Hydrogen Generation Using Integrated Photovoltaic and Photoelectrochemical Cells

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Objectives

The primary objective of this project is to develop novel nanostructures with improved optical and electronic properties for photoelectrochemical (PEC) hydrogen generation from water splitting. Specifically, we seek to design and demonstrate new strategies based on combining quantum dot (QD)-sensitization and elemental doping to significantly enhance visible light absorption and thereby PEC properties of metal oxide (MO) nanostructures, e.g. TiO_2, WO_3, and ZnO. Interesting synergistic effect has been discovered from the combined use of QD sensitization and N-doping of TiO_2 nanoparticle (NP) and nanorods.[1] Similarly, combining Au NPs with CdSe QD sensitization of TiO_2 has shown strong synergistic effect as well in terms of PEC performance.[2] The fundamental mechanisms behind the observed synergistic effects have been proved using a combination of experimental techniques including spectroscopy, microscopy, and ultrafast laser.

Technical Barriers

Towards the development of efficient PEC cells for hydrogen generation based on nanomaterials, one of the technical barriers is to control the surface properties of all the components involved, e.g. the MO nanostructures, QDs, and metal NPs. The second technical barrier is to determine the local structures and exact energy levels of the dopant, e.g. N, since this is critical to develop appropriate models to explain the synergistic effects observed.[1] The third technical barrier is to probe and understand the exact role of metal NPs in the enhanced PEC performance, which has been tentatively attributed to increased light scattering of Au NPs, leading to enhanced light absorptions of the CdSe QDs.[2]

Abstract

Hydrogen is an extremely attractive fuel for clean alternative energy. New nanocomposite structures and advanced strategies have been developed to improve the performance of PEC cells for hydrogen generation from water splitting. Systematical studies have been carried out to probe the fundamentals behind, including charge carrier properties at interfaces. One of the most important discoveries we have made is strong synergistic effects in ternary nanocomposites that show significantly enhanced PEC properties compared to binary or single component systems. These strategies are promising for advancing energy conversion technologies in the future.

Progress Report

1. Generating hydrogen by PEC with CdSe QD sensitized and N-doped TiO_2 nanostructures

TiO_2 is the most researched material for PEC water splitting. Since the bandgap of the TiO_2 is large (E_g=3.2eV), it cannot absorb most of the sunlight. One effective way to increase the absorption of the sunlight is by using semiconductor QDs to sensitize the TiO_2 film. Another approach is elemental doping. PEC measurements carried out on TiO_2 NPs and nanorods demonstrated that there is a strong synergistic effect when QD sensitization is combined with N-doping.[1] The reason for the increase in photocurrent when CdSe sensitizes N-doped TiO_2 vs. TiO_2 alone is attributed to the increase in hole transport from the valence band of CdSe to the oxygen vacancies in N-doped TiO_2.

2. PEC Properties of CdSe/TiO_2 Mesoporous Hybrid Structures

In sensitizing metal oxides such as TiO_2 using QDs, small molecules are often used to link semiconductor quantum dots to TiO_2 films. Since these small molecules are mainly dielectric materials, they will block the transfer of the photoelectrons from the quantum dots to the TiO_2 film. In this project, we have developed a new method to link QDs and TiO_2 without using the small linking molecules by assembly the QDs and TiO_2 NPs together into colloid spheres.[2] The PEC characterization of CdSe/TiO_2 hybrid spheres shows an increase in the photocurrent when compared to TiO_2 alone and CdSe sensitized to TiO_2 using a linking molecule. The overall increase in photocurrent

from the CdSe/TiO_2 hybrid structure is believed to be due to better or stronger coupling between the CdSe and the TiO_2 when compared to the CdSe sensitized TiO_2 linked by short chain organic linker molecules.

3. Enhanced PEC Performance of CdSe QD-Sensitized Au/TiO_2 Hybrid Mesoporous Films

Metal NPs have also been considered for sensitizing of enhance PEC properties of metal oxides. We have demonstrated the first Au/TiO_2 hybrid structure (0-5%) that has also been sensitized with CdSe QDs for PEC water splitting. For the pristine TiO_2 film sample, the absorption onset is around 360 nm, with minimal visible light absorption. In contrast, the Au/TiO_2 film showed strong absorption in the visible region due to the surface plasmon resonance (SPR) of Au NPs, and the absorption increases with increasing amount of Au NPs loading. The strong enhancement for the photocurrent when Au is introduced with CdSe can be explained by an increase in scattering due to presence of the metal. The increase in scattering allows the CdSe to absorb more light and inject electrons into the conduction band of TiO_2. Since enhancement occurred over the entire visible spectral range and increased with decreasing wavelength, increased light scattering by Au NPs is suggested to be responsible for the enhanced PEC performance.

4. N-Doped ZnO Nanowire Arrays for PEC Water Splitting

N-doped zinc oxide (ZnO:N) nanowire arrays have also been studied as photoanodes in PEC hydrogen generation from water splitting. In comparison to ZnO nanowires without N-doping, ZnO:N nanowires show an order of magnitude increase in photocurrent density with photo-to-hydrogen conversion efficiency of 0.15% at an applied potential of +0.5 V (versus Ag/AgCl). These results suggest substantial potential of metal oxide nanowire arrays with controlled doping in PEC water splitting applications.

5. Photocatalytic Performance Improved in Nanorod Arrays

One way to effectively increase the photocatalytic performance of TiO_2 is to couple it with a metal, such as Ag, in order to create an effective charge-separation between the photogenerated electron-hole pairs. Ag NPs with different loadings were systematically coated onto uniformly aligned TiO_2 nanorod arrays, and their photocatalytic performance was found to be enhanced compared to bare TiO_2, and increased linearly with the Ag NP loading until a maximum photodecay rate was reached at 0.25 wt.% Ag loading, and then decreased linearly with further increasing Ag loading. A simple reaction model was developed to explain the experimental results. Using two consecutive glancing angle depositions (GLAD) at different deposition angles and with different material, a WO_3-core TiO_2-shell nanostructure has been fabricated. The core-shell nanostructures are much more efficient in the amount of photodegradation abilities that can be extracted per nm of TiO_2 deposited. For the core-shell nanostructures annealed at T_a =300°C, this ratio is 470 times, 90 times, and 18 times more efficient than the amorphous TiO_2, anatase TiO_2, and multi-layered TiO_2/WO_3 films. This huge improvement can be directly correlated to the larger interfacial area between TiO_2 and WO_3, which is optimized in this core-shell morphology.

Both WO_3/TiO_2 and TiO_2/WO_3 core/shell nanorod films were used to make electrodes for PEC water splitting. IPCE analysis showed that the WO_3/TiO_2 samples were more efficient at water splitting. The maximum efficiency for the TiO_2/WO_3 sample was under 5% at about 340 nm. The WO_3/TiO_2 achieved near 12% IPCE at 350 nm but the efficiency decreased sharply around 390 nm. These preliminary data show that the WO_3 is the better core material for these core/shell structures but improved efficiency in the visible region through sensitization or doping may allow these structures to achieve greater efficiency. Additional characterization will be needed to determine why the two structures showed such a marked difference in water splitting efficiency.

6. Double-Sided QD Co-Sensitized ZnO Nanowire Arrays for PEC Hydrogen Generation

An analogue of the typical tandem cell for PV devices has been produced by designing a photoanode which is coated on both sides with conductive substrate (FTO) and ZnO nanowires. To increase the visible light absorption, both sides have been coated in either CdS or CdSe. This unique structure integrates the motif of QD sensitization and tandem cell to provide a simple approach to enhance simultaneously the visible light absorption and carrier collection of nanostructured metal oxide photoelectrodes. The electrode with the highest photocurrent and efficiency was when the CdS/ZnO nanowire side was illuminated with light loading compared to the CdSe/ZnO on the opposite end. Controls were done on various double sided as well as single sided structures. Linear sweep measurements for the CdS/ZnO-ZnO/CdSe double sided nanowire electrodes showed enhanced photocurrent when compared to control structures. This is due to the elevation of the CdSe when the Fermi energies are aligned increasing electron and hole transport. Recombination of electrons and holes is also less in these devices which increases their overall performance.

Future Directions

Our plan for next year include optimization of composite structures in terms of ratio and morphology of constituent components, validation of the enhanced hole transport model proposed using ultrafast laser techniques using the new fs laser system acquired recently, and improvement of overall PEC performance by carefully considering, determining and controlling the key factors involved, including electrode, interfacial interaction, and optical absorption. A combination of microscopy, spectroscopy, dynamics, and electrochemistry techniques will be employed. Collaboration with appropriate groups will be

sought, including possible theoretical modeling in relation to the experimental work.

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