

SiO₂@ZnIn₂S₄ Core-shell Nanoparticles for Photocatalytic Hydrogen Evolution

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Extended Abstract

ZnIn₂S₄ (ZIS) is a visible-light-driven photocatalyst with the energy band gap of 2.25 eV, suitable for hydrogen production from water splitting [1]. Similar to other photocatalysts, ZIS suffers electron-hole recombination and slow oxygen evolution reaction kinetics. In our previous studies, gold–silver nanoshells (GS-NSs) with a tunable surface plasmon resonance (SPR) were employed to facilitate charge separation of photoexcited carriers. We developed a microwave-assisted hydrothermal method to generate ZIS particles [2]. In particular, GS-NSs were used as the seeds during the ZIS synthesis. Note also that an interlayer of SiO₂ between the GS-NSs and the ZIS photocatalyst provided another key parameter to control the hydrogen production. Our studies showed that this unique GS-NS@SiO₂@ZIS core-shell particles exhibited a unique plasmonic-enhanced photocatalytic hydrogen production [3][4]. The matching of the absorptions between GS-NSs and ZIS, and the thickness of SiO₂ interlayer play important roles on the charge transfer mechanism [4]. However, the coverage, thickness, and crystallinity of ZIS on top of the SiO₂ interlayer were not systematically investigated. Control over the core-shell particles enables us to study structure-property relationships. We initiated the preparation of SiO₂@ZIS core-shell particles, since the SiO₂ surface properties can be tethered using self-assembled monolayers. Additionally, the method developed in this study can further be generalized to synthesize metal sulfide photocatalysts on top of other metal oxide surfaces. Our initial results showed that, the thickness of ZIS shell can be varied and the coverage of ZIS shell can be improved on SAM-modified SiO₂ particles, using hydrothermal method. However, the poor crystallinity suppressed the hydrogen evolution rate, perhaps due to more electron-hole trap sites. In this work, we focused on improving the coverage and crystallinity of ZIS shells synthesized using microwave-assisted solvothermal method by pH control in H₂O or ethanol [5]. The surface modification on SiO₂ surfaces was also critical to generate a homogeneous coverage [6][7]. The results showed that SiO₂@ZIS exhibits the best coverage but poor crystallinity while synthesized in the pure ethanol, and exhibits the best crystallinity but poor coverage in the pure H₂O. All SiO₂ particles were modified with (3-mercaptopropyl) trimethoxysilane (MPS). Particles synthesized in lower pH would improve the crystallinity, both in H₂O and ethanol. However, the ZIS coverage was worse in H₂O, and better in ethanol solution. Thickness of ZIS shell could easily be control in ethanol at different pH. In order to further enhance the performance of SiO₂@ZIS, increasing precursor concentration of ZIS coating onto SiO₂ in ethanol with lower pH condition gave rise to a better crystallinity and homogeneous coverage for better photocatalytic hydrogen production. The reason is that at a lower pH condition and higher precursor concentration, thioacetamide releases more H₂S gas during solvothermal process. Higher H₂S concentration at a higher pressure reaction cell is suggested to assist crystalline ZIS growth selectively on the MPS-modified SiO₂ surface. Thus, our facile procedure paves the way to generate a more complex structure GS-NS@dielectric@photocatalyst, for optimization of solar hydrogen production.

Keywords: Core-shell particle, hydrogen production, solar energy

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