doi:10.1017/S1431927613003632
Microsc. Microanal. 19 (Suppl 2), 2013

CdSe Heterostructures for Photocatalytic Hydrogen Generation

Pornthip Tongying, Masaru Kuno and Galyna Krylova

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556 USA

The demands of energy consumption grow each year due to an increasing world population. Major energy sources, such as fossil fuels, are rapidly depleting, making renewable energy an immediate concern. Hydrogen is a potentially clean alternative energy carrier for the system composed of fuel cell. Photocatalytic water splitting under visible light is an attractive environmental-friendly approach to produce hydrogen, which utilizes two renewables: water as a raw material and solar light as an abundant energy source. Semiconducting materials can be used as a photocatalyst if they meet the following requirements: (i) it should possess a suitable energy band gap which is able to absorb solar light in the UV and visible regions; (ii) their conduction band energy level (E_{CB}) should be more negative than hydrogen's reduction potential [E_{CB} < -0.41 V versus Normal Hydrogen Electrode (NHE), pH=7] while their valence band energy level (E_{VB}) should be more positive than oxygen's reduction potential (E_{VB} > 0.82 V versus NHE, pH=7).

Cadmium and zinc chalcogenides have received a lot of attention because they absorb both visible and UV light. For example, CdS (E_g = 2.4 eV) powder has been reported as a photocatalyst for water splitting in a sulfide/sulfite solution[1]. Recently, Osterloh et al. demonstrated that the confinement properties of semiconductors play an important role in photocatalytic H_2 generation. Namely, higher H_2 production rates are observed in CdSe quantum dots (QDs) with diameters in the range of 2.25-3 nm[2]. The H_2 generation efficiencies can also be enhanced by incorporating semiconductor with noble metals (such as Pt, Pd and Au) to improve charge separation[3]. To better understand the role of heterostructure play in photocatalytic H_2 generation, in this work focuses on designing of heterostructure models based on one-dimensional (1D) high-quality CdSe nanowires (NWs). This is composed of core/shell NWs (CdSe/CdS core/shell) as well as the decoration of CdSe and core/shell NWs with Pt NPs.

CdSe NWs with diameters (*d*) of ~14.0 ≤ 2.6 nm and lengths (*l*) ~6 μm have been synthesized using Solution-Liquid-Solid (SLS) growth [4]. Representative transmission electron microscope (TEM) micrographs are shown in figures 1a-b. To produce CdSe/CdS core/shell NWs, the obtained CdSe NWs were then coated with a ~5 nm thick dot-like CdS shell at mild temperature (~120 °C) using elemental sulfur and dimethylcadmium precursors (figures 1c-d). Subsequently, both CdSe and CdSe/CdS core/shell NWs were decorated by Pt NPs using a thermal deposition approach which is the injection of $Pt(acac)_2$ and NWs precursor into the mixture solution of oleic acid and oleylamine at 200 °C[5]. NPs uniformly coat the surface of NWs and have diameters of ~3-5 nm. Low- and high-resolution TEM images of these hybrid nanostructures are shown in figures 1e-h. The photocatalytic H_2 generation of all NWs obtained and their heterostructures has been performed under visible light in the presence of Na_2S/Na_2SO_3 as sacrificial electron donors, which also prevent photocorrosion of NWs contributing materials stability during photocatalytic reactions. The observed photocatalytic activity for H_2 generation increases in the order: CdSe< CdSe/CdS< CdSe/CdS/Pt NP NWs. A maximum H_2 generation rate of 434.29 μmol h^{-1} g^{-1} for CdSe/CdS/Pt NP heterostructure is approximately 220 and 8 times better than that of bare CdSe and CdSe/CdS core/shell NWs, respectively. Adding Pt NPs dramatically improves H_2 generation rates because it improves charge separation in the system while simultaneously acting as a cocatalyst for the reduction of surface adsorbed protons [6].

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[6] This research is supported by the Center for Sustainable Energy at Notre Dame (cSEND). The authors thank the Center's Materials Characterization Facility (MCF), the Notre Dame Integrated Imaging Facility (NDIIF), as well as the Notre Dame Radiation Laboratory/Department of Energy (DOE), Office of Basic Energy Sciences, for use of their facilities and equipment. P.T. thanks the Royal Thai Government Scholarships for partial financial support.

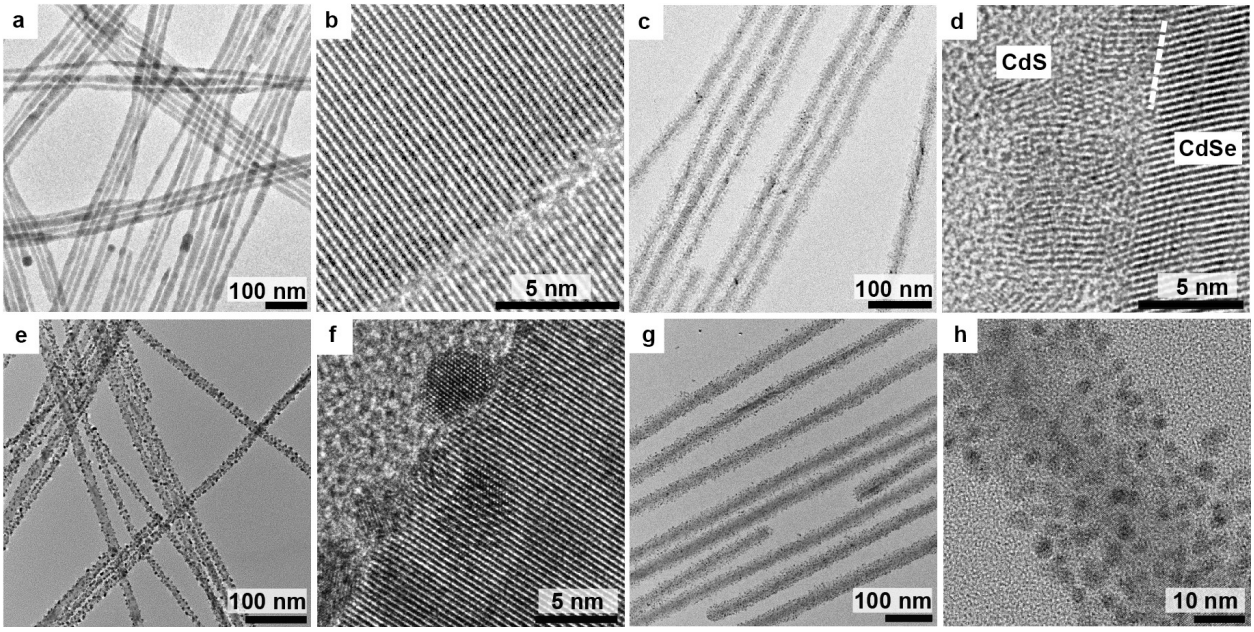

Figure 1. Low- and high resolution TEM images of CdSe NWs (a-b) and CdSe/CdS core/shell NWs (c-d), Pt decorated CdSe (e-f) and CdSe/CdS core/shell (g-h) NWs.

https://doi.org/10.1017/S1431927613003632 Published online by Cambridge University Press