SURFACE ENHANCED NANOSTRUCTURED ELECTRODE
MATERIALS FOR SOLAR ENERGY HARVESTING
AND CONVERSION

by

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ABSTRACT

This dissertation presents surface enhanced photoanodes and oxygen evolution reaction (OER) catalysts for solar water splitting to produce hydrogen. The enhancement could be achieved by either introduced surface plasmon enhanced metallic nanostructures, such as Au or Ag nanoparticles, or adjusted surface structure, chemical composition and band structure of TiO₂. This dissertation also presents various electrochemical and spectroscopic techniques used to characterize nanostructured materials for solar water splitting reactions.

Firstly, a model photoanode comprised of Ag@Ag₂S core-shell nanoparticles (NPs) on a nanostructured TiO₂ substrate is presented for visible light sensitive photoelectrochemical properties. The nanostructured electrode is coated with TiO₂ nanowires (NW) on Ti plate to provide a high surface area for efficient light absorption and efficient charge collection from Ag@Ag₂S NPs. Pronounced photoelectrochemical responses of Ag@Ag₂S NPs under visible light responses were obtained. These responses were attributed to collective contributions of local surface plasmon enhancement, enhanced charge collection by Ti@TiO₂ NWs, and high surface area of the nanostructured electrode system. The shell thickness and core size of the Ag@Ag₂S core-shell structure can be controlled and the optimal photoelectrochemical performance with a core size of 17 nm (in diameter) and shell thickness of 8 nm was formed.

Secondly, a Au@CdS/Ti@TiO₂ nanostructured photoanode was prepared by decorating a CdS thin film layer onto a Au/Ti@TiO₂ NWs substrate. Compared to CdS/Ti@TiO₂ NWs photoanode, Au@CdS/Ti@TiO₂ exhibits a significant enhancement to water splitting efficiency. The enhanced photoelectrochemical catalytic activity is attributed to the surface plasmon
enhancement of Au nanoparticles. XPS, XRD, SEM, EDS, high resolution TEM, AC impedance and other electrochemical methods were applied to resolve the structure-function relationship of the nanostructures of Ag@Ag₂S/Ti@TiO₂ NWs and Au@CdS/Ti@TiO₂ NWs electrodes. The studies of the photocatalytic activity of the core-shell structure, as well as a core-shell structure predictive model can further improve the understanding of the interplay between the shell thickness and core size and guide the design of highly efficient core-shell materials.

Lastly, chapter 5 of this dissertation presents a high efficiency, durable, and low-cost oxygen evolution reaction (OER) catalyst based on earth-abundant elements, carbon, oxygen, and titanium for renewable energy conversion and storage devices. In this study, we report a highly active nanostructured electrode NanoCOT (C, O and Ti) for an efficient OER in alkaline solution. The NanoCOT electrode is synthesized from the carbon transformation of nanostructured TiO₂ in an atmosphere of methane, hydrogen and nitrogen by a CVD process. The NanoCOT exhibits highly enhanced OER catalytic activity in alkaline solution, providing a current density of 1.33 mA/cm² at an overpotential of 0.42 V, which is about 4 times higher than an IrO₂ electrode and 15 times higher than a Pt electrode because of its nanostructured high surface area and favorable OER kinetics. The enhanced OER catalytic activity of NanoCOT is attributed to the presence of a continuous energy band of the titanium oxide electrode with predominantly reduced defect states of Ti (e.g., Ti¹⁺, Ti²⁺ and Ti³⁺) formed by chemical reduction with hydrogen and carbon. OER performance of NanoCOT can also be further enhanced by decreasing its overpotential 150 mV at a current density of 1.0 mA/cm² after coating its surface electrophoretically with 2.0 nm IrOₓ nanoparticles (NPs).
DEDICATION

I would like to dedicate this dissertation to my family, in particular my wife Wei Li and my son Willian Shan, who stood by me throughout the PhD program.
LIST OF ABBREVIATIONS AND SYMBOLS

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>AC</td>
<td>Alternating Current</td>
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<tr>
<td>C</td>
<td>Capacitance</td>
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<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
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<tr>
<td>CCD</td>
<td>charge-coupled device</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
</tr>
<tr>
<td>Co-Bi</td>
<td>Cobalt Borate</td>
</tr>
<tr>
<td>Co-Pi</td>
<td>Cobalt Phosphate</td>
</tr>
<tr>
<td>Co(TCPP)Cl</td>
<td>Cobalt Meso-5,10,15,20-Tetrakis(4-Carboxyphenyl)Porphyrin Chloride</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>DSSC</td>
<td>Dye Sensitization Solar Cell</td>
</tr>
<tr>
<td>E</td>
<td>Potential</td>
</tr>
<tr>
<td>E_{fb}</td>
<td>Flat Band Potential</td>
</tr>
<tr>
<td>E_{on}</td>
<td>Turn On Potential</td>
</tr>
<tr>
<td>EDS</td>
<td>Electron Dispersive Spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectra</td>
</tr>
<tr>
<td>eV</td>
<td>Electron Volt</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine-doped Tin Oxide</td>
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<td>HER</td>
<td>Hydrogen Evolution Reaction</td>
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</table>
HRTEM  High Resolution Transmission Electron Microscopy
I-V    Current-Voltage
Isc    Short-Circuit Current
IPCE   incident photon-to-current efficiency
λ      Wavelength
LSPR   Localized Surface Plasmon Resonance
N      Carrier Density
NP     Nanoparticle
NW     Nanowire
NHE    Normal Hydrogen Electrode
N3     C_{26}H_{16}N_{6}O_{8}RuS_{2}
N719   C_{58}H_{86}N_{8}O_{8}RuS_{2}
N749   C_{69}H_{116}N_{9}O_{6}RuS_{3}
OER    Oxygen Evolution Reaction
OEC    Oxygen Evolution Catalysis
PEC    Photoelectrochemical
pH     The acidity or basicity of an Aqueous Solution
RDE    Rotating Disc Electrode
Rs     Series Resistance
Rct    Charge Transfer Resistance
P123   Poly(ethylene glycol)-Poly(propylene glycol)-Poly(ethylene glycol)
P25    Titanium(IV) Oxide Nanopowder, Degussa (Evonik) P25
PMMA   Poly(methyl methacrylate)
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>3D</td>
<td>Three Dimension</td>
</tr>
<tr>
<td>RC</td>
<td>Resistor–Capacitor</td>
</tr>
<tr>
<td>RET</td>
<td>Resonant Energy Transfer</td>
</tr>
<tr>
<td>RHE</td>
<td>Reversible Hydrogen Electrode</td>
</tr>
<tr>
<td>SCE</td>
<td>Saturated Calomel Electrode</td>
</tr>
<tr>
<td>sccm</td>
<td>Standard Cubic Centimeter per Minute</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transmission Electron Microscope</td>
</tr>
<tr>
<td>STP</td>
<td>Standard Temperature and Pressure</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
<tr>
<td>TEOA</td>
<td>Triethanolamine</td>
</tr>
<tr>
<td>TEOS</td>
<td>Tetraethyl Orthosilicate</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultra-Violet Visible Spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>ΔG</td>
<td>Change in Gibbs Free Energy</td>
</tr>
<tr>
<td>ΔE</td>
<td>Change in Energy of the System</td>
</tr>
<tr>
<td>η</td>
<td>Overpotential</td>
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ACKNOWLEDGMENTS

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1. INTRODUCTION

1.1 Solar energy for water electrolysis.

The United States is one of the world’s largest energy consumers. In 2010, around 70% of this energy was derived from fossil fuels, such as petroleum, coal, and natural gas. 8.4% of this energy was supplied by nuclear power and only 8% was supplied by renewable energy. Rapid economic and population growth will potentially exhaust the traditional fossil fuel supply around the world. The world’s energy consumption is predicted to grow by 56% between 2010 and 2040. Additionally, fossil fuels also cause air pollution and contribute to global warming by increasing greenhouse gas emissions. Energy-related carbon dioxide emission in 2040 are projected to increase 46% from 2010. To meet the future energy demands while minimizing these negative impacts on environment issues by traditional fuel resources, the development of renewable resources with sustainable supply is in high demand. Solar energy presents a promising source of renewable clean energy. Sunlight is an abundant resource that could meet the world’s future energy challenge. Every hour the sunlight projects more energy onto Earth (4.3×10^{20} J) than is needed to meet global energy needs for an entire year (4.1×10^{20} J).\textsuperscript{1} The world energy consumption can be easily satisfied by sunlight with minimal environmental impact.

Hydrogen is the most abundant element in the universe and has been considered as the ultimate energy carrier to replace fossil fuels in the future.\textsuperscript{2} Hydrogen has high calorific value per mass unit, which is triple that of gasoline and quadruple that of natural gas. The major advantage of the combustion of hydrogen is that it produces only water in contrast to hydrocarbon fuels, such as gasoline and diesel, which produce carbon monoxide and carbon dioxide causing global
warming and other toxic byproducts. However, the current industrial hydrogen production mainly relies on steam reforming methods; these methods use fossil fuels as the starting material and produce toxic and greenhouse gases. On the other hand, the electrolysis of water, has been regarded as a green chemical process to obtain pure hydrogen because the only byproduct is oxygen. Yet conventional electrolysis requires electrical energy produced by fossil fuels and negative impacts on environment remain. It is highly desirable to develop water electrolysis systems powered solely by solar energy because solar energy and water are the cleanest and most abundant natural resources to address the global energy challenges. There are already a number of systems developed to split water using sunlight. Photocatalytic or photoelectrochemical (PEC) methods for splitting of water into H₂ and O₂ were shown by Honda and Fujishima’s work on the first PEC cell for water splitting using TiO₂ as a photoelectrode in 1972. As shown in Figure 1.1, the key components of the PEC water-splitting are a semiconductor photocatalyst that harvests the solar spectrum, followed by charge carrier generation and separation at the semiconductor/aqueous interface to be used for water reduction and oxidation reactions. The free energy change for the water splitting reaction H₂O→H₂ + 1/2O₂ under standard conditions is ΔG =237.2 kJ/mol corresponding to ΔE°=1.23 eV. As shown in Figure 1.2, the band gap of a semiconductor must be larger than 1.23 eV, with the valence band position more positive (or below) than water oxidation potential (1.23 eV) and the conduction band position more negative (or above) than water reduction potential (0 eV at pH=0).

In the past few decades, enormous effort has been invested in identifying and optimizing efficient photoactive materials for solar water splitting by tailoring their compositions and morphologies. TiO₂ remains one of the most widely studied photocatalysts although its wide bandgap (3.2 eV) limits its operation only to UV light (λ < 400nm), leading to low power
conversion efficiency for hydrogen production with the entire solar spectrum.\textsuperscript{8-11} Several ways have been taken to broaden visible light absorption by a photocatalytic electrode material for more efficient solar water splitting, including designing heterojunction structures: CdS/TiO$_2$,\textsuperscript{12} BiVO$_4$/WO$_3$;\textsuperscript{13} nanostructures: core/shell,\textsuperscript{14} quantum dots;\textsuperscript{15} dopant: Ce doped TiO$_2$,\textsuperscript{16} Cr doped TiO$_2$ and N doped TiO$_2$;\textsuperscript{17} co-catalysts: C$_3$N$_4$,\textsuperscript{18} cobalt meso-5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin chloride (Co(TCPP)Cl);\textsuperscript{19} and surface plasmon enhancement: Ag@Ag$_2$S,\textsuperscript{20} Au/Fe$_2$O$_3$.\textsuperscript{21} In the first part of this research dissertation, the synthesis and design of catalytic semiconductor electrodes for water-splitting will be introduced. This is composed of two main sections: (1) surface plasmonic enhancement of photoelectrochemical solar energy conversion systems for water splitting and (2) surface-enhanced nanostructured electrode for efficient oxygen evolution.
Figure 1.1 Schematic and operating mechanism of a photoelectrochemical cell.
Figure 1.2 Schematic of energy diagram of semiconductor photocatalytic water splitting system.
1.2 Surface plasmon enhancement of photoelectrochemical solar water splitting conversion system.

Metal nanoparticles (NPs), such as Au, Ag, Cu, Pt and Al, possess localized surface plasmon resonance (LSPR) properties when their surface electron cloud is excited by incident electromagnetic wave whose frequency matches the natural frequency of the metal NPs surface electrons. Different types and sizes of metals show distinct plasmon absorption in the visible region. For example, spherical Ag (38 ±12 nm diameter), Au (25 ±5 nm) and Cu (133 ±23 nm) nanostructures exhibit LSPR absorption peaks at nearly 420, 520 and 610 nm, respectively. The LSPR wavelength and intensity can also be tuned by tailoring the size and shape of metal nanostructures. For example, Ag wire (90 ±12 nm diameter and >30 aspect ratio), sphere (38 ±12 nm) and cube (79 ±12 nm) nanostructures show distinct absorption peaks around 380 nm, 420 nm, and 480 nm, respectively. Moreover, LSPR absorption peaks of Ag nanocubes of edge length 56 nm, 79 nm and 129 nm correspond to orange, red and blue spectra respectively. Therefore, plasmonic nanostructures interacting with the entire solar spectrum could be achieved by adjusting the chemical composition, shape and size of plasmonic nanostructures. Furthermore, LSPR can generate an enhanced electromagnetic field concentrating the incident light energy. Such localized electromagnetic (EM) field enhancements can approach $10^3$ at the surface of an isolated plasmonic particle compared with that of the incoming light, and can achieve more than $10^6$ between two particles separated by ~1 nm under resonance conditions. The spaces between plasmonic nanostructures with very high-intensity fields are often referred to as hot spots. These hot spots exhibit multiple resonances that can yield very strong EM fields. This unique capability of plasmonic nanostructures make them suitable for various applications, such as single-molecule spectroscopy, surface-enhanced Raman spectroscopy, molecular sensing and detection, and solar energy conversion systems. For example, semiconductor photocatalysts
can be coupled to plasmonic nanostructures to enhance photocatalytic efficiency. Plasmonic metals that can interact with light through the excitation of LSPR can enhance the rate of photocatalytic reactions on nearby semiconductors.\textsuperscript{28-30} In general, there are three energy-transfer mechanisms by which LSPR can enhance the photocatalytic activities.\textsuperscript{31} The first mechanism is plasmon-mediated electron transfer in which hot electrons are directly injected from excited plasmonic-metal nanostructures into the semiconductor conduction band (Figure 1.3).\textsuperscript{32} This enhancement is observed in metallic plasmonic nanoparticle sensitized semiconductors. When there is direct interaction of plasmonic particles and light, the excitation of a surface plasmon can generate hot electrons within the metal nanostructures. These electrons can rapidly transfer to the conduction band of nearby semiconductors and lead to Fermi level equilibrium between the two materials.\textsuperscript{33} Usually, the minimum potential for the conduction band of the semiconductor for water splitting is somewhere between -1.0 and 0 V versus normal hydrogen electrode (NHE). For plasmonic nanoparticles, the energy of the hot electron that formed in the process of the SPR excitation is between 1.0 and 4.0 eV above on the metal Fermi level. The Fermi level for noble metals is around 0 V vs. NHE.\textsuperscript{22} Due to this alignment of the electronic states, in the plasmonic-metal/semiconductor composite, the energetic excited electrons can transfer from the metal to the semiconductor. Thus, the surface plasmon hot electron injection process should play a significant role for the high-energy electrons to execute half-reactions on semiconductors under visible light irradiation, such as the hydrogen evolution reaction. The second mechanism involves the interaction of a semiconductor with a strong localized SPR-induced electromagnetic field nearby metallic nanostructures, as shown in Figure 1.4.\textsuperscript{34, 35} In these systems, an increased local electromagnetic field can be generated upon irradiation of the plasmonic nanoparticles. Radiative energy can transfer from the plasmonic metal to the semiconductor through the interaction of this
localized electromagnetic field with the semiconductor. This interaction increases the generation of charge carriers near the surface of the semiconductor. The separated electron–hole pairs in the semiconductor can reach the respective surface sites on the surface of a semiconductor readily, leading to enhanced photocatalytic efficiency. Local electromagnetic field induced carrier formation only occurs when the energies of the excitation wavelength and larger than the band gap of the semiconductor and requires a short distance from plasmonic metals to the semiconductor. The illumination energy can also be transferred from plasmonic metals to the semiconductor when the energy is lower than the band gap of the semiconductor through the form of a resonant energy transfer (RET) process. The RET process involves the direct excitation of electron-hole pairs through the nonradiative relaxation of the localized surface plasmon dipole and does not require a direct connection. RET enhancement happens where the semiconductor and plasmonic metal are separated by a non-conductive layer preventing any direct charge exchange. The third mechanism is based on the excellent light scattering efficiency of plasmonic nanostructures, as shown in Figure 1.5. The efficiency of a light absorption of semiconductor thin film or particles is low. Here, the plasmonic nanostructure essentially acts as a nano-mirror between plasmonic metals and thus increasing the average optical path length to enhance the light absorption of the semiconductor. Based on Rayleigh scattering theory, the intensity of scattered radiation is strongly dependent upon the ratio of particle size to wavelength that scattering efficiency increases with increasing particle size. This increase in illumination energy increases the absorption efficiency, causing an increased in the rate of electron–hole pair formation in the semiconductor.
Figure 1.3 Mechanism of surface plasmon resonance induced charge transfer with approximate energy levels on the NHE scale.
Figure 1.4 Mechanism of SPR-induced electromagnetic field enhancement of the semiconductor charge excitation process.
Figure 1.5 Schematic illustrating the scattering mechanism to increase the average optical path length.
1.3 Oxygen evolution catalysts for electrochemical oxygen evolution.

Coupling solar cell panels with oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) electrocatalysts to split water is a promising approach toward direct production of hydrogen fuel from sunlight, as shown in Figure 1.6. The OER is a very critical half-reaction of solar water splitting and is more complicated than HER due to its four electrons process. Efficient OER holds the promise for addressing the challenge of solar water splitting for large-scale storage of intermittent energy using hydrogen from the sun, wind, and other renewable sources. However, the OER involves sluggish kinetics at most electrodes, while makes it less viable on an industrial scale. Nowadays, electrocatalysts used for the OER consist of precious metals such as Pt, Ru, and Ir, which have shown excellent OER performances to date. However, Pt forms a poorly conductive oxide film and shows a high overpotential. Pure Ru metal, in particular, have shown to be the most active catalyst for OER but very unstable. IrO₂ was found to be the next most active and stable at higher current densities. However, its scarcity and prohibitive cost renders its use impractical for large-scale applications. Thus, it is important to develop inexpensive and highly active OER catalysts to overcome these obstacles. Applications and synthesis for earth abundant catalyst have drawn great attention in recent years. The most intensive studies of earth abundant catalysts can be categorized into two main classes. The first main class of novel oxygen evolution catalysis (OEC) includes oxides or hydroxides of earth abundant transition metals such as Mn, Co, Ni, and Fe. For example, MnO₂, NiO, Ni(OH)₂, CoOOH, NiOOH, and FeOOH have been developed for enhancing water electrolysis efficiency. The second main class includes complex ternary oxides that have a specific crystal structure, such as spinel and perovskite. For example, perovskite structure Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃₋δ (BSCF) has been reported as the optimal intrinsic catalyst; spinel type
ZnCo$_2$O$_4$,\textsuperscript{55} M$_x$Fe$_{3-x}$O$_4$ (M= Ni, Co, Mn, Fe, or Zn),\textsuperscript{56} and mesoporous Ni$_x$Co$_{3-x}$O$_4$\textsuperscript{57} were also studied for their OER efficiency. The goal of these studies were to synthesize earth abundant OEC and to understand the structure–function relationship of these catalytic electrode materials.
Figure 1.6 Structure and operating mechanism of a solar water splitting cell.
1.4 Dye Sensitized Solar Cell.

Solar cells are primary solar energy harvesting and conversion devices that can convert the incident photon energy of sunlight directly into electricity by the photovoltaic effect.58 Solar cells are categorized into three generations.59 The traditional first and second generation solar cells are made of single layer and p/n junction semiconductors, respectively. In the second generation solar cell system, light exited-electrons in the p-type portion flow across the interface and transfer into the n-type side to produce an output potential. For example, 0.7 V DC voltage can be generated from a crystalline p/n junction silicon solar cell with an efficiency of 25%.60 Different from the conventional solid p/n junction solar cell, the dye sensitized solar cell (DSSC) is the third generation photoelectrochemical device. It consists of a photoanode, cathode, and electrolyte solution in between. Since 1991 when Grätzel and O’Regan first reported that DSSCs could be a feasible alternative photovoltaic device and attained a remarkable efficiency of 7%,61 DSSCs have received considerable attention as a new generation of sustainable solar cell because of their high Incident Photon to Charge Carrier Efficiency (IPCE), durability, flexibility, decorative nature, and low cost.62 The scheme and operation steps of DSSCs are shown in Figure 1.7. A standard DSSC has three primary components: a dye sensitized wide band gap oxide photoanode, such as TiO₂, an iodide/triiodide (I⁻/I₃⁻) redox electrolyte, and a counter electrode. Two electrodes are assembled together and sealed to prevent the electrolyte from leaking.62 The photoanode is made of transparent fluoride-doped tin dioxide (FTO) glass, on the conductive side is a thin layer of nanosized carrier transport oxide material such as TiO₂ with a highly porous and high surface area. The anode modified with photosensitive dye adsorbed and bonded onto TiO₂ surface. The electrolyte is made of a thin layer of I⁻/I₃⁻ redox couple spread over a conductive counter electrode, usually, a platinum film sputtered on FTO.
Under light illumination the electrons in the ground state ($S$) of dye can be excited into excited state ($S^*$), then injected into the conduction band of the TiO$_2$. The electrons flow through the external circuit toward the Pt/FTO electrode, then go through the I$_3$/I$^-$/redox system in the electrolyte to regenerate the oxidized dye to complete the circuit.\textsuperscript{62}

In the past two decades, photosensitive dyes, electrolyte systems, nanostructured photoanode and counter electrode with different composition and morphologies have been widely investigated and optimized. Typical carrier transports in DSSCs are nanostructure wide band gap oxide semiconductor, such as TiO$_2$, ZnO, or NiO.\textsuperscript{63,64} The photosensitizer dye molecules for the sensitization of the oxides are the key material issues in DSSCs, and determine the efficiencies in the conversion of solar energy to electricity.\textsuperscript{64} Metal complex molecules such as, ruthenium,\textsuperscript{65} osmium,\textsuperscript{66} rhenium\textsuperscript{67} and platinum\textsuperscript{68} have been widely investigated as sensitizers for DSSCs due to their excellent redox properties, highly efficient metal-to-ligand charge transfer, long excited lifetime, and high photoelectric conversion efficiencies. Among these metal complex dyes, polypyridyl ruthenium is the most widely studied. The most used ruthenium complex dyes for DSSCs are C$_{26}$H$_{16}$N$_6$O$_8$RuS$_2$ (N3), C$_{58}$H$_{86}$N$_8$O$_8$RuS$_2$ (N719) and C$_{69}$H$_{116}$N$_9$O$_6$RuS$_3$ (N749), which show conversion efficiencies higher than 10\% (Figure 1.8).\textsuperscript{65}
Figure 1.7 Structure and operating mechanism of a dye-sensitized solar cell.
Figure 1.8 Structure of the dye, N3 (A), N719 (B) and N749 (C).
Although the polypyridyl ruthenium dyes provide high efficiency, there are still several disadvantages of using noble metals complexes. Their scarcity, prohibitive cost, and complicated synthesis restrict their large-scale application. To overcome these obstacles, efforts are being made in developing inexpensive noble metal free complex dyes with highly active for DSSCs applications. Abundant metals (Zn, Cu and Fe) coordinated by porphyrin or phthalocyanine rings, and metal-free organic dyes such as triarylamine-based dyes, triphenyl-amino-vinyl dyes, and thiophene-based dyes have been reported to show fair conversion efficiencies. Now, the record for DSSCs is 15% power conversion efficiency, as reported by Graetzel. This was achieved by using hybrid perovskite CH$_3$NH$_3$PbI$_3$ dye, subsequently deposited from separated solutions of CH$_3$NH$_3$I and PbI$_2$. The electrolyte is based on a mixed solvent containing an iodide/tri-iodide redox pair in fairly polar organic solvents. The electrolyte is a key component in DSSCs, which has great influence on the internal charge carrier transport, long term stability, and continuously reduces the photosensitive dye and itself during DSSC operation. An example of the typical electrolyte composition is a solution of anhydrous LiI, I$_2$, 1, 2-dimethyl-3-n-propylimidazolium iodide, and 4-tert-butylpyridine in dehydrated acetonitrile. The counter electrode is also a crucial component in the DSSC for collecting external circuit electrons and catalyzing the reduction of the tri-iodide ions in the electrolyte. In conventional DSSCs, a Pt film deposited on Indium-Tin Oxide (ITO) or Fluorine doped Tin Oxide (FTO) substrate is used as counter electrode. Pt serves as the catalytic material and counter electrode due to its excellent conductivity and high catalytic activity toward the (I$^-$/I$_3^-$) redox pair regeneration. However, as a noble metal, its high cost and low abundance are major drawbacks in large-scale commercial application of DSSCs. Thus, it is important to reduce production costs while maintaining a highly catalytic activity. Much effort has been devoted to investigating earth-abundant catalysts...
for the replacement of Pt. Among these materials, carbon nanotube,\textsuperscript{74} graphene,\textsuperscript{75} sulfides and selenides, such as NiS,\textsuperscript{76} FeS\textsubscript{2},\textsuperscript{77} MoSe\textsubscript{2},\textsuperscript{78} and Cu\textsubscript{2}FeSnS\textsubscript{4}\textsuperscript{79} have been intensively studied and showed fair activities in DSSCs.

This dissertation is focused on developing nanostructured electrode materials and surface plasmonic structures for light energy harvesting and energy conversion. Chapter 1 briefly introduces the research background, the main idea and the importance of the dissertation. Chapter 2 describes the details of the kinds of experimental techniques and material synthesis procedures used throughout this dissertation. Chapter 3 discusses the synthesis of Au/CdS/TiO\textsubscript{2} and its visible light PEC properties. Chapter 4 shows the study of visible light driven photoelectrochemical properties of Ti@TiO\textsubscript{2} nanowire electrodes sensitized with core–shell Ag@Ag\textsubscript{2}S nanoparticles. Chapter 5 extends the NanoCOT work to Dye-sensitized solar cell (DSSC) applications. The NanoCOT could be used as the counter electrode of DSSC, which should a superior efficiency than Pt film electrode. Chapter 6 discusses the conclusions and the future work of the dissertation. It will detail a few systems that could be further studied and developed to improve the fields of solar energy conversion.
REFERENCES


2. EXPERIMENTAL

This chapter provides a brief outline of electrochemistry and structural characterization methods and all the experimental procedures for sample preparation. Materials preparation procedures for TiO2 nanowires (NWs), NanoCOT, Ag2S, CdS, Au and Ag nanoparticles (NPs) are presented in this chapter along with assembly procedures of a dye-sensitized solar cell (DSSC). Electrochemistry techniques such as cyclic voltammetry (CV), rotating disc electrode (RDE) and electrochemical impedance spectroscopy (EIS) are used to studies electrochemical properties of nanostructured electrodes. Photoelectrochemical measurements including I-V curves and action spectrum are briefly discussed. Other techniques briefly discussed at the end of the chapter include scanning electron microscopy (SEM), transmission electron microscopy (TEM), absorption spectroscopy, X-ray techniques, including X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

2.1 Materials Synthesis.

2.1.1 Synthesis of Ti@TiO2 NWs.

The Ti@TiO2 NWs substrates were prepared using a hydrothermal reaction process. Ti plates of 99% purity with dimensions of 15 × 15 mm and thickness of 0.50 mm were first cleaned with acetone in an ultrasonic bath for 20 min and then rinsed in excess DI water. The cleaned Ti plates were loaded into a 23 mL Teflon-lined stainless steel autoclave containing 10 mL 0.6 M HCl solution and heated at 190 °C for 12 h. After cooling to room temperature, the as-prepared Ti NWs substrates were thoroughly washed with distilled water and dried in air.
Subsequently, the samples were annealed at 450 °C for 2 h (in air) and allowed to cool to room temperature to form a thin TiO$_2$ layer on Ti NWs substrate.

2.1.2 Synthesis of Ag@Ag$_2$S Core–Shell NPs on Ti@TiO$_2$ NW Substrates.

Ag NPs were synthesized by the Tollens reaction.

$$\text{RCHO} + 2[\text{Ag(NH}_3)_2]^+ + 3\text{OH}^- \rightarrow \text{RCOO}^- + 2\text{Ag} + 4\text{NH}_3 + 2\text{H}_2\text{O}$$

The mechanism of Ag deposit on TiO$_2$ via Tollens reaction is shown as follows

Typically, 0.2 mL 0.1 M NaOH was added to 10 mL of 0.01 M AgNO$_3$ solution prior to dropwise addition of 1.0 M ammonia solution until a clear solution containing a silver–ammonia complex [Ag(NH$_3$)$_2$]$^+$ was obtained. 10 mL of 0.05 M Dextrose (C$_6$H$_{12}$O$_6$) solution was then added into the above fresh [Ag(NH$_3$)$_2$]$^+$ solution then freshly prepared Ti@TiO$_2$ NW substrates were quickly dipped into the above solution under stirring. The color of the solution changed to a dark brown, indicating the formation of Ag NPs in the solution. The amount of the Ag NPs attached to the Ti@TiO$_2$ NW substrates was varied by altering the substrate dipping time. The Ag NPs/Ti@TiO$_2$ NWs were taken out and washed in excess DI water. Ag@Ag$_2$S core–shell NPs were obtained by sulfurizing the Ag NPs in 20 mL of 8 mM sulfur/DMSO solution at 100 °C to convert the surface of Ag NPs to Ag$_2$S shells. The shell thickness was controlled by the reaction time duration. The as-prepared sample was finally washed with CS$_2$ (caution: highly
flammable, toxic, and irritant) and acetone and dried, sequentially, at room temperature to obtain Ag@Ag$_2$S core–shell NPs on Ti@TiO$_2$ substrates.

2.1.3 Synthesis of Au NPs on Ti@TiO$_2$ NW Substrates.

Au NPs were electrodeposited onto Ti@TiO$_2$ NWs obtained previously. Typically, a piece of Ti@TiO$_2$ NW electrode was immersed in 0.1 M NaCl containing 1 mM HAuCl$_4$ for cyclic voltammogram (CV) measurement. Ti@TiO$_2$ NW substrates was immersed in 0.1 M NaCl containing 1 mM AuCl$_3$ for CV to select the potential for two pulse potential deposition using a CHI 760C potentiostat. $E_1$ and $E_2$ are two potentials selected to grow polydisperse gold nanoparticles on the nanowire-coated electrode. $E_1$ is a potential with large over potential for gold nucleation sites on Ti@TiO$_2$ NW. $E_2$ is a potential more negative than the thermal dynamic potential of gold deposition for growing the nucleation sites to large gold nanoparticles because of the sluggish kinetics of reduction on Ti@TiO$_2$ NW surface. $^1$

2.1.4 Deposition of CdS on Au/Ti@TiO$_2$ and Ti@TiO$_2$ NWs Substrates.

CdS films can be deposited on Au/Ti@TiO$_2$ or Ti@TiO$_2$ NWs substrates by chemical bath method. 1 mL of 0.1 M cadmium acetate, followed by 1 mL of 0.2 M thiourea, was added to 15 mL of 0.2 M Triethanolamine (TEOA) in a beaker under constant stirring. Then 0.1 mL of 30% ammonia aqueous solution was subsequently added. After vigorous stirring, the 100 µl solution was transferred to Ti@TiO$_2$ or Au/Ti@TiO$_2$ NWs substrate, then thermostated the substrate at 80 °C. After 30 min, the substrate was removed and rinsed with deionized water. To obtain thicker films, this procedure was repeated. After the final deposition, the substrates were again rinsed with deionized water and then dried in air.
2.1.5 Fabrication of NanoCOT Electrode.

NanoCOT electrode was fabricated by hydrothermal reaction of a Ti substrate to form Ti nanowires (NWs) on its surface, using the same procedure as described in section 2.1.1, followed by air annealing and carbon transformation of the oxidized Ti NWs in a chemical vapor deposition (CVD) system. The thermally annealed TiO$_2$ NWs substrates were then treated with 0.5 M Fe(NO$_3$)$_3$ for 20 min and dried in air. The Fe catalyst-coated substrates were horizontally placed into a quartz boat with a quartz plate cover on top to allow sufficient mixture gas retention time for the carbon transformation reaction. The boat was loaded in a tube furnace (1100, MTI Corporation, Richmond, CA). The chamber was purged by several vacuum/N$_2$ purge cycles to dispose of the oxygen in the furnace, followed by a constant N$_2$ gas flow. The furnace temperature was set to 900 °C with a ramp rate of 50 °C/min and a dwell time of 1 h. At ~600 °C, the N$_2$ gas was turned off, and the CH$_4$/H$_2$/N$_2$ gas mixture was turned on at a flow rate of ~1000 sccm and reduced to ~100 sccm when the temperature reached 800 °C. After the carbon transformation reaction, the furnace was allowed to cool under CH$_4$/H$_2$/N$_2$ flow until the temperature of the furnace reached ~600 °C. At this temperature, the CH$_4$/H$_2$/N$_2$ was turned off, and the N$_2$ flow was turned back on. The samples were allowed to cool to room temperature in a N$_2$ stream before being removed from the furnace. The CVD furnace is shown in Figure 2.1.
Figure 2.1 CVD system for NanoCOT fabrication.
2.1.6 Synthesis of Planar COT Electrode.

Planar COT electrode fabrication followed the same procedure as for the NanoCOT electrode described above, except for using electropolished Ti substrates instead of nanostructured Ti NW substrates. The electropolished Ti substrates were obtained by anodizing a Ti substrate in a methanol solution containing 3 vol % sulfuric and 3 vol % hydrochloric acid at a current density of 0.1 mA/cm² at −40°C. The electropolished Ti substrates were then calcined at 550 °C for 10 h in air to form a thin layer of TiO₂. The TiO₂ layer was then converted to a COT electrode by following the same procedure outlined in section 2.1.5.

2.1.7 Synthesis of COT NPs.

COT NPs were obtained by direct carbon transformation of TiO₂ NPs using the same CVD setup described above for both NanoCOT and planar COT samples; 100 mg P25, 20 mg P123, and 20 mg PMMA were then added to 30 mL of 3 mM Fe(NO₃)₃ acetone solution and stirred for 5 h at room temperature in a capped beaker. The resultant precipitate of Fe and surfactant-modified P25 were then centrifuged and dried prior to being grounded to a powder in a mortar. The obtained powder was placed horizontally in a quartz boat and heated at 450 °C in air for 1 h to remove the surfactant. N₂ gas was then used to purge the tube furnace to remove residual O₂ within the chamber prior to the carbon transformation process, as described in section 2.1.5.

2.1.8 Synthesis of NiMoZn/NanoCOT Cathode.

NiMoZn alloy was electrodeposited onto a NanoCOT electrode.² Briefly, a solution of nickel(II) chloride hexahydrate (9.51 g L⁻¹), sodium molybdate dihydrate (4.84 g L⁻¹), anhydrous zinc chloride (0.0409 g L⁻¹), tetrabasic sodium pyrophosphate (34.57 g L⁻¹), and sodium bicarbonate (74.77 g L⁻¹) was used as an electrodeposition solution. Hydrazine hydrate (1.21 mL L⁻¹) was added immediately before plating. The NiMoZn alloy was deposited onto the
NanoCOT electrode at a potential of $-1.5 \ \text{V vs Ag/AgCl}$ for 20 min. The obtained electrodeposited film was then stored in 10 M KOH for 16 h to obtain suitable stoichiometry for enhanced proton reduction.

2.1.9 Electrophoretic Deposition of 2.0 nm IrO$_x$ NPs onto NanoCOT Electrode. $^3$

2.4 mM aqueous K$_2$IrCl$_6$ at pH 13 was heated at 90 °C for 20 min and immediately cooled in an ice-bath, producing a blue 2.0 nm IrO$_x$ nanoparticle solution. The 2.0 nm IrO$_x$ particles were deposited by electrophoresis onto NanoCOT wire at 1.0V vs Ag/AgCl.

2.1.10 Fabrication of Dye-Sensitized Solar Cell (DSSC).

1.5 cm×1.5 cm Fluorine doped Tin oxide (FTO) coated glass substrates were cleaned with soap solution and warm water followed by ultrasonication in acetone and isopropanol for 15 minutes each. The cleaned substrates were then dried in a stream of nitrogen. A thin layer of titania sol made by 3 mL ethanol, 0.25 g Titanium isopropoxide, 1 mL acetic acid, and 0.3 g polyvinyl pyrrolidone was spin coated on FTO substrates and dried in air. A square mask of 0.5×0.5 cm was made by a 3M scotch tape and pasted on the FTO substrates. Titania nanoparticles paste prepared by mixing 0.1g of P25 (Sigma Aldrich) powder with 8 drops of Triton X surfactant and ultrasonicated for 1 hour for homogenous mixing. The paste was doctor bladed on the mask to get an area of 0.25 cm$^2$. The films were kept in the fume hood to dry for 15 minutes and the scotch tapes masks were removed. The FTO substrates were annealed in air at 500°C for 30 mins and cooled to room temperature and soaked in 0.5 mM cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) dye (N3, Solaronix, Switzerland ), in 1:1 mixture of acetonitrile and t-butanol for 24 hours. The dye sensitized photoanodes were washed with ethanol to remove any unanchored dye and dried in air. A 40 μm Parafilm spacer was placed over the dye anchored TiO$_2$ and filled with 50 mM of iodide/tri-
iodide electrolyte (Iodolyte AN-50, Solaronix, Switzerland). NanoCOT was used as a counter electrode. A Pt sputtered FTO counter electrode was used as a control. The current voltage characteristics of the devices in dark and under 1 Sun illumination conditions were recorded with a potentiostat (Princeton Applied Research Model: M270).

2.2 Electrochemistry Techniques.

2.2.1 Cyclic Voltammetry (CV).

CV is an electrochemical technique for studying electrochemical mechanisms, the redox potential, rates of oxidation and reduction processes, intermediates in redox reactions, the reversibility of a reactions, mass transfer, as well as analyzing quantitative information about redox processes under various conditions. A typical CV system is composed of an electrochemical workstation with a working electrode, a reference electrode, a counter electrode and electrolyte. In CV experiment, the electrolyte is to provide redox species to the working electrodes during oxidation and reduction. The potential of a working electrode is ramped linearly versus time and scanned back and forth at certain scan rate between maximum and minimum potential relative to the reference electrode. Meanwhile the current between the working electrode and counter electrode is measured and reported versus applied potential. During the process, oxidized species can be generated during the forward scan and then the oxidized species will be probed in the reverse scan. The scan cycles can be repeated as many times as desired.

2.2.2 Rotating Disc Electrode (RDE).

The cyclic voltammetry technique is usually done at stead-state solution and mass transfer is controlled by the diffusion of substrate. Under such condition, the redox diffusion layer grows as a function of time and there is no linear diffusion layer to reach a limiting current. To obtain
predictable results, and investigate reaction mechanisms and other chemical phenomenon, it is very important to achieve a controlled mass transfer. Hydrodynamic voltammetry is different from the cyclic voltammetry that can alter the convection in solution to provide a constant mass transport rate and a linear growth diffusion layer so that a limiting current can be achieved on the working electrode. A rotated disk electrode (RDE) is one of the hydrodynamic electrodes used in three electrode system. During experiments the electrode rotates at constant angular velocity to make redox species flow perpendicularly to the electrode and flings the solution away from the center of the electrode. The potential scan is applied like a regular CV, while the steady-state current is controlled by the solution flow rather than diffusion. The higher the rotating speed the faster solution flow, result in a thinner the mass transfer layer to produce a higher current density. By rotating at various rates, different electrochemical phenomena can be investigated, such as multi-electron transfer, the kinetics of electrons transfer, and electrochemical reaction mechanisms. In my experiments, the OER activities of COT NPs catalysts were measured using a rotating disc electrode (RDE) system (RRDE-3A, ALS, Co., Ltd., Tokyo, Japan) in a three-electrode cell. (Figure 2.2).

2.2.3 Electrochemical impedance spectroscopy (EIS).

EIS is an experimental method of characterizing impedance of a system opposing the flow of direct and/or alternating current with a range of frequencies. The frequency response of the impedance is dependent on the actual electrochemical system and its detailed configuration of electrical circuit elements such as resistor and capacitor and inductor. The data obtained by EIS can be plotted as a Nyquist plot composed of a real impedance part in x-axis and an imaginary part on y-axis indicating the resistant and capacitance of the working electrode, respectively, at various frequencies. Impedance spectra of many electrochemical systems can be fitted using an
equivalent RC circuit model, mostly, comprised of a resistor ($R_s$) representing the resistivity of the electrolyte between the working and reference electrode, a charge transfer resistance ($R_{ct}$) representing the catalytic charge transfer resistivity, and a capacitance (C) in parallel with the ($R_{ct}$) analogous to the double layer charging capacity of the solid–liquid junction. EIS is a powerful tool used broadly to study the presence of corrosion, quality of coating, and kinetics of electrochemical reaction. In our experiments, EIS of samples were measured in a three-electrode cell using a CHI 760C potentiostat at DC potential of 0 V versus Ag/AgCl and an AC potential frequency range of 10000-0.1 Hz with an amplitude of 10 mV in 0.1 M NaOH electrolyte.

2.3 Photoelectrochemical (PEC) Cell Test.

A PEC cell consist of a semiconductor as a photoanode that absorbs light, and a metal cathode, such as Pt. The electrodes are immersed in an electrolyte and connected by an external circuit. During water splitting process, water is oxidized at the anode and $H^+$ is reduced to form $H_2$. The water splitting efficiency can be determined by photocurrent density, especially, the photocurrent response to the incident light (action spectra) and I-V curves. The PEC photocurrent test system for Ag@Ag$_2$S/Ti@TiO$_2$ or Au@CdS/Ti@TiO$_2$ photoanode is exhibited in Figure 2.3. Action spectra and I–V curves were obtained using a home-built two electrode photocurrent testing system composed of a glass cell, a Keithley 2400 source meter, and a xenon arc lamp (Newport 66902) coupled with an Oriel 1.5 air mass (AM) spectral filter. An additional 400 nm long pass filter was used when only visible light was needed. For the action spectrum an additional monochromator (MD 1000, Optical Building Blocks) coupled to the solar simulator was added. The photocurrent was plotted versus the bias potential and wavelength of the incident light to generate I-V curves and action spectra respectively to study the photoelectrochemical properties of a photoanode.
Figure 2.2 Rotating disc electrode (RDE) system.
Figure 2.3 PEC testing system containing a light source, a monochromator, a two electrode PEC cell, and a Keithley source meter for I-V and action spectrum measurements.
2.4 Scanning Electron Microscopy (SEM).

SEM is used for imaging a solid specimen by focusing a high energy electron beam to scan the surface of a specimen. The electron beam is formed from a cathode filament and accelerated towards the specimen through applying a voltage. The accelerated electron beam in the SEM interacts with atoms in the specimen and generates significant amounts of kinetic energy signals, including secondary electrons, backscattered electrons, and X-rays. Secondary electrons are emitted from the surface of specimen, which is most commonly used for producing very high resolution images of morphologies, revealing details from 1-5 nm in size. Backscattered electrons are the electrons reflected by elastic scattering from a deeper location within the sample, and their signal intensity is related to the atomic number. Backscattered electrons are able to provide the distribution of different elements in the specimen by illustrating contrast of elements. When the incident electron beam excites the inner shell electrons in the specimen, the higher energy electrons fill the vacancies and release X-rays. The frequencies of X-rays are related to the different energy levels of the corresponding elements. Thus, these characteristic X-rays are used to analyze the composition and the quantities of elements in the specimen. In this dissertation, nanostructure morphologies and high-resolution images were characterized with a JEOL 7600F field emission scanning electron microscope.

2.5 Transmission electron microscopy (TEM).

TEM is a microscope technique for imaging that uses a high energy electron beam that is transmitted through and interacts with an ultra-thin sample. An image with significantly high magnification and resolution can be formed from the transmitted electrons and detected by a charge-coupled device (CCD) camera. Due to the short de Broglie wavelength of electrons, TEM is able to characterize a single column of atoms, which makes TEM as an ideal analysis method.
for morphological, compositional, and crystalline information. In this dissertation, TEM images were acquired using an FEI Tecnai F-20 transmission electron microscope.

2.6 X-Ray Diffraction (XRD).

X-ray diffraction crystallography is a technique can probe the order of atoms in a crystal lattice which can be used for identifying the phases of crystalline materials. X-rays are a form of electromagnetic radiation. X-ray’s energy can range from 120 eV to 120 keV and a wavelength ranging from 0.01 to 10 nanometers. This energy is generated by the colliding between high energy electrons and a metal target in a cathode ray tube. The wavelength of an X-ray is close to the lattice spacing that the crystalline atoms can diffract the incident X-rays into specific directions when the conditions satisfy the Bragg’s law: \( n\lambda = 2d \sin \theta \), where \( d \) is the lattice spacing, \( \theta \) is incident angles, \( n \) is the order of diffraction and \( \lambda \) is the wavelength of X-rays. By measuring the peak positions and intensities, the crystalline structure, as well as their chemical bonds can be determined. In my experiments the XRD patterns were obtained using a Bruker D2 or D8 phaser diffractometer.

2.7 X-ray Photoelectron Spectroscopy (XPS).

XPS is a surface sensitive quantitative analysis technique that is done by irradiating a solid material with a beam of X-ray, as well as directly probing the kinetic energies of the photoelectrons ejected by X-ray to identify the elements in the sample. An XPS can obtain the chemical information within 10 nm of the sample surface, such as the chemical composition, chemical states, chemical bonds and relative concentrations of elements. XPS results described in this dissertation was performed using a Kratos XIS 165 system.
REFERENCES


3. VISIBLE LIGHT DRIVEN PHOTOELECTROCHEMICAL PROPERTIES OF Ti@TiO$_2$ NANOWIRE ELECTRODES SENSITIZED WITH CORE-SHELL Ag@Ag$_2$S NANOPARTICLES

3.1 Introduction.

Coupling plasmonic nanostructures with photocatalytic semiconductors have been used to enhance activities of photocatalytic semiconductors. ¹⁻³ Core–shell nanostructures have been recently explored as an important structure to enhance the efficiency of charge collection by shortening the charge carrier transport distances.⁵⁻⁷ Photocatalytic performance of these core-shell NPs can be optimized by their constituent materials⁸⁻¹¹ as well as their core size, shell thickness, and core-to-shell ratio. ¹²⁻¹⁴ In order to maximize the surface enhanced efficiency, there are several technical challenges which need to be addressed: 1) How to maintain the stability of the plasmon nanostructures during the course of the photocatalytic reaction? 2) How to systematically control the thickness of the catalytic layer near a plasmonic antenna system in order to understand the distance dependence of the surface enhanced mechanism? 3) How to maximize the light absorption of the photocatalytic layer while maintaining its thickness suitable for optical plasmon enhancement? As shown in Figure 3.1, we present a nanostructured photoanode comprised of Ag@Ag$_2$S core-shell NPs attached to a Ti@TiO$_2$ NWs substrate. This large surface structures will greatly help address the challenging issues outlined above regarding plasmon enhanced photocatalytic applications. The Ag$_2$S shell thickness and Ag core size can be controlled by simply controlling the chemical reaction time with sulfur. Pronounced visible light responses are obtained and attributed to collective contribution of enhanced charge collection
configuration, large surface area of the nanostructured electrode and plasmon local field enhancement.

3.2 Results and Discussion.

3.2.1 Morphology and structural characteristics of Ti@TiO$_2$ NWs, Ag NP/Ti@TiO$_2$ NWs, and Ag@Ag$_2$S NPs /Ti@TiO$_2$ NWs.

Figure 3.2A shows the diameters of the synthesized Ti@TiO$_2$ NWs varying from 50 to 100 nm and lengths of up to 500 nm. The estimated surface coverage of Ti@TiO$_2$ NWs from SEM is about $6 \times 10^9$ per 1 cm$^2$. The estimated oxide layer from high resolution TEM is around 2 nm with some variation from wire to wire. Figure 3.2B shows a top-view SEM image of Ti@TiO$_2$ NWs deposited with Ag NPs obtained by Tollens reaction. Small Ag NPs with sizes around 25 nm in diameter are densely coated onto the Ti@TiO$_2$ NWs with their density and sizes determined by the deposition time. The top-view of Ag@Ag$_2$S/Ti@TiO$_2$ NWs obtained by dipping a Ag/Ti@TiO$_2$ NWs electrode in S/DMSO solution for 10 sec at 100°C is shown in Figure 3.2C. Due to its robustness and low temperature, the simple dipping method in S/DMSO solution provides a dense shell of Ag$_2$S on top of Ag NPs. SEM studies show no significant morphological difference before and after converting Ag NPs to Ag$_2$S NPs. The presence of Ag@Ag$_2$S NPs is also confirmed by scanning transmission electron microscopy (STEM) as shown in Figure 3.3.

The Ag$_2$S shell serves as a visible-response photocatalytic layer and an insulating protection layer for the Ag core. To confirm how well the Ag$_2$S shell would prevent corrosion of the Ag core, the obtained Ag@Ag$_2$S NPs have been tested using linear sweep voltammetry in 0.1 M NaOH. An anodic peak is expected for the bare or partly exposed Ag NPs in NaOH solution due to the formation of Ag$_2$O as shown in Figure 3.4. Longer dipping time for Ag NPs in S/DMSO solution yield lower anodic current; there is no Ag anodic current observed after dipping the Ag NPs longer than 5 sec, indicating the Ag NP cores are fully covered by a Ag$_2$S layers.
Figure 3.1 Schematic Ti@TiO₂ NW electrodes modified with core-shell Ag@Ag₂S NPs for surface enhanced photoelectrochemical studies under visible light. Reprinted with permission from The Journal of Physical Chemistry B 118 (49), 14037-14046. Copyright 2014 American Chemical Society.
Figure 3.2 Typical SEM images of bare Ti@TiO$_2$ NWs prepared on Ti substrate using hydrothermal reaction (A), Ti@TiO$_2$ NWs coated with Ag (B), and Ag@Ag$_2$S NPs (C) using electroless deposition method. Reprinted with permission from The Journal of Physical Chemistry B 118 (49), 14037-14046. Copyright 2014 American Chemical Society.
Figure 3.3 Typical STEM image of Ag@Ag$_2$S particles scratched from a Ag@Ag$_2$S/Ti@TiO$_2$ nanostructured electrode. Reprinted with permission from The Journal of Physical Chemistry B 118 (49), 14037-14046. Copyright 2014 American Chemical Society.
Figure 3.4 Anodic polarization curves of freshly-prepared Ag/Ti@TiO$_2$ NW electrodes in 0.1 M NaOH before and after being treatment with S/DMSO solution for 1, 3, 5, and 10 sec. Scan rate: 0.2V/s. Reprinted with permission from The Journal of Physical Chemistry B 118 (49), 14037-14046. Copyright 2014 American Chemical Society.
The anodic current turn-on potential $E_{on}$, which is defined by the potential where the anodic current starts rising, increases when the substrate dipping time increases from 1 sec to 5 sec and is accompanied with a decrease in the anodic current, indicating the coated Ag NPs are resistive to corrosion in NaOH. This is essential for the direct observation of possible surface enhanced photoelectrochemical studies because a background current as low as possible is needed from the Ag NP electrode while benefiting from its plasmon enhancement under visible light irradiation. We also ensured the Ti@TiO$_2$ NWs are coated with thin layer of TiO$_2$ to decrease the dark current density as we scan the potential in positive direction for following photoelectrochemistry studies. In addition, the Ag@Ag$_2$S core-shell structures were also confirmed by XPS. The XPS datas for Ag and Ag@Ag$_2$S are illustrated in Figure 3.5. The peak positions at 368.5 eV and 374.5 eV are attributed to the Ag 3d$_{5/2}$ and 3d$_{3/2}$ core levels. These two peaks shift to 368.1 eV and 374.1 eV, respectively, after converted the surface of Ag NPs to Ag$_2$S, after 10 sec dipping in S/DMSO solution. This result is consistent with the previously reported data for Ag$_2$S, and further confirms that the Ag NP cores are fully coated by a Ag$_2$S shells. To study the crystallinity, lattice spacing, core size and shell thickness of Ag@Ag$_2$S, XRD, high resolution TEM and EDS line profile been used to investigate the properties. Figure 3.6 shows the XRD patterns of bare Ti@TiO$_2$ NWs, Ag NPs/Ti@TiO$_2$ NWs and Ag@Ag$_2$S NPs/Ti@TiO$_2$ NWs. XRD of the bare Ti@TiO$_2$ NWs show diffraction peaks of Ti metal substrate and both of the two phases of TiO$_2$, anatase and rutile. After coating with Ag NPs, two Ag diffraction peaks, $<200>$ and $<220>$, are observed at 44° and 64°, respectively. After converting the Ag NPs to Ag@Ag$_2$S NPs, four Ag$_2$S diffraction peaks are observed at 28.7°, 31.2°, 33.3° and 34.1°, corresponding to Ag$_2$S $<111>$, $<-112>$, $<120>$ and $<-121>$, respectively. Other peaks from Ag, Ti and TiO$_2$
remain after the Ag\textsubscript{2}S converting, further confirming that Ag and Ag\textsubscript{2}S coexist on the Ti@TiO\textsubscript{2} NW electrode.

To resolve the Ag@Ag\textsubscript{2}S core-shell structure and measure the core size and shell thickness, high resolution TEM was used to determine the lattice spacing and spatial distribution of bare Ag and Ag@Ag\textsubscript{2}S NPs. The high resolution TEM images of Ag and Ag@Ag\textsubscript{2}S are shown in Figure 3.7 A and B for more detailed structural information. The bare Ag NP with size of 22 nm in diameter shows a lattice spacing of 2.3 Å, corresponding to the $<111>$ plane of Ag. After treating with S/DMSO solution for 10 sec, a single Ag@Ag\textsubscript{2}S NP is imaged and found the lattice spacing of 2.8 Å attributed to $<1\overline{2}2>$ plane of Ag\textsubscript{2}S. The Ag core located near the side of a Ti@TiO\textsubscript{2} NW has a lattice spacing of around 2.04 Å, corresponding to the $<200>$ plane of Ag. The asymmetric spatial distribution of Ag\textsubscript{2}S shell thickness with the thickest portion pointing far away from the surface of the Ti@TiO\textsubscript{2} NW is attributed to the limited mass transfer of sulfur to the interior of the Ti@TiO\textsubscript{2} NWs and Ag NPs. To further probe the concentration spatial distribution at the nanometer scale for S and Ag in single core-shell unit, combined STEM and EDS line profile methods are used to probe the element spatial distribution with electron beam scan across a selected Ag@Ag\textsubscript{2}S NP. As shown in Figure 3.7D, the black and red patterns show concentration profiles of S and Ag across a selected Ag@Ag\textsubscript{2}S particle with size of 23 nm in diameter indicated by the red arrow in Figure 3.7C. For the 23 nm particle, the shell thickness is about 8 nm thick, and the core size is about 15 nm. Based on the TEM images and EDS line profile data, Ag@Ag\textsubscript{2}S core-shell structures prepared with a 10 sec dipping time in S/DMSO solution produces NPs with a top shell thickness around 8 nm.
3.2.2 Absorption spectra and average Ag\textsubscript{2}S shell thickness measurement.

To eliminate the strong surface plamonic effect of Ti@TiO\textsubscript{2} NWs, UV-Vis absorption spectra of Ag and Ag\textsubscript{2}S are obtained on glass slides to characterize the light absorption characteristics of the nanostructured Ag\textsubscript{2}S and bare Ag NPs. As shown in Figure 3.8, the Ag NPs deposited on glass substrate by Tollens reaction has a major plasmon absorbance peak near 450 nm. After converting Ag NPs to Ag\textsubscript{2}S NPs, the plasmon peak was dramatic decreased and accompanied with an obvious absorption peak broadening in both the UV and visible light region shorter than 600 nm. The extrapolated band gap $E_{bg}$ of Ag\textsubscript{2}S is estimated to be around 2 eV. Control of the shell thickness for the Ag@Ag\textsubscript{2}S NPs is obtained by varying the dipping time of Ag NPs in S/DMSO solution. Yet analysis the average shell thickness of all NPs using high resolution TEM would be time prohibitive. As shown in Figure 3.9, to determine the average shell thickness, the total charge for reduction of Ag\textsubscript{2}S layer to Ag is measured and used to calculate the thickness of Ag\textsubscript{2}S layer by following the Faraday’s law. The 25 nm of the average core-shell NPs size were obtained from previous TEM study for the shell thickness calculation. The collected total charge of Ag\textsubscript{2}S reduction reaction increases with the dipping time; the reduction peak position shifts towards a more negative potential because of the increase in the film resistivity with the increase of the shell thickness. The 25 nm Ag NPs will be total converted to Ag\textsubscript{2}S when the dipping time longer than 100 sec. Ag\textsubscript{2}S shell thickness increases from 5 nm to 25 nm when the dip coating time increases from 5 to 100 sec as shown in the inset of Figure 3.9. Especially, a 8 nm of shell thickness is achieved when the dipping time is 10 sec, which comes up to the high resolution TEM results.
Figure 3.5 XPS spectra of Ag/Ti@TiO$_2$ NWs and Ag$_2$S/Ti@TiO$_2$ NWs showing shift in binding energy of Ag 3d peaks. Reprinted with permission from The Journal of Physical Chemistry B 118 (49), 14037-14046. Copyright 2014 American Chemical Society.
Figure 3.6 XRD patterns of Ti@TiO$_2$ NWs, Ag/Ti@TiO$_2$ NWs, and Ag@Ag$_2$S/Ti@TiO$_2$ NWs. Reprinted with permission from The Journal of Physical Chemistry B 118 (49), 14037-14046. Copyright 2014 American Chemical Society.
Figure 3.7 High resolution TEM images of a selected single Ag (A) and Ag@Ag\(_2\)S (B) NPs detached from a Ti@TiO\(_2\) NW electrode with lattice structure and spacing labeled in the Figures. STEM image of a selected Ag@Ag\(_2\)S NP attached to a Ti@TiO\(_2\) NW and element concentration profiles of S and Ag are shown in panel C, and D, respectively. Reprinted with permission from The Journal of Physical Chemistry B 118 (49), 14037-14046. Copyright 2014 American Chemical Society.
Figure 3.8 UV-Vis spectra of Ag NPs before (black) and after (red) treatment with S/DMSO solution to form Ag$_2$S NPs. The spectra were taken for Ag NPs prepared on bare cover glass rather than Ti@TiO$_2$ NW substrate in order to eliminate strong light scattering and background signal. Reprinted with permission from The Journal of Physical Chemistry B 118 (49), 14037-14046. Copyright 2014 American Chemical Society.
Figure 3.9 Cathodic reduction behavior of Ag\textsubscript{2}S shell of Ag@Ag\textsubscript{2}S/Ti@TiO\textsubscript{2} NW electrode for estimating the average thickness of the shell thicknesses obtained by controlling the dipping time in DMSO/S solution. The total reduction charge is calculated and converted to Ag\textsubscript{2}S shell thickness as shown in inset. Reprinted with permission from The Journal of Physical Chemistry B 118 (49), 14037-14046. Copyright 2014 American Chemical Society.
3.2.3 Photoelectrochemistry results and enhancement mechanism.

To investigate the effect of coating with Ag NPs and Ag@Ag$_2$S core-shell NPs on the photoelectrochemical activities of the Ti@TiO$_2$ NWs electrodes, we measured the photocurrents of Ti@TiO$_2$ NWs, Ag/Ti@TiO$_2$ NWs, and Ag@Ag$_2$S/Ti@TiO$_2$ NWs with various shell thicknesses. As shown in Figure 3.10, the Ti@TiO$_2$ NW electrode shows a better photocurrent response in the UV region, with barely any photocurrent response in the visible light region. In contrast, the Ag/Ti@TiO$_2$ NWs electrode exhibit pronounced photocurrent action under visible light illumination above 400 nm and extended to 550 nm. The visible light response at the surface plasmon resonance region of Ag NPs in NaOH electrolyte is attributed to the hot electron injection from excited Ag NPs to Ti@TiO$_2$.\textsuperscript{44} The photocurrent intensity decrease in the UV area upon Ag NP coating due to the decreased UV light absorption by the underlying Ti@TiO$_2$ NWs in the presence of Ag NPs, which partially blocks the UV light illumination on the Ti@TiO$_2$ NWs. After coating the Ag NPs with Ag$_2$S layer, the obtained Ag@Ag$_2$S/Ti@TiO$_2$ photoelectrode shows an enhanced and broad photocurrent response to visible light in contrast to the pristine Ag/Ti@TiO$_2$ photoelectrode. In the UV region, increase in the amount of Ag$_2$S results in an enhanced photocurrent intensity, due to the UV absorbance of Ag$_2$S. In the visible region, the photocurrent increases with increasing thickness of Ag$_2$S shell and then decreases if the Ag NPs are over-developed in the S/DMSO solution, which reduce the surface plasmon enhancement of Ag NPs. As shown in Figure 3.11, visible light response of bare Ag NPs are sensitive to the particle size and their coverage on Ti@TiO$_2$ NWs. Peak broadening and smaller amplitude photocurrent appeared when the deposition time longer than 1.5 min due to plasmon coupling and increase in light reflection by the dense silver nanoparticles (Figure 3.11 A). Another notable feature of the action spectra is that the peak of Ag is disappeared and only single
peak in visible region is obtained for Ag$_2$S after extended period of sulfurization treatment (Figure 3.11 B), and the peak position shifts to longer wavelength as we increase the silver particle coverage and sizes as shown in Figure 3.11 C.

Figure 3.12 shows the I-V curves of the photoelectrodes under visible light irradiation from a solar simulator with its UV light removed by a broad-band filter (>400 nm). Photocurrent density of Ag/Ti@TiO$_2$ NWs electrode is 39 μA/cm$^2$ at 0.2 V, which is slightly higher than 32 μA/cm$^2$ of the bare Ti@TiO$_2$ NWs electrode. After coating Ag$_2$S layer, Ag@Ag$_2$S/Ti@TiO$_2$ show improved photocurrent and the amplitude of enhancement depends on the Ag$_2$S shell thickness. About two times increase in photocurrent is obtained for Ag@Ag$_2$S NP electrodes with the Ag$_2$S shell thickness of 5 nm and 8 nm. Further increase of shell thickness would yield smaller amplitude of increase as shown by photocurrent density of Ag@Ag$_2$S with 14 nm and 20 nm Ag$_2$S layer.
Figure 3.10 Action spectra of photoanodes comprised of Ti@TiO$_2$ NWs and Ag/Ti@TiO$_2$ NWs and Ag@Ag$_2$S/Ti@TiO$_2$ NWs with various shell thickness. Inset is the zoom-in figure showing only visible light region of the action spectra. Reprinted with permission from The Journal of Physical Chemistry B 118 (49), 14037-14046. Copyright 2014 American Chemical Society.
Figure 3.11 (A) action spectra of bare Ag/Ti@TiO$_2$ in (with different length of silver mirror reaction time) prior to be sulfurized; (B) action spectrum of Ag$_2$S/Ti@TiO$_2$ in UV and visible light area (1.5 min for silver mirror reaction); and (C) Action spectra of Ag$_2$S/Ti@TiO$_2$ in visible light region obtained by complete sulfurization of silver film grown with extended silver mirror reaction time indicated in the figure. The sulfurization was done by dipping the silver film in S/DMSO longer than 3 min to convert Ag to Ag$_2$S. Reprinted with permission from The Journal of Physical Chemistry B 118 (49), 14037-14046. Copyright 2014 American Chemical Society.
Figure 3.12 Dark and light I-V curves of photoanodes comprised of Ti@TiO$_2$ NWs (A) and Ag/Ti@TiO$_2$ NWs (B), Ag@Ag$_2$S/Ti@TiO$_2$ NWs with 5 (C), 8(D), 14(E), and 20 (F) nm. Photocurrent was taken with an AM1.5 solar simulation with its UV light modified with a > 400 nm long pass filter to remove UV excitation. The I-V curves were taken in a two electrode system with a Pt counter electrode was used. Reprinted with permission from The Journal of Physical Chemistry B 118 (49), 14037-14046. Copyright 2014 American Chemical Society.
Table 3.1 Estimated photocurrent peak positions ($\lambda_1$ and $\lambda_2$) as indicated in Figure 9 and corresponding peak current without background current subtraction, and dependence on growth times of silver film and sulfurization. Reprinted with permission from The Journal of Physical Chemistry B 118 (49), 14037-14046. Copyright 2014 American Chemical Society.

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Table 3.1 summarizes photocurrent measurable peak positions and their relative photocurrent intensities from samples obtained under various conditions of silver deposition, sulfurization time. The enhancement photocurrent with the 1.5 min silver mirror reaction and 0-40 sec dipping time from entry 1 to 5 is due to the Ag surface plasmon enhanced photoactivity of Ag$_2$S. This is confirmed by the presence of the first photocurrent peak $\lambda_1$ near 460 nm, corresponding to the plasmonic absorption of the silver core (Figure 3.8). Hot electron injection from the Ag is unlikely because of the complete coating of the Ag$_2$S layer as evidenced by our previous TEM, XPS and electrochemical reduction of Ag$_2$S shell studies. 10 sec dipping time, corresponding to shell thickness of 8 nm is a short distance to produce improved photoexcitation showed the optimal photocurrent intensity because of the local field effect of the silver core architecture. On the other hand, the Ag cores also have excellent electrical contact to the Ti@TiO$_2$ NWs as shown by the anodic polarization curve in Figure 3.4, therefore electron-hole pairs can separate more effectively at the interface of Ag$_2$S and Ag prior to be collected by the Ti@TiO$_2$ NWs. Moreover, a large number of Ag NPs could be deposited on Ti@TiO$_2$ NWs, due to the high surface area of NWs structure. This structure yields a high optical density for effective light absorption by increasing the average effective optical path length, causing an increase in the population of the excited states in the ultra-thin Ag$_2$S shell layer. Further growth of Ag$_2$S shell thickness leads to a small Ag core size, the thick Ag$_2$S shell will block the light absorption on Ag core that will not provide plasmon enhanced photocurrent. Ag@Ag$_2$S NPs always produces more photocurrent than bare Ag NPs (entry 6-9 of Table 3.1) because of the semiconductor characteristic of Ag$_2$S itself. The quantum effect of Ag$_2$S is also evidenced by the dependence of photocurrent of Ag$_2$S NPs size and coverage as shown by entry 10-14 of Table.
3.1. Large Ag$_2$S particle size and higher coverage produce red-shift in photocurrent peak from 470 nm to 620 nm and photocurrent decrease from 0.15 $\mu$A to 0.03 $\mu$A.

3.2.4 Ag$_2$S photoanode Stability testing.

To determine the stability of Ag@Ag$_2$S NPs for long-term photocatalytic applications, we tested their temporal electrochemical stability properties in various electrolytes and at various electrode potentials. Stability testing results of Ag@Ag$_2$S/Ti@TiO$_2$ photoanode in NaOH, sodium citrate, and mixture of sulfate and sulfide electrolytes are shown in Figure 3.13 by repeating the action spectra scanning under constant potential. Photocurrent in the visible light region of 450 nm decreases over the cycles in NaOH and sodium citrate as shown in Figure 3.13A and 13B, which due to the oxidation of silver and silver sulfide via half reaction $2\text{Ag} + 2\text{OH}^- - 2e^- \rightarrow \text{Ag}_2\text{O} + \text{H}_2\text{O}$ and/or $\text{Ag}_2\text{S} + 2\text{OH}^- - 2e^- \rightarrow 2\text{Ag}_2\text{O} + \text{S} + \text{H}_2\text{O}$ to form Ag$_2$O layer. In contrast, photocurrent of Ag@Ag$_2$S/Ti@TiO$_2$ NWs in mixed sulfate and sulfide electrolyte is very stable as shown in Figure 3.13C because S$^{2-}$ works as a holes sacrifice can fill the holes in Ag$_2$S upon photoexcitation. Figure 3.13D shows the variation of Ag@Ag$_2$S photocurrents at 465 nm over the action scanning cycles in the three different electrolytes. It clearly shows that photocurrent decreased 37% and 18% in NaOH and sodium citrate, respectively, and no obvious photocurrent decrease is observed in sulfide and sulfate electrolyte. To better understand the function of the Ag$_2$S shell of a Ag@Ag$_2$S/Ti@TiO$_2$ electrode, we repeat the same stability testing experiment for bare Ag/Ti@TiO$_2$ NWs electrode. Figure 3.14 shows stability results of Ag/Ti@TiO$_2$ in three different electrolytes. Similar to Ag@Ag$_2$S/Ti@TiO$_2$ electrode, bare Ag NP electrodes show decrease photocurrent intensity in the visible light region of 460 nm over the cycles in NaOH and sodium citrate due to the oxidation of silver in basic aqueous solution, although the photocurrent density is less than Ag@Ag$_2$S/Ti@TiO$_2$ electrode. Ag/Ti@TiO$_2$
electrode showed very large background current in mixed electrolyte of sulfide and sulfate because of the chemical reaction on Ag in the presence of sulfide as shown in Figure 3.14C. A stable action spectrum was obtained after 16 cycles because of the formation of a stable Ag$_2$S layer. As summarized in Figure 3.14D, the visible light photocurrent of bare Ag/Ti@TiO$_2$ showed 35% decrease in NaOH and 11% decrease in sodium citrate. It should also be noted that Ag$_2$O does not generate appreciable photocurrent at a bias as low as 0.2 V unless a high potential is applied under light excitation to produce AgO. 17,18 For the dark current, it is a well-known that silver particles can be oxidized during anodic polarization. As shown in Figure 3.15, there are two main oxidation peaks generally observed in the linear sweep and cyclic voltametry curve of Ag. The first current peak at 0.6 V vs NHE is due to the oxidation of Ag to Ag$_2$O and the second current peak is attributed to the generation of AgO around 0.9 V vs NHE. However, after the surface of Ag converted to Ag$_2$S layer there is no Ag oxidation peak observed at a potential <1.0V. Anodic current can be observed for Ag$_2$S electrode at a potential >1.0V due to the oxidation of S$^{2-}$ to S. All these observed redox potentials of bare silver, silver sulfide are listed in an energy diagram in Figure 3.16.
Figure 3.13 Action spectra cycles of Ag@Ag$_2$S/Ti@TiO$_2$ NWs (10 nm shell thickness) in (A) 0.1 M NaOH, (B) 0.1 M sodium citrate (Na$_2$C$_6$H$_5$O$_7$), (C) 0.1 M Na$_2$SO$_4$ + 0.05 M Na$_2$S, and (D) the photocurrent at 465 nm with various cycle, bias potential is 0.05V. Reprinted with permission from The Journal of Physical Chemistry B 118 (49), 14037-14046. Copyright 2014 American Chemical Society.
Figure 3.14 Action spectrum cycles of Ag/Ti@TiO₂ NWs in (A) 0.1 M NaOH, (B) 0.1 M Na₃C₆H₅O₇, (C) 0.1 M Na₂SO₄ + 0.05 M Na₂S, and (D) the photocurrent at 465 nm with different cycle, the bias potential is 0.05V. Reprinted with permission from The Journal of Physical Chemistry B 118 (49), 14037-14046. Copyright 2014 American Chemical Society.
Figure 3.15 Linear scanning voltammetry of Ag/Ti@TiO$_2$ NWs and Ag@Ag$_2$S/Ti@TiO$_2$ NWs (10 nm shell thickness) in 0.1 M NaOH. Scan rate: 50 mV/sec. Reprinted with permission from The Journal of Physical Chemistry B 118 (49), 14037-14046. Copyright 2014 American Chemical Society.
Figure 3.16 The band potential of TiO$_2$, Ag$_2$S and the oxidation potential of Ag$_2$O/Ag, AgO/Ag$_2$O, and O$_2$/H$_2$O in basic solution. Reprinted with permission from The Journal of Physical Chemistry B 118 (49), 14037-14046. Copyright 2014 American Chemical Society.
3.2.5 AC impedance and Mott–Schottky plot.

To elucidate the photo-induced charge transfer processes and to obtain more quantitative information about the photoanode, electrochemical AC impedance spectroscopy (EIS) has been studied. Figure 3.17 shows the Nyquist plots of the Ag@Ag₂S/Ti@TiO₂ NWs (8 nm Ag₂S shell thickness) electrode in the dark, under visible light irradiation (>400 nm), and a full simulated solar spectrum (visible light + UV light). Impedance spectra of other control electrodes, such as bare Ti@TiO₂ NWs, Ag@Ag₂S/Ti@TiO₂ NW (20 nm Ag₂S shell thickness) electrodes, are shown in Figure 3.18. All AC impedance spectra are fitted using an equivalent RC circuit model, shown in Figure 3.17, comprised of a resistor (Rₛ) representing the resistivity of the electrolyte between the working and reference electrode, a charge transfer resistance (Rₜ) representing the photo-induced charge transfer resistivity, and a capacitance (C) in parallel with the (Rₜ) analogous to the double layer charging capacity of the solid-liquid junction. All fitting results are summarized in Table 2. There is no major differences in Rₛ and C for all three electrodes. For the Ti@TiO₂ NW electrode, Rₜ is smaller under visible irradiation than in the dark due to the photocatalytic events that provide photocurrent from the photoanode to the Ti substrate. Rₜ is further decreased under full solar irradiation because of the greater UV sensitivity of the Ti@TiO₂ NW electrode. For the Ag@Ag₂S /Ti@TiO₂ (8 nm) photoanode, Rₜ under visible light irradiation is only about 50 % of the Ti@TiO₂ photoanode, and decreases 30% in contrast to the Ag@Ag₂S/Ti@TiO₂ (20 nm), indicating a more effective visible light induced photoelectrochemical activity due to the localized surface plasmon enhancement of the Ag core. Rₜ of Ti@TiO₂ after adding UV light is 9585 Ω, which is smaller than Ag@Ag₂S/Ti@TiO₂, because of the strong UV sensitivity of TiO₂.
Figure 3.17 Nyquist plots of Ag@Ag$_2$S/Ti@TiO$_2$ NW (8nm) photoanode in dark, under visible irradiation (> 400 nm), and 1 sun solar (AM 1.5) irradiation, respectively. Inset is the equivalent circuit used to fit the experimental data. Fitting results are shown in Table 2. Reprinted with permission from The Journal of Physical Chemistry B 118 (49), 14037-14046. Copyright 2014 American Chemical Society.
Figure 3.18 Nyquist plots of Ag@Ag$_2$S /Ti@TiO$_2$ with 20 nm shell (A), and bare Ti@TiO$_2$ NWs(B), in dark, under visible irradiation (> 400 nm), and 1 sun solar (AM 1.5) irradiation, respectively. Fitting results are shown in Table 2. Reprinted with permission from The Journal of Physical Chemistry B 118 (49), 14037-14046. Copyright 2014 American Chemical Society.
Figure 3.19 Mott–Schottky plots obtained at 1000 HZ in dark from a bare Ti@TiO₂ NW electrode in contrast to Ag@Ag₂S/Ti@TiO₂ NWs. Reprinted with permission from The Journal of Physical Chemistry B 118 (49), 14037-14046. Copyright 2014 American Chemical Society.
Table 3.2 AC impedance results obtained by fitting the experimental data fitting in Figure 14 and Figure S5, and carrier density results calculated from Figure 15. Reprinted with permission from The Journal of Physical Chemistry B 118 (49), 14037-14046. Copyright 2014 American Chemical Society.

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Visible

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AM 1.5 UV+Vis

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Carrier Density

| 7.14x10<sup>20</sup>/cm<sup>3</sup> | 2.78x10<sup>20</sup>/cm<sup>3</sup> | 1.24x10<sup>19</sup>/cm<sup>3</sup> |
Figure 3.19 shows Mott–Schottky plots at 1000 HZ, which are used to determine the flat band potential ($E_{fb}$) and carrier density ($N$) of the Ti@TiO$_2$ NW and Ag@Ag$_2$S/Ti@TiO$_2$ (8 nm and 20 nm) electrodes in order to estimate the conduction band position and the conductivity of the photoanode, respectively. The estimated $E_{fb}$ values of Ti@TiO$_2$ NW, Ag@Ag$_2$S /Ti@TiO$_2$ (8 nm), and Ag@Ag$_2$S /Ti@TiO$_2$ (20 nm) electrodes are very close that around -0.5 V vs. NHE, indicating that the $E_{fb}$ is still determined by the thick Ti@TiO$_2$ NW electrode which has its conduction band aligned with the conduction band of Ag@Ag$_2$S NPs for effective charge injection upon light irradiation. The estimated $N$ values obtained from the slopes of the Mott–Schottky plots are summarized in Table 3.2. The $N$ of Ag@Ag$_2$S /Ti@TiO$_2$ (8 nm) is found to be around 3 times higher than Ag@Ag$_2$S /Ti@TiO$_2$ (8 nm) and 60 times higher than Ti@TiO$_2$ NW. The higher number of carriers of Ag@Ag$_2$S/TiO$_2$ is from the strong surface plasmon enhancement of Ag core to increase the photocatalytic activity of the Ag$_2$S shell.

3.3 Conclusions.

A model nanostructured electrode of Ag@Ag$_2$S/Ti@TiO$_2$ NW is reported for surface plasmon enhanced photocatalytic process. Structural and detailed electrochemical studies are performed in order to confirm the core-shell structure of Ag@Ag$_2$S formed by a robust and simple dipping method in S/DMSO solution. An optimal Ag$_2$S shell thickness of 8 nm is used to demonstrate the concept of a surface plasmon enhanced photoelectrochemical reaction at the nanostructured electrode system. Electrochemical polarization curves show that the Ag$_2$S shell serves not only as a photoactive layer, but also an ideal insulating layer to prevent corrosion of the Ag core structure. The enhanced visible light response of the core-shell structure is attributed to (1) plasmon induced local field enhancement, (2) a large interface area for interfacial charge
transfer, and (3) effective charge collection of Ti@TiO$_2$ NWs. Further efforts are needed to quantitatively analyze these contribution factors.
REFERENCES


(9) Park, G.; Lee, C.; Seo, D.; Song, H. Full-Color Tuning of Surface Plasmon Resonance by Compositional Variation of Au@Ag Core–Shell Nanocubes with Sulfides. *Langmuir* 2012, 28, 9003-9009.


4. SYNTHESIS OF Au@CdS/Ti@TiO$_2$ NWs AND CdS/Ti@TiO$_2$ NWs PHOTOANODE FOR SURFACE ENHANCED VISIBLE LIGHT SENSITIVE PHOTOCATALYST

4.1 Introduction.

Nanostructured n-type CdS is a typical visible light photocatalyst because its a band gap of 2.4 eV and its band positions are suitable for water splitting. CdS has been considered to be an promising visible light active photocatalyst for photocatalytic water splitting and pollutant degradation. 1-3 However, it is well known that there are two main inherent defects in CdS: the low separation efficiency of photogenerated electron-hole pairs and its unstability in aqueous media during photocatalytic process. 4,5 Many attempts have been made to increase its photoactivity and photostability. For example, changing the composition of CdS with other semiconductor and using cocatalysts and/or sacrificial reagents are commonly used methods to address these issues. 6-8 Recently, metal plasmonic nanostructures have also been used to enhance the photocatalytic efficiency of CdS. 9,10 Herein, nanostructured Au electrode is used to enhance visible-light-driven photoelectrochemistry at CdS/TiO$_2$ NWs photoanode.

4.2 Results and Discussion.

4.2.1 Electrodeposition of Au NPs. 11

As shown in Figure 4.1, because of the AuCl$_4^-$ reduction, cathodic current density increases follow the negative scan direction, and there is no obvious reversible oxidation peak, indicating the deposition of Au onto Ti@TiO$_2$ NW surface. Two electrodeposition potentials were selected based on the CV to grow polydisperse Au NPs on the Ti@TiO$_2$ NW electrode, which is located at $E_1$ (-1.2 V vs. Ag/AgCl) and $E_2$ (-0.7 V vs. Ag/AgCl), respectively. As shown in Figure 4.2 $E_1$ and $E_2$ were pulse potentials for Au NPs growth on a Ti@TiO$_2$ NW substrate. $E_1$ is a potential
with large over potential for gold nucleation sites. E2 is a potential close to the thermal dynamic potential of gold deposition for growing the nucleation sites to large gold nanoparticles without developing new nucleation sites. The duration time $t_1$ and $t_2$ for $E_1$ and $E_2$, respectively, were adjusted to control the NP density and size. The density of Au NPs would be controlled by either increasing $E_1$ and/or $t_1$. Large Au NP size can be obtained by increasing the duration time of $t_2$. In my experiments, $E_1$ is selected near -1.2 V (vs. Ag/AgCl) for 1.5 sec, and $E_2$ is selected lower than the thermal dynamics potential of gold deposition at -0.5 V vs. Ag/AgCl for 300 sec. The synthesis of CdS on Au NPs is described in section 2.1.4.

4.2.2 Morphology of Au@CdS/Ti@TiO2 NWs and CdS/Ti@TiO2 NWs.

Figure 4.3 shows a top-view SEM images of Au@CdS/Ti@TiO2 NWs (A) and CdS/Ti@TiO2 (B) and the corresponding EDS. The length of Ti@TiO2 is estimated to be around 500 nm, and the edge length varies from 20 nm to 100 nm. As shown in Figure 4.3 A, polydisperse Au NPs from 20 nm to 80 nm are electrodeposited onto the Ti@TiO2 NWs. 10 nm CdS NPs were uniformly coated on Au/Ti@TiO2 NWs (Figure 4.3 A) and Ti@TiO2 NWs (Figure 4.3 B) respectively to form a heterojunction structure.

4.2.3 Photoelectrochemistry results and enhancement mechanism.

To investigate the effect of Au NPs on the photoelectrochemical activities of the CdS/Ti@TiO2 heterjunction electrodes, we measured the photocurrents of CdS/Ti@TiO2 NWs and Au@CdS/Ti@TiO2 NWs. As shown in Figure 4.4 (A), the CdS/Ti@TiO2 NWs electrode shows a higher photocurrent in the 330-400 nm wavelength region than Au@CdS/Ti@TiO2 NWs. Au NPs deposition leads to the photocurrent intensity decrease in the UV area, because the presence of Au NPs partially blocks the UV light absorption by the underlying Ti@TiO2 NWs. In contrast, the Au@CdS/Ti@TiO2 NWs electrode exhibit obviously higher photocurrent action
in the visible light region that above 500 nm and extended to 700 nm. Figure 4.4 (B) shows the I-V curves of the photoanodes under visible light irradiation from a solar simulator with its UV light removed by a broad-band filter (>400 nm). Photocurrent density of Au@CdS/Ti@TiO$_2$ NWs electrode is 23.8 A/cm$^2$ at 0 V, which is 4.9 A/cm$^2$ higher than 18.9 A/cm$^2$ of the CdS/Ti@TiO$_2$ NWs electrode. The enhanced visible light response at the surface plasmon resonance region of Au NPs in sodium acetate electrolyte is attributed to the hot electron injection from excited Au NPs to Ti@TiO$_2$, as well as surface plasmon resonance-induced electromagnetic field enhancement. Further, the high conductivity for efficient charge collection over Au NPs lead to a higher e--h+ pair generation and efficient charge separation of the PEC system.

4.3 Conclusions.

A nanostructured heterojunction photoelectrode of Au@CdS/Ti@TiO$_2$ NW is prepared using combined methods of hydrothermal reaction, electroless deposition and CBD deposition to compare with CdS/Ti@TiO$_2$ for surface plasmon enhanced photocatalytic study. Photoelectrochemical studies are performed that enhancement of photocurrent in visible light area in the presence of Au NPs can be observed due to both the high conductivity for efficient charge collection, high electron-hole pair generation and separation efficiency, and surface plasmon resonance of Au NPs.
Figure 4.1 Cyclic voltammetry of Ti@TiO$_2$ NW electrode in 0.1 M NaCl aqueous solution containing 1.0 mM AuCl$_3$. Scan rate: 100 mV/s.
Figure 4.2 Two-stage stepwise potential function applied to the Ti@TiO$_2$ NW electrode for polydisperse Au NP growth and typical current response. $E_1 = -1.2$ V and $E_2 = -0.5$ V (vs Ag/AgCl) are selected potentials from panel B for growing nucleation sites of Au and particle growth with duration time $t_1$ and $t_2$, respectively.
Figure 4.3 SEM images and EDS of Au@CdS/Ti@TiO$_2$ NWs (A) and CdS/Ti@TiO$_2$ NWs (B).
Figure 4.4 Photocurrent action spectra and I-V curve (400 nm long pass filter) of CdS/Ti@TiO₂, Au@CdS/Ti@TiO₂. 0.1 Sodium acetate, Pt wire counter electrode.
REFERENCES


5. LOW COST NanoCOT ELECTRODE MADE OF CARBON, OXYGEN, TITANIUM FOR EFFICIENT CATALYTIC WATER OXIDATION

5.1 Introduction.

The NanoCOT electrode is a low-cost electrode material containing carbon, oxygen and titanium, and has a nanostructured surface with excellent activity for OER in alkaline solutions. As shown in Figure 5.1, NanoCOT is synthesized by the facile carbon thermal transformation of nanostructured TiO$_2$ film or TiO$_2$ NPs in an atmosphere of methane, hydrogen and nitrogen. The lower inset of Figure 5.1 shows a photograph of the NanoCOT electrode formed directly on a Ti plate. Color changes of a Ti plate before and after the hydrothermal reaction and carbon transformation are shown in Figure 5.2 along with the photograph of a NanoCOT wire sample.

In comparison to semimetallic titanium oxycarbides synthesized by carbothermal reactions as reported previously in the literature, $^{1,2}$ the NanoCOT is the first Ti based material possesses enhanced OER reactivity that is comparable to IrO$_2$ or Pt in alkaline solution and can be engineered to serve as cathode and anode for complete water splitting. Moreover, the NanoCOT can be also used as an alternative to expensive Pt/FTO counter electrodes of dye-sensitized solar cell (DSSC). Here, the synthesized NanoCOT plate is directly used as counter electrodes for TiO$_2$ DSSC application and showed the significant improvement compare to Pt film.
Figure 5.1 Schematic of preparation procedures for the NanoCOT electrode and a photograph of NanoCOT electrode (lower right inset) after carbon transformation of a nanostructured TiO₂ film. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
**Figure 5.2** Photographs of bare Ti plate (a), hydrothermally treated Ti plate with Ti NWs (b), and NanoCOT coated Ti substrate (c) after carbon transformation reaction in a CVD system. (d) shows a NanoCOT sample made from a 0.5 mm (in diameter) Ti wire. Detailed experimental details are included in experimental section of the manuscript. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
5.2 Characterization of NanoCOT.

Figure 5.3 shows the top-view SEM images of TiO$_2$ NWs (A) and NanoCOT NWs after the carbon transformation reaction at 900 °C (B), (C) and 1000 °C (D), respectively. The diameters of the synthesized TiO$_2$ NWs are around 20 to 100 nm and lengths of up to 500 nm. After carbon thermal treatment at 900 °C, the NW shape is still retained and covered by a thin layer of carbon film and nano-chunks. Carbon nanotubes with diameters around 80 nm are formed at a CVD temperature of 1000 °C. TiO$_2$ NWs can be melted at a temperature as high as 900 °C, and that this melting process can be avoided in presence of hydrogen and methane gas atmosphere due to the formation of NanoCOT, which has a higher melting temperature than pristine TiO$_2$ NWs. Raman spectra in the range of 300-2000 cm$^{-1}$ of the as-synthesized TiO$_2$ NWs and NanoCOT were recorded for investigation of TiO$_2$ phase and carbonaceous species formation (Figure 5.4). Raman peaks from 300 to 700 cm$^{-1}$ indicated the formation of TiO$_2$ NWs.$^3$ These peaks are weakened after the formation of NanoCOT because of chemical reduction and carbon doping dramatic change in the electronic structure TiO$_2$. After carbon transformation, the main Raman lines corresponding to the D and G bands of carbon can be detected around 1350 cm$^{-1}$ and 1600 cm$^{-1}$. This implies that there is trace amount of carbon precipitates on the NanoCOT substrate during thermal annealing in methane and hydrogen. XRD in Figure 5.5 shows that NanoCOT is isostructural with TiO (PDF Card: 01-086-2352), and that there are a large amount of additional reduced Ti oxide phase corresponding to Ti$_2$O$_3$ (PDF Card: 00-043-1033), Ti$_2$O (PDF Card: 00-011-0218), as well as carbon (PDF Card: 00-013-0148). As labeled in the figure, the peaks around 36.2°, 42°, 61°, 73° and 76.9°, correspond to <111>, <200>, <220>, <311> and <222> phases of TiO, respectively. The crystals sizes of reduced Ti oxide can be estimated by Scherrer equation: \( D = \frac{k\lambda}{\beta \cos \theta} \), which D is the mean size of the crystalline domains, k is the shape factor.
with a typical value of about 0.9, $\lambda$ is the X-ray wavelength (Cu K-alpha 1, 0.154056 nm), $\beta$ is the line broadening at half the maximum intensity, and $\theta$ is the Bragg angle. The estimated crystal sizes are 27 nm, 25 nm and 11 nm for TiO, Ti$_2$O and Ti$_2$O$_3$, respectively.
Figure 5.3 SEM images of TiO$_2$ NWs (A) formed on Ti substrate after hydrothermal reaction in 0.6 M HCl, and low-resolution (B) and a zoom-in (C) SEM images of a NanoCOT electrode surface prepared by hydrothermal reaction of 1×1 cm$^2$ Ti plate (0.5 mm in thickness) followed by carbon transformation at 900 °C, and (D) surface morphology of a NanoCOT surface after carbon transformation at 1000°C. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
Figure 5.4  Raman spectra of NanoCOT electrode and TiO\textsubscript{2} NW electrode. The TiO\textsubscript{2} NW electrode was formed on a 1×1 cm\textsuperscript{2} Ti substrate (0.5 mm in thickness) via hydrothermal reaction followed by thermal annealing in air. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
Figure 5.5 XRD spectrum of a planar COT electrode synthesized using carbon transformation method at 900 °C in CH₄/H₂/N₂ atmosphere. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
Further insights into the effect of carbon thermal transformation on the structure were obtained by HRTEM observations as shown in Figure 5.6. A representative HRTEM image of TiO$_2$ NW is shown in Figure 5A, revealed lattice spacing of 2.99 Å and 3.26 Å, corresponding to $<001>$ and $<110>$ planes of rutile TiO$_2$. The upper left inset (Figure 5.6 A) is the electron diffraction of the TiO$_2$ NW, which further confirmed its single crystalline nature. After carbon transformation, HRTEM images of NanoCOT (Figure 5.6 B, C, and D) showed polycrystalline titanium oxides in a reduced state. The close examination at the NanoCOT revealed lattice spacing of 1.51 Å and 2.15 Å corresponding to the $<220>$ and $<200>$ planes of TiO; 2.4 Å corresponding to the $<002>$ plane of Ti$_2$O; 2.19 Å corresponding to the $<111>$ plane of TiO$_2$; as well as a large amount of amorphous structure possibly attributed to a mixture of C, O and Ti, in good agreement with the XRD analysis.

As illustrated in Figure 5.7, the chemical states and composition of Ti, O and C in NanoCOT were investigated by high-resolution XPS. Before data acquisition, samples were sputtered by Ar ion beam with incident energy of 3 keV for 30 sec to clean the surface. Compared to the XPS of TiO$_2$, there are four doublet peaks corresponding to four chemical states of Ti, namely, Ti$^{1+}$/Ti$_2$O (Ti 2p$_{3/2}$, 455.1 eV; Ti 2p$_{1/2}$, 461 eV), Ti$^{2+}$/TiO (Ti 2p$_{3/2}$, 455.6 eV; Ti 2p$_{1/2}$, 461.4 eV), Ti$^{3+}$/Ti$_2$O$_3$ (Ti 2p$_{3/2}$, 456.8 eV; Ti 2p$_{1/2}$, 462.7 eV), and Ti$^{4+}$/TiO$_2$ (Ti 2p$_{3/2}$, 458.7 eV; Ti 2p$_{1/2}$, 464.3 eV). The Ti atomic percentage was calculated base on the XPS that the percentage of Ti$^{1+}$, Ti$^{2+}$, Ti$^{3+}$ and Ti$^{4+}$ are 9%, 21%, 34% and 36%, respectively. The intense O 1s peak at 530.4 eV in Figure 5.7 B can be attributed to the O$^{2-}$ anions of the Ti-O bond. Another relatively peak at 532.1 eV is assigned to carbonate-like species due to the carbon dopant in TiO$_{2-x}$ lattice. The spectra for core level C 1s are shown in Figure 5.7 C. The major peak at 284.6 eV is assigned to external graphitic-like C–C SP$_2$ bond, as well as the peak at 285.6 eV is
attributed to diamond C–C sp³ bond, as evidenced in the Raman analysis (Figure 5.4). The peaks at 286.7 eV and 290.8 eV are ascribed to C–O and O–C=O bonds, respectively, whose concurrent presence indicates the formation of Ti–O–C bond due to interstitial carbon in the TiO_{2−x} phase. Moreover, the composition results calculated from the XPS also showed that the formula of NanoCOT can be estimated to be TiO_{1.3}C_{0.3}.

The electrochemical activities of the synthesized NanoCOT electrode were studied by using dynamic control of electrode potential in the presence of a standard redox couple of Ru(NH₃)₆^{2+/3+} and compared with the performance of other electrodes, including a bare Ti electrode, Pt, and IrO₂ wire electrode. As shown in Figure 5.8, a highly reversible CVs of Ru(NH₃)₆^{3+} can be obtained at the NanoCOT electrode with ΔE around 65 mV, which is close to that of the Pt or IrO₂ electrode. The slightly higher ΔE than theoretical value of 2.3RT/nF (or 59mV at 25 °C for Ru(NH₃)₆^{3+} +e → Ru(NH₃)₆^{2+}) is due to the concentration overpotential at the large surface area (0.5 cm×1 cm) of a NanoCOT electrode for the CV measurement. The faradaic current density on NanoCOT electrode is about two-fold higher than that of Pt or IrO₂ wire electrode, due to the larger specific surface area, as well as highly conductivity of NanoCOT. This is consistent with the increase in its double layer charging current in the potential region from 0 to 0.4 V (vs. Ag/AgCl).
Figure 5.6 HRTEM images and electron diffraction patterns of oxidized Ti NWs (A) prior to the formation of NanoCOT and HRTEM images of selected regions of a NanoCOT electrode (B, C and D). Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
Figure 5.7 XPS analysis of Titanium (A), Oxygen (B) and Carbon (C) in the NanoCOT electrode. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
Figure 5.8 CVs of NanoCOT, Pt, IrO₂ wire, and a bare Ti electrode in 1.0 M Na₂SO₄ containing 5.0 mM Ru(NH₃)₆Cl₃ at a scan rate of 100 mV/s. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
Figure 5.9 (A) Polarization curves of a bare ITO, a NanoCOT (on 1×1 cm² Ti substrate), a NanoCOT prepared on 0.5 mm (in diameter) Ti wire, a planar COT obtained on electropolished Ti substrate, IrO₂ wire, and a Pt wire electrodes (0.45 mm in diameter) in 0.1M KOH solution for OER; Scan rate: 5 mV/sec. Reference electrode: Ag/AgCl. Electrode potential is corrected to be relative to RHE using formula E (vs. RHE)=E(vs. Ag/AgCl)+0.197V+0.059 pH; (B) Tafel plots for anodic branches of the log current density (mA/cm²) vs. overpotential (η) for OER reaction obtained under the same conditions as panel A. η=applied potential (vs. RHE)-1.23 V. Tafel plots are fitted in the region of η=0.42-0.52 using a linear function to obtain their slope and intercept (or exchange current density j₀) as listed in Table 5.1. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
5.3 Water oxidation performance.

The polarization curves in Figure 5.9 A for OER show that the OER current density per geometric surface area at NanoCOT, NanoCOT wire is much higher than ITO, IrO$_2$ and Pt wires. The current at planar COT is lower than NanoCOT, while close to IrO$_2$ due the minimum surface nanostructure. The log current density for all control electrodes is plotted against the overpotential ($\eta$) for OER as shown by Tafel plots in Figure 5.9 B. Appreciable OER current is observed beginning at $\eta=0.3$ for NanoCOT, NanoCOT wire, or planar COT, which is the same as IrO$_2$ wire and much lower than Pt wire, and ITO (Figure 5.9 B). All Tafel plots were fitted using a linear function and their slopes and intercepts are listed in in Table 1 along with the current density at $\eta=0.42$. NanoCOT prepared on Ti plate or wire generates a current density of 1.33 mA/cm$^2$ or 1.18 mA/cm$^2$ at $\eta=0.42$, respectively, which is more than 4 times higher than the 0.32 mA/cm$^2$ of IrO$_2$ wire and 15 times higher than 0.08 mA/cm$^2$ of Pt wire. Moreover, the OER efficiency of a planar COT electrode is also comparable with IrO$_2$ wire. All slopes obtained are comparable as the slope is a function of $(1-\alpha)F/2.3RT$, where $\alpha$ is the transfer coefficient for oxygen reduction reaction. The applied overpotential in the data-fitting region was not high enough for ITO electrode to show reasonable OER activity as shown in Figure 5.9A. The exchange current density values obtained from data fitting are consistent with the current density at $\eta=0.42$ V, indicating a significant catalytic OER at NanoCOT surface.

To optimize the OER performance, we also studied the impact of CVD temperature on the water oxidation reaction in 0.1 M KOH as shown in Figure 5.10. The current density of NanoCOT synthesized by 800 °C is only 10 mA/cm$^2$ at 2 V vs RHE. The maximum activity is observed for the electrode treated in CVD at 900 °C, which achieved a current density of 25 mA/cm$^2$. A temperature higher than 900 °C leads to a decreased current density due to greater
carbon accumulation and carbon nanotubes formed on the NanoCOT surface, which block the active surface of NanoCOT from interacting with redox species. Thus, the ideal temperature for optimal carbon transformation is kept at 900 °C to achieve optimal OER performance. Beside high activity, the long-term stability is another important factor to determine the applicability of OER electrode. Water splitting capability and stability of a NanoCOT electrode was tested in 0.1 M KOH when at 1.8 V bias potential against a Pt wire cathode. As shown in Figure 5.11, the current density remains around 5.5 mA/cm² after 17 hours and no apparent morphology change was observed after the electrolysis experiment as shown by SEM image of the sample after 17 hours test in Figure 5.12.
Table 5.1: Current density at $\eta=0.42$ V, slope and exchange current density $j_0$ for OER of NanoCOT (on 0.5 mm diameter Ti wire and 1x1 cm$^2$ Ti plate), NanoCOT on Ti wire, planar COT, 0.5 mm diameter IrO$_2$ and 0.45 mm diameter Pt wire electrodes. Results are obtained from Figure 5.9. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.

<table>
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<th>Electrode</th>
<th>$j$ (mA/cm$^2$) at $\eta=0.42$ V</th>
<th>slope $\log$(A/cm$^2$)/V</th>
<th>$j_0$ A/cm$^2$</th>
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</thead>
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<tr>
<td>NanoCOT on 0.5 mm Ti wire</td>
<td>1.18</td>
<td>9.2</td>
<td>2.0$x10^{-7}$</td>
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<tr>
<td>NanoCOT on 1x1 cm$^2$ Ti plate</td>
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<td>7.7</td>
<td>9.3$x10^{-7}$</td>
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<tr>
<td>Planar COT</td>
<td>0.22</td>
<td>10.6</td>
<td>1.0$x10^{-8}$</td>
</tr>
<tr>
<td>IrO$_2$ wire (0.5 mm)</td>
<td>0.32</td>
<td>9.3</td>
<td>4.5$x10^{-8}$</td>
</tr>
<tr>
<td>Pt wire (0.45 mm)</td>
<td>0.08</td>
<td>8.4</td>
<td>2.6$x10^{-8}$</td>
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<tr>
<td>Planar ITO</td>
<td>0.04</td>
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Figure 5.10 The OER current density of NanoCOT plate dependence on different carbon modification temperature in 0.1M KOH solution, at 5 mv/sec. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
Figure 5.11 Current density monitored for NanoCOT (anode) and Pt (cathode) electrodes in 0.1M KOH solution for long-term water electrolysis over several hours at 1.8 V. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
**Figure 5.12** Typical SEM image of NanoCOT electrode surface morphology after 17 hours of water oxidation test as shown in Figure 5.12. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
5.4 AC impedance.

To elucidate the OER kinetics and charge transfer process and to obtain more quantitative information about the electrodes, AC impedance spectroscopy (EIS) was performed. Figure 5.13 shows typical Nyquist plots of the NanoCOT wire, IrO$_2$ and Pt electrodes at 1.664 V (vs. RHE). All impedance spectra are fitted using an equivalent RC circuit model as shown as inset of Figure 5.13, which is comprised of a resistor ($R_s$) representing the resistivity of the electrolyte between the working and reference electrode, a charge transfer resistance ($R_c$) representing the charge transfer resistivity of the redox reaction, and a capacitance (C) in parallel with the (R) analogous to the double layer charging capacity of the solid-liquid junction. All fitting results are summarized in Table 5.2. No major differences in $R_s$ of three different electrodes were observed. $R_c$ of NanoCOT wire is as low as 71 $\Omega$, which was much lower than that found for wire electrodes of IrO$_2$ (243 $\Omega$) and Pt (3600 $\Omega$). This means that NanoCOT wire is more kinetically favorable than IrO$_2$ and Pt electrode for OER. Pt shows much poorer OER activity compared to NanoCOT wire and IrO$_2$, because of the formation of a non-active oxide layer as shown by the increase in its $R_c$. Moreover, the capacitance is greatly enhanced for NanoCOT wire because of its high surface area.
Figure 5.13 Nyquist plots of NanoCOT, IrO₂ and Pt wire samples at 1.664 V (vs. RHE). Inset is the equivalent circuit used to fit the experimental data. Fitting results are shown in Table 5.2. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
<table>
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<tr>
<th>Impedance</th>
<th>NanoCOT</th>
<th>IrO₂</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_s$ (Ω)</td>
<td>20</td>
<td>19</td>
<td>13</td>
</tr>
<tr>
<td>$R_c$ (Ω)</td>
<td>71</td>
<td>243</td>
<td>3600</td>
</tr>
<tr>
<td>$C$ (μF)</td>
<td>180</td>
<td>26</td>
<td>14</td>
</tr>
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</table>
5.5 Characterization and electrochemical catalytic performance of COT NPs.

Besides, the NanoCOT samples that prepared on Ti plate or wire substrate for OER testing and device fabrication (e.g., electrolyzer and solar cell). COT NPs are highly desirable for many other applications because of their high surface areas, allowing formation of electrode materials on other substrates, such as flexible transparent electrodes. Figure 5.14 shows photographs of TiO$_2$ NPs before and after carbon transformation towards COT NPs. Figure 5.15 A shows the SEM of COT NPs. After carbon treatment at 900 °C, the nano-particles are agglomerated, and the BET surface area is found to be 2.3 m$^2$/g (Figure 5.16). Figure 5.15 B shows the XRD pattern of the COT NPs catalyst. The XRD pattern is similar to NanoCOT, but shows poorer crystallinity with lower amounts of Ti$_2$O, TiO and Ti$_2$O$_3$ phase. Five new peaks around 29°, 31°, 33°, 54° and 55° are observed, which can be attributed to the formation of other reduced titanium oxide phases, such as Ti$_9$O$_{17}$ (PDF Card: 01-085-1061) and Ti$_3$O$_5$ (PDF Card: 04-008-6988), respectively.

The chemical states of O, Ti, and C in COT NPs were also investigated by XPS. The chemical composition of COT NPs was quite similar to NanoCOT. As shown in Figure 5.17, there are also four doublet peaks corresponding to four chemical states of Ti, namely, Ti$^{1+}$/Ti$_2$O (Ti 2p$\!/2$, 455.2 eV; Ti 2p$\!1/2$, 461.4 eV), Ti$^{2+}$/TiO (Ti 2p$\!/2$, 456.2 eV; Ti 2p$\!1/2$, 462.3 eV), Ti$^{3+}$/Ti$_2$O$_3$ (Ti 2p$\!/2$, 457.7eV; Ti 2p$\!1/2$, 463.6 eV), and Ti$^{4+}$/TiO$_2$ (Ti 2p$\!/2$, 459.3 eV; Ti 2p$\!1/2$, 465.2 eV). However, compared to the NanoCOT, the COT NPs has a lower amount of Ti$^{1+}$, Ti$^{2+}$, Ti$^{3+}$ and a higher amount of Ti$^{4+}$, which is in a good agreement with the COT NPs’ XRD. The calculation of Ti atomic percentage based on the COT NPs’ XPS shows that the percentage of Ti$^{1+}$, Ti$^{2+}$, Ti$^{3+}$ and Ti$^{4+}$ are 3%, 5%, 25% and 67%, respectively. The intense O 1s peak at 530.7 eV in Figure 5.17 B can be attributed to the O$^{2-}$ anions of the Ti-O bond. Another relatively
weaker peak at 531.8 eV can be assigned to C-O bond. The results show a similar C-O content in COT NPs compared to NanoCOT with about one third O atoms being bonded with C. The spectra for core level C 1s are shown in Figure 5.17 C. The major peak at 284.6 eV is assigned to external graphitic-like C–C sp² bond, as well as the peak at 285.4 eV is attributed to diamond C–C sp³ bond. The peaks at ca. 286.6 eV and 290.2 eV are associated to C–O and O–C=O bonds, respectively. Based on the XPS analysis results, the chemical formula of COT NPs is estimated to be TiO_{1.9}C_{0.3}.

Figure 5.18 shows the OER catalytic characteristics of COT NPs on RDE glass carbon electrodes. As shown in figure, the OER onset potential of the COT NPs is around 1.53 V (vs. RHE), and generates a current density of 10mA/cm² at a potential of 1.72 V (vs. RHE), which is superior or comparable to nanostructured IrO₂ and other OER nano catalysts reported in the literature, such as Co₃O₄,⁶ anodized Ni,⁷ layered double hydroxide of Zn and Co,⁸ Mn₃O₄/CoSe₂⁹ or Co/Mn/O,¹⁰ depending on surface area. The average OER performances of COT NPs, NanoCOT, IrO₂ and planar COT, respectively, at 1.77 V vs RHE are shown in Figure 5.19. COT NPs shows the highest OER current density that from 13-16.5 mA/cm² due to higher surface area than other catalysts. The OER efficiency of NanoCOT is around 2-4 times of IrO₂ depending on the surface areas of the different substrates. In addition, the Planar COT shows efficiency close to IrO₂ wire.
Figure 5.14 Photographs of dried and grounded TiO$_2$ NPs (P25) modified with Fe catalyst and polymer surfactant (A) and COT NPs after carbon transformation (B). SEM image of the COT NPs is shown in the results and discussion section of the manuscript. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
Figure 5.15 Typical SEM image of COT NPs obtained from TiO$_2$ NPs (A) and their XRD spectrum (B) in comparison with XRD of NanoCOT. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
Figure 5.16 Nitrogen adsorption isotherm for COT NPs. Analysis of the nitrogen adsorption isotherm using the Brunauer-Emmett-Teller method \(^4\) gives a surface area of 2.3 \(\text{m}^2/\text{g}\), consistent with no micropores and very limited mesoporosity. The hysteresis loop is closest to type H\(_3\) from plate-like particles agglomerated to give slit shaped pores. \(^5\) Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
Figure 5.17 XPS Ti, O and C contents of COT NPs. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
**Figure 5.18** OER performance of COT NPs in 0.1 M O₂-saturated KOH analyzed from a RDE system. COT NPs loading is 0.1 mg/cm² on a glassy carbon electrode; rotation speed: 1,600 r.p.m.; scan rate: 10mV/s. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
Figure 5.19 Average OER performances of COT NPs, NanoCOT, IrO₂ and planar COT, respectively, at 1.77 V (vs. RHE). The error bar represents distribution of measured current density from five independent measurements. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
5.6 Water reduction performance of NanoCOT and complete water electrolysis at NanoCOT electrodes.

A cathode is necessary for complete water splitting and Pt is always the best candidate due to its favorable proton reduction at its surface. Proton reduction is sluggish at the NanoCOT cathode in contrast to Pt electrode as shown by Figure 5.20. To overcome this problem, we electrochemically coated NanoCOT electrode with NiMoZn alloy film. Enhanced proton reduction efficiency at NanoCOT can be achieved with surface coating of NiMoZn as shown in Figure 5.20. SEM and a photograph of the NiMnZn coated NanoCOT electrode are shown in Figure 5.21. In order to demonstrate the superior water splitting capability of NanoCOT, various combinations of a NanoCOT anode and Pt, IrO₂ wire, or NiMoZn/NanoCOT cathode were evaluated using linear scanning voltammetry for water splitting in 0.1 M KOH as shown in Figure 5.22. The combination of NiMoZn/NanoCOT (cathode) and NanoCOT (anode) exhibited the highest current density of 99 mA/cm² at 3 V, which is higher than the 70 mA/cm² of IrO₂ and 26 mA/cm² of Pt. We have attempted to wire this pair of electrodes of NanoCOT to a silicon solar cell whose potential output is set to 2.0 V by using a potentiometer wired to the solar cell panel in order to generate oxygen and hydrogen as shown in bottom inset of Figure 5.22.

5.7 Enhanced OER reaction at NanoCOT using IrOₓ NPs.

It is well-known that the OER properties of Ir oxide with an undefined stoichiometry (IrOₓ) are strongly dependent on particle size. Especially, 2 nm IrOₓ exhibits thermodynamically and kinetically favorable OER capability with the minimum overpotential reported.¹¹,¹² To compare NanoCOT electrode with 2 nm IrOₓ, OER performance of NanoCOT coated with 2 nm IrOₓ NPs nanoparticles are studied. The amount of 2 nm IrOₓ NPs on NanoCOT can be controlled by the electrophoretic deposition time. The IrOₓ NPs coating thickness increases with deposition time. As shown in Figure 5.23 A, 36 min deposition of IrOₓ onto NanoCOT yields 140 mV less
overpotential than as synthesized NanoCOT at current density of 0.1 mA/cm². NanoCOT’s current density of 10.3 mA/cm² at 1.75 V (vs. RHE) can be improved to 30 mA/cm² with 36 min coating with IrOₓ NPs. Figure 5.23B shows that the OER onset potential decreases with increasing loading of 2 nm IrOₓ NPs onto NanoCOT, accompanied with an increase in its current density at 1.6V (vs. RHE). The OER performance of IrOₓ/NanoCOT electrode can be improved with longer deposition time and its onset potential can reach 1.38 V (vs. RHE) after 20 min, which is equivalent to η=150 mV for water oxidation, and current density at 1.6V vs RHE reaches as high as 15 mA/cm² at deposition time of 32 min.
Figure 5.20 Proton reduction at the NanoCOT, Pt and NiMoZn/NanoCOT plate cathodes in 0.1M KOH solution, at 5 mV/sec. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
Figure 5.21 Photograph (A) and a typical SEM image, (B) of electrodeposited NiMoZn/NanoCOT electrode for proton reduction reaction. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
Figure 5.22 Linear scanning voltammetry curves and O$_2$/H$_2$ fluxes at standard temperature and pressure (STP) of three pairs of anode and cathode electrodes in 0.1M KOH solution for complete water electrolysis at scan rate of 5 mv/sec. Bottom inset is the optimal combination of NiMoZn/NanoCOT (cathode) and NanoCOT (anode) electrode for complete water splitting at 2.0 V DC output provided by a 12.5 % silicon solar cell panel wired to a potentiometer under sun light outside the Shelby Hall of the University of Alabama in Fall 2014. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
Figure 5.23 Polarization curves of 2 nm IrO\textsubscript{x} NPs/NanoCOT (36 min deposition time) and NanoCOT electrode in 0.1 M KOH at 5 mV/sec (A). Applied potential at current density of 0.1 mA/cm\textsuperscript{2} (black) and current density at 1.6 V (vs. RHE) (red) of 2 nm IrO\textsubscript{x} nanoparticles coated NanoCOT as a function of electrophoresis deposition time (B). The error bar represents the distribution of measured current density of four independent measurements. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
5.8 Mechanism.

NanoCOT surface is highly active due to the predominant reduced Ti (Ti\(^{1+}\), Ti\(^{2+}\), Ti\(^{3+}\)) defect states provide a high concentration of active sites for water absorption and dissociation, which is a critical first step in the process of OER. The rich and unusual valence states of Ti (Ti\(^{1+}\), Ti\(^{2+}\), Ti\(^{3+}\) and Ti\(^{4+}\)) that hybridized with C 2p and O 2p state in the NanoCOT electrode form a continuous energy band that plays an important role in enhancing carrier conductivity and active sites performance, leading to a higher OER performance with a low overpotential. Furthermore, the direct growth of NanoCOT on Ti substrate, which can efficiently collect and transfer electrons, enables a strong bonding between NanoCOT and the Ti electrode and thus an enhanced OER stability is presumably another important reason for the enhanced OER performance. Such carbon modified titanium oxide electrode material could be achieved by oxidizing and/or anodizing TiC directly, although it is nontrivial to achieve the right composition with such a facile and economical method as shown by our preliminary test result in Figure 5.24 and Figure 5.25.

It should be noted that residual Fe content in our NanoCOT is not responsible for the obtained OER activity. To assess the possible effect of residual Fe on OER activity of NanoCOT electrode, we have performed four control experiments to conclusively demonstrate that the trace of Fe or Fe/C on the surface is not responsible for highly OER efficiency of NanoCOT. This includes OER performance of 1) NanoCOT electrode with Fe leached out using strong acid (Figure 5.26 and 5.27); 2) CVD treated bare Fe plate with and without Fe(NO\(_3\))\(_3\) treatment (Figure 5.28); 3) thermally annealed NanoCOT sample in air (Figure 5.29); and 4) CVD treated TiO\(_2\) nanowire substrate without Fe(NO\(_3\))\(_3\) treatment (Figure 5.30). Based on all above control investigation, we conclude that the residue amount of Fe is not responsible for the enhanced
OER. We believe that the role of reduced Fe(NO$_3$)$_3$ by hydrogen in our CVD system is to help decompose CH$_4$ into carbon and hydrogen for TiO$_2$ reduction and carbon doping, which is helpful for converting TiO$_2$ into the NanoCOT with high OER activity.
Figure 5.24 OER current density of 30 nm TiC NPs (Alfa Aesar) before and after being annealed in air at 350 °C, 400 °C, 500 °C, and 600 °C. Rotating disc electrode (RDE) measurements were conducted in 0.1M KOH solution at 25 °C with a scan rate of 10 mV/s. The counter electrode of Pt, and a reference electrode of Ag/AgCl were used. The working electrode was prepared by loading NPs (0.15 mg/cm²; an ink mixture of 20 mg TiC or oxidized TiC NPs, 20 µl Nafion solution and 2 ml ethanol) on the glassy carbon electrode and dried prior to test with RDE. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
Figure 5.25 OER current density of TiC NPs before and after anodization. 100 mg 30 nm TiC NPs (Alfa Aesar) was mixed with 1 ml 15% PVA aqueous, then pasted onto a Ti plate, and then air dried at 80 °C. The film was anodized in ethylene glycol containing 2% (w/w) H2O and 0.3% (w/w) NH4F at a voltage of 40 V for 1 h. The OER characterization of the TiC and anodized TiC films were measured in 0.1 M KOH in a three-electrode cell using at a scan rate of 10 mV/s. The electrochemical cell comprised of a catalytic electrode as the working electrode, a graphite rod counter electrode, and a Ag/AgCl reference electrode. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
Figure 5.26 XPS of Fe content in NanoCOT electrode before (A) and after (B and C) HNO₃ leaching; NanoCOT electrode was dipped in concentrated HNO₃ (69.2%, Fisher Chemicals) for three hours to leach out external Fe. The leached NanoCOT electrode was then washed in DI water. In order to confirm that Fe has been definitely removed, two different areas on the NanoCOT electrode were selected as shown in panel B (top surface) and C (bottom) and no Fe signal was identified in the XPS spectrum. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
Figure 5.27 The OER of NanoCOT before and after leaching obtained in 0.1M KOH. To completely remove residual HNO$_3$ after DI water rinsing, the leached NanoCOT was annealed at 400 °C in CH$_4$/H$_2$/N$_2$ for 20 min. The polarization curves indicate that residual Fe does not affect the OER performance of NanoCOT. The anodic current per geometric surface area for leached NanoCOT actually shows more activity than that of original NanoCOT because of the increase of surface area after removal of Fe and amorphous carbon. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
Figure 5.28 OER current density of CH₄/H₂/N₂ CVD treated bare Fe plate and Fe plate coated with Fe(NO₃)₃. 99% Fe plates with and without 0.5 M Fe(NO₃)₃ modification were loaded in a tube furnace, followed by thermal carbon modification in CH₄/H₂/N₂ under 900 °C for 1 hour as we used for synthesis of NanoCOT. The current density of surface Fe/C decorated plate is very similar to that of the Fe substrate. Moreover, its current density of 2 mA/cm² at 1.8 V is much lower than 14 mA/cm² of NanoCOT. The result confirms that the trace of Fe/C cannot provide improved OER activity. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
Figure 5.29 OER current density of air-annealed NanoCOT. The as-prepared NanoCOT was annealed at 500 °C in air for two hours to convert NanoCOT into iron-based oxides and TiO$_2$. The NanoCOT electrode treated in such way mainly contains iron oxide/TiO$_2$ and barely exhibits any anodic current, and the current density is as low as 0.15 mA/cm$^2$ at 1.8 V. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
Figure 5.30 OER current density of a CH₄/H₂/N₂ treated TiO₂ electrode without Fe(NO₃)₃ coating in comparison with NanoCOT. TiO₂ nanowire substrate without Fe(NO₃)₃ decoration was loaded in a tube furnace, followed by carbon thermal modification in CH₄/H₂/N₂ under 900 °C for 1 hour. The existent Fe³⁺ is very important during the carbon thermal modification process. The surface Fe³⁺ works as CH₄ decomposition catalyst to form carbon and hydrogen for TiO₂ reduction and carbon doping. As shown in Figure S18, TiO₂ cannot be transformed to NanoCOT in the absence of Fe³⁺ treatment, thus leading to very poor OER performance. Reprinted with permission from Journal of the American Chemical Society 137 (37), 11996-12005. Copyright 2015 American Chemical Society.
5.9 Dye-Sensitized Solar Cell.

As shown in Figure 5.3, compares the cyclic voltammograms of NanoCOT (900 °C) and conventional Pt counter electrodes were carried out to characterize their electrocatalytic activity under I$_3^-$ / I redox pair. The marked oxidation and reduction peaks were assigned to the I$_3^-$ / I redox reaction.

$$I_3^- + 2e^- \leftrightarrow 3I^-$$ (1)

$$3I^- - 2e^- \leftrightarrow I_3^-$$ (2)

The conventional Pt electrode showed enhanced redox kinetics and the peak-potential separation, $\Delta E$, of the Pt is 170 mV, which lower than 340 mV of NanoCOT. However, the NanoCOT electrode provided much higher current density than that of the Pt electrode due to the larger surface area. Figure 5.32 shows the I–V curves of DSSCs based on NanoCOT (900°C and 1000°C) counter electrode and Pt counter electrode. Under 1 sun illumination, the DSSC with the conventional Pt counter electrode gave $I_{sc} = 5.2$ mA/cm$^2$ and $V_{oc} = 0.71$. While, the DSSC achieves a higher performance that the $I_{sc}$ was 6.4 mA/cm$^2$ and $V_{oc}$ was 0.69 V with the 900 °C NanoCOT, moreover, the $I_{sc}$ and $V_{oc}$ could increase to 9.3 mA/cm$^2$ and 0.77 V, respectively, based on 1000 °C NanoCOT, due to the higher surface area. The action spectra of the DSSCs with Pt and NanoCOT (900°C) counter electrodes are shown in Figure 5.33. It is observed that the action spectra of the DSSCs using the Pt and NanoCOT electrodes both show good photovoltaic responses in the 350–700 nm wavelength range. It is noticeable that the DSSC based on NanoCOT exhibits a higher photocurrent than that of Pt in the wavelength range of 400–700 nm, which means that more incident light is harvested by the NanoCOT. Thus, based on the I-V and action spectra, as well as cyclic voltammograms of NanoCOT and Pt electrodes,
the NanoCOT as a catalytic counter electrode for DSSCs exhibited higher current density and overall conversion efficiency than the Pt counter electrode.
Figure 5.31 Cyclic voltammograms (CVs) of NanoCOT and Pt counter electrodes at 5mv/s scan rate. The electrolyte solution was composed of 0.1 M LiClO₄, 10 mM LiI, and 1 mM I₂ in acetonitrile. Graphit electrode was used as counter electrode and Ag/AgCl works as reference electrode.
Figure 5.32 I–V characteristics of DSSCs with NanoCOT counter (900°C and 1000°C) electrode and Pt counter electrode.
Figure 5.33 Action spectra of the DSSCs with Pt and the NanoCOT (900°C) counter electrodes.
5.10 Conclusions.

In summary, a low-cost NanoCOT electrode is synthesized that containing earth-abundant elements carbon, oxygen and titanium. NanoCOT operating efficiently in alkaline solution for OER with appreciable catalytic current and only about 300 mV overpotential. The NanoCOT is prepared by facile carbon thermal transformation of nanostructured Ti substrate or TiO₂ NPs in an atmosphere of methane, hydrogen and nitrogen in the presence of Fe catalyst. This catalytic OER performance of NanoCOT can be further improved by coating its surface with 2 nm IrOₓ NPs. Based on the characterization provided by structural analysis, we conclude the superiorly OER performance of NanoCOT is contributable to the predominant valence and defect states of Ti (Ti⁺, Ti²⁺, Ti³⁺ and Ti⁴⁺), significant hybridization of C 2p and O 2p states, as well as, the intimate electrical contact between NanoCOT and the Ti substrate. With its lower cost and superior performance for OER over IrO₂ and Pt samples, NanoCOT can potentially benefit efficient water splitting and other electrochemical applications by replacing precious metals. NanoCOT can be engineered to form COT NPs in order to enhance their current density of OER and applications of NanoCOT onto other electrical conductive substrates (e.g., glassy carbon, indium-tin-oxide, and stainless steel). In addition, the NanoCOT is successfully applied as a substitute for Pt film used in DSSCs as catalytic counter electrode. DSSCs based on low-cost NanoCOT exhibited higher current density and overall conversion efficiency than the Pt counter electrode.
REFERENCES


6. CONCLUSION AND PERSPECTIVE

Photoanode materials made of Ag@Ag$_2$S/Ti@TiO$_2$ NWs and Au@CdS/Ti@TiO$_2$ NWs have been successfully prepared to show significant surface plasmon enhancement of photoelectrochemical characteristics, although the photocurrent density of 89 $\mu$A/cm$^2$ for Ag@Ag$_2$S/Ti@TiO$_2$ NWs and 50 $\mu$A/cm$^2$ for Au@CdS/Ti@TiO$_2$ NWs at 0.2 V under the visible light needs further improvement by optimizing the nanostructures due to their high overpotential, inefficient electron-hole pair separation and carrier transportation. Further improvement of their photoelectrochemical performance is critical and can be obtained by followings.

First, oxygen-evolving cocatalysts (OEC), such as cobalt borate (Co-Bi) or cobalt phosphate (Co-Pi) can be potentially used to modified Ag@Ag$_2$S/Ti@TiO$_2$ NWs or Au@CdS/Ti@TiO$_2$ NWs photoanodes decrease the overpotential for water oxidation. Second, Ti@TiO$_2$ NWs substrate can be replaced with pure NanoCOT substrate to improve carrier transport and collection for high efficiency surface plasmon enhanced OEC/photocatalyst/NanoCOT composite photoanode. Thirdly, our study has shown that the thickness of the catalytic layer of Ag@Ag$_2$S/Ti@TiO$_2$ NWs system and plasmonic core size can be controlled, and an optimal Ag$_2$S shell thickness of 8 nm with a Ag core size of 17 nm can be obtained. However, the interaction strength which depends on the separation distance between the photocatalyst shell and the plasmonic core still needs to be fully investigated in order to study the variation of photocatalytic activities based on the separation distance. A tri-layer plasmonic semiconductor core-shell structure nanostructure photocatalyst containing a Ag core, SiO$_2$ interlayer, and a CdS shell (Ag@SiO$_2$@CdS) with a controllable interlayer and shell thickness is highly desirable in
order to address this issue. The SiO₂ interlayer electronically insulates the metal from the semiconductor and effectively blocks electron transfer between the Ag and photocatalyst shell, while electromagnetic field energy is still allowed to play roles in local field enhancement. The SiO₂ interlayer thickness can be controlled by varying the Tetraethyl Orthosilicate (TEOS) concentrations to study the effect on photocatalytic activity. ¹ Lastly, the Ag core can be replaced by an AgₓAuᵧ alloy nanostructure as an alternative synthesis strategy for tuning the surface plasmon resonance wavelength in a broad wavelength region for photocurrent enhancement. The AgₓS/AgₓAuᵧ nanostructured composites will be obtained by dipping the AgₓAuᵧ alloy nanostructures into S/DMSO solution. The photoelectrochemical performance of the photocatalysts will be studied.

The low-cost NanoCOT plates and NPs OER catalysts, containing earth-abundant elements, have been successfully synthesized and tested in alkaline solutions. Even though NanoCOT and COT NPs showed excellent OER efficiency, the limited surface area of NanoCOT plate and large particle size of COT NPs lead to a lower anodic current density than previously reported nano-sized OER catalysts, such as nanostructured CoSe₂ with a much smaller particle size and higher surface area.² To further improve the OER efficiency of COT NPs, surface area increase by reducing the particle size is still necessary and but challenging. For the NanoCOT plate, improvement of surface area could be done by depositing TiO₂ thin film on Ni foam, which has a very high porosity with 75-95% void spaces. Moreover, a ball mill will be applied to reduce the particle size of COT NPs. The OER efficiency will be significantly improved after reduce the particle size from 1 μm to 100 nm. Even though, based on the evidence provided by surface structural analysis, we find that unusual valence states of Ti and significant hybridization of the C 2p and O 2p states play important roles and lead to a higher OER performance. The band
structure of NanoCOT and the process of OER at Ti defect are still not clear. A computational study will be carried out to obtain an improved understanding of the NanoCOT’s performance for OER.
REFERENCES
