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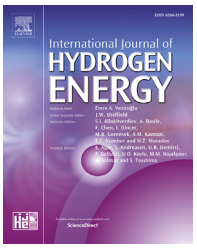

Efficient photo-catalytic hydrogen production performance and stability of a three-dimensional porous CdS NPs-graphene hydrogel

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ABSTRACT

We designed a novel CdS nanoparticles composite graphene hydrogel. Under sunlight, the CdS nanoparticles (NPs) -reduced graphene oxide hydrogel (rGH) had the highest hydrogen production rate of 6.44 mmol/g, which is 1.3 times that of CdS nanoparticles (5.12 mmol/g) and 1.4 times that of CdS (4.6 mmol/g). The enhanced photo-catalytic activity can be attributed to several positive factors such as the formation of composite hydrogels and the quantum size effect of the CdS nanoparticles nanomaterials. The formation of the composite hydrogel improves the specific surface area of the catalyst and increases the active site on the catalyst surface. The quantum size effects of the CdS nanoparticles effectively reduce the recombination probability of electrons and holes. The close contact between the CdS nanoparticles and the graphene gel can effectively separate photo-generated electrons and holes via the unique large π-bond structure of graphene. These positive factors effectively improve the photocatalytic activity of composite materials for water decomposition. In addition, recovery experiments show a composite catalyst recovery rate of up to 95%. The results show that the composite photo-catalyst can effectively avoid secondary pollution during photo-catalytic hydrogen production. This eliminates powder recovery problems. The hydrogen production efficiency of the catalyst remains unchanged after 5 cycles indicating that the formation of the gel system stabilizes the catalyst and inhibits light corrosion of CdS nanoparticles.

Introduction

New energy vehicles are important to major car manufacturers and research institutes. Fuel-cell vehicles (FCV) are widely recognized as a new type of vehicle with promising development prospects because of its high efficiency and near-zero emission [1].

Hydrogen is a renewable, non-polluting, and abundant source of clean energy that is recognized in all countries. Therefore, hydrogen fuel cells have received widespread attention. Hydrogen production is mainly through the conversion of fossil fuels (coal, natural gas, petroleum) and steam at elevated temperatures. Another major method is electrocatalytic hydrogen production. However, both of these methods can result in environmental pollution. Solar

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photocatalytic decomposition of water is a promising solution to the global energy crisis and environmental pollution [2–7] and has aroused widespread concern in the scientific community. Solar energy is clean, energy-rich, and long-lasting. It is an important choice for human beings to cope with energy shortage, climate change, and energy conservation. In 1972, Fujishima et al. [8] converted solar energy directly into chemical energy because the TiO_2 single crystal electrode decomposes water to produce hydrogen under light irradiation. However, the solar conversion efficiency (STH) of UV-responsive semiconductors is too low, and high STH semiconductors are the focus of current research.

In TiO_2 [9–12], transition metal sulfide [13–25], Transition metal phosphide [26,27], carbon nitride [28–30], ZnO [31,32], and other photo-catalytic materials, CdS has a narrower band-gap width of ~2.4 eV; thus sunlight can be absorbed more effectively. In addition, the band position of CdS completely satisfies the thermodynamic requirements of many mainstream photo-catalytic reactions, such as hydrolysis [33,34]. More importantly, the edge position of the conduction band (CB) of CdS is more correct than most of studied semiconductors such as TiO_2, $SrTiO_3$, and ZnO indicating that the photo-generated electrons of CdS have a strong reduction ability toward the photo-catalytic reaction. Therefore, CdS has been extensively explored in various fields of photo-catalysis. However, the photo-catalytic activity of pure CdS semiconductor materials has not yet been improved. This is because the CdS particles have poor photo-stability, and serious aggregation with each other, which increases the recombination of photo-generated carriers. Finally, cadmium sulfide is difficult to recover and it is likely to cause secondary pollution.

By reducing the particle size of CdS, the photo-catalytic efficiency and photo-stability of CdS during water decomposition can be improved. Zero-dimensional (0D) nanomaterials such as quantum dots (QDs) with small particle size and large specific surface area facilitate rapid migration of photo-generated electrons and holes and alleviate the problem of photo-corrosion [35,36]. At the same time, conductive carbon nano-materials can effectively promote the transfer of photo-generated electrons, thus far, graphene, carbon nanotubes, and fullerenes are widely used to achieve these advantages [37–42].

In addition, High surface matrix can not only improve the stability and photocatalytic activity of CdS nanoparticles, but also promote the recovery of catalysts, such as silica, alumina, and polymers (such as polystyrene, polyacrylamide, sodium alginate shell polysaccharides) as a matrix to support the use of inorganic nanoparticles [43–50].

Hydrogels are three-dimensional network structures formed by hydrophilic polymer chains that are interconnected by covalent or secondary interactions (electrostatic, van der Waals, hydrogen bonds, etc.) [51]. Hydrogels can be swollen by absorbing large amounts of water through internal functional group hydrophilic groups such as -COOH, $-SO_3H$, $-NH_2$, -OH, and $-CONH_2$ [52,53]. These groups bind strongly to metal ions [47], and the hydrogels adsorb heavy metal ions. Because of these properties, hydrogels with specific functional groups provide a unique water environment, and hydrogels also show good biocompatibility and environmental friendliness. Thus, they show great potential for environmental protection [54–56].

The high specific surface area and low density three-dimensional porous structure of graphene hydrogel are widely used in photo-catalytic hydrogen production and degradation. For example, a graphene hydrogel is loaded with TiO_2 [57–59], g-C_3N_4 [60], Ag_3PO_4 [61], and AgBr [62] to degrade pollutants and adsorb heavy metal ions and graphene hydrogel is loaded with C_3N_4 QDs [63],TiO_2 [64], MoS_2 [65] to photocatalytic hydrogen production. The specific surface area and porous structure reduce the recombination of photo-generated electrons and holes. This can improve the stability and recovery efficiency of the catalyst. However, the application of graphene hydrogel in the photo-catalytic hydrogen production is still relatively small. Therefore, it is reasonable to expect that CdS NPs can be loaded on the graphene hydrogel to improve its photocatalytic hydrogen production activity and stability.

Here, we designed a solar-induced gel system that produces hydrogen. Hydrothermal synthesis of CdS NPs-rGH composite catalyst not only inhibited the photo-corrosion of CdS, but also increased the active site of the composite catalyst and also improved the separation of photo-generated charges rate. The morphology, microstructure, and optical properties of the composites were studied in detail especially the interaction between CdS NPs and graphene. The photocatalytic hydrogen evolution activity of CdS NPs-rGH composite hydrogels was evaluated under simulated sunlight. In this experiment, the photocatalytic activity of CdS NPs-rGH composite hydrogel was tested by photochemical, UV–Vis and fluorescence spectroscopy. The recovery of CdS NPs-rGH and CdS was compared and reflected the low cost and high recovery rate of composite hydrogel. We used these results to study the hydrogen production mechanism.

Experimental

Methods for preparing CdS NPs, graphene hydrogel and CdS NPs-rGH

Preparation of CdS NPs

First, stable CdS NPs aqueous solutions were synthesized by improving the synthetic methods in the literature [66]. Subsequently, an equal volume of $CdCl_2$, Na_2S, and EDTA aqueous solutions were mixed at room temperature under ultrasonic agitation in order to mix them thoroughly. Prior to mixing, the pH of the aqueous EDTA solution was adjusted to 5 by addition of HCl. At pH = 5, the EDTA molecules dissociate and behave as negative ions (anions). As a result, they become ligands for Cd. When the solution is shaken, the EDTA-anion forms an amphipathic negatively charged shell rendering the QD water-soluble. The pH of CdS-EDTA quantum dots in water is close to the initial pH value of EDTA aqueous solution. The best molar ratio of Cd^{2+}/HS^-/EDTA is 1/0.9/1.

Preparation of graphene hydrogel

(Graphene oxide was purchased from TIMES-NANO (Chengdu, Sichuan, China) Purity: > 98 wt%; layers: <3; diameter: 8–15 μm). The GO was placed in water and sonicated until the

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