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Preparation of a novel recyclable cocatalyst wool–Pd for enhancement of photocatalytic H_2 evolution on CdS

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ABSTRACT

In recent years, the research of photocatalyst splitting of water to hydrogen by using semiconductor has been developed rapidly. CdS are attractive photocatalytic materials for the conversion of solar energy into chemical energy under visible-light irradiation. In this paper, a kind of recyclable cocatalyst that the wool supported palladium cocatalyst was synthetized and characterized by X-ray diffraction, diffuse reflectance UV–vis spectroscopy, energy-dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopic (XPS) studies and transmission electron microscopy (TEM). The optimal weight percentage of wool–Pd was found to be 3.0 wt %, which resulted in a high visible-light photocatalytic average H_2-production rate of 1555 μ mol/h. It showed that the recycled cocatalyst wool–Pd could improve the efficiency of photocatalytic hydrogen production because of introducing oxidation cocatalyst PdS and reduction cocatalyst Pd. This study indicated that the prepared recyclable cocatalyst wool–Pd not only could improve the efficiency of photocatalytic hydrogen production, but also eco-friendly and recyclable.

1. Introduction

Hydrogen energy, which can be produced from water and has no pollution when used as fuel, is considered to be one of the most promising substituting energy for the exhausting fossil fuel [1,2]. One major source of energy available to the world is water, which is very abundant but not as easily as transported as hydrogen energy. Major research efforts are therefore underway to find ways to convert by water to hydrogen energy [3–5]. Heretofore, more attention has been given to use

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semiconducting photocatalytic materials for hydrogen generation from water under light irradiation [6–9].

II–VI group semiconductor compounds have attracted great attention due to their electrochemical properties [10,11]. Although there has developed the vast majority of photocatalysts, cadmium sulphide (CdS) continues to be a favored material because of its capability of converting light energy into chemical energy. We know CdS semiconductor with a direct band gap of 2.42 eV displays superior optical, photophysical and photochemical properties [12,13]. However, there exist some problems in using CdS. For instance, one is high recombination rate of photogenerated electron hole pairs, which to some extent limited its application [14–16]. Therefore, how to greatly enhance the activities of photocatalysts is most important. Many researchers have made efforts to promote the activity of CdS particles, such as synthesis of CdS with different morphologies (flower-like [17–19], belt-like [20]and tube-like) and combination with other components, including noble metals, semiconductors, and carbon materials. Many studies reportedly showed that certain semiconductor photocatalysts could exhibit high photocatalytic activity even without cocatalysts [21,22]. Nevertheless, the cocatalysts loaded on semiconductor photocatalysts enable or increase the photocatalytic activity of the photocatalysts [23].

So far, a number of studies indicated that mainly noble metals were used as the cocatalysts [24–26], but the noble metals are costly and also their utilization rate is low. Based on the above two points, we supported noble metal palladium on the wool to form a recycled cocatalyst wool–Pd. Our group have used wool–Pd as a highly active heterogenous catalyst for heck reaction [27]. We found that for the wool supported palladium catalyst, the loaded palladium particles could be distributed evenly in the surface of fibers due to the structurally ordered amino acids chains, so the formation and aggregation of Pd-black could be prevented, which was regarded as the most critical problem to the performance of palladium catalyzed conversions. Herein, we report that wool–Pd as a recycled cocatalyst loaded on CdS for photocatalytic H_2 production using sulfide and sulfite as sacrificial reagents under visible light. The activity of CdS could be enormously increased by introducing wool–Pd as a recycled cocatalyst under the same reaction conditions. In addition, the recycled cocatalyst wool–Pd exhibited excellent catalytic performance and ability of reusing, which would have a good application prospect.

2. Experimental

All starting materials and reagents were commercially available and used without further purification.

2.1. Synthesis the serial WPC samples

In typical synthesis process, 15 mg of wool–Pd complex catalyst prepared in our laboratory [28] (Pd 11.74%) were dipped in deionized water (20 mL) by sonication for 10 min. An aqueous solution of Na_2S (20 mL, 0.01 M) was added slowly to wool–Pd under vigorous stirring. Then, $Cd(Ac)_2 \cdot 2H_2O$ (20 mL, 0.01 M) aqueous solution was added dropwise to the mixture (40 mL, as prepared above), followed by combination of vigorous stirring and sonication for 30 min. The yellow mixture was then stirred at 80 °C for 2 h. The weight ratios of wool–Pd to $Cd(Ac)_2 \cdot 2H_2O$ were 0, 0.5%,1.0%, 2.0%, 3.0%, 4.0% and 5.0%, and the obtained samples were labeled as WPC0, WPC0.5, WPC1.0, WPC2.0, WPC3.0, WPC4.0 and WPC5.0, respectively. Finally, the resulting serial WPC samples were centrifuged and subsequently washed with deionized water and then dried in a vacuum at 80 °C for 12 h.

2.2. Recycling of the wool–Pd cocatalyst

An important point concerning the use of wool–Pd cocatalyst is its lifetime, particularly it might have a good application prospect in the future. The successive operations were depicted as follows: after the end of the reaction, the mixture was cooled down to room temperature and took wool–Pd catalyst out of the mixture with tweezers, then washed with deionized water (5 × 10 mL) and then dried in a vacuum at 40 °C for 12 h. In the next synthesis process, a certain of wool–Pd was dipped in reactor for preparing the same ratio of WPC samples, which can be recycled and reused for a plurality of times.

2.3. Characterization

X-ray diffraction patterns (XRD) of the metal oxides prepared were recorded on a Rigaku X-ray diffractometer D/MAX-2200/PC equipped with Cu K_α radiation (40 kV, 20 mA). UV–vis diffuse reflectance spectra were measured using Shimadzu UV-3100 spectrophotometer. The reflectance spectra were transformed to absorption intensity by using Kubelka–Munk method. XPS measurement was recorded on PHI5702 photoelectron spectrometer. Binding energy was referred to C1s (284.80 eV). ICP-AES were measured on IRIS Advantage. TEM study was carried out on a TECNAI TF20 instrument. Elemental analysis of the photocatalyst was conducted by EDX attached to the transmission electron microscope.

2.4. Photocatalytic activity

About 0.15 g of photocatalyst powders was dispersed in 100 mL of aqueous solution containing 0.5 M Na_2S and 0.5 M Na_2SO_3 as the sacrificial reagents in the reactor under the vertical irradiation of a 300 W Xe lamp. The suspension was then thoroughly degassed and irradiated by a 300 W Xe lamp (Aulight, CEL-HXF300) which is equipped with an optical filter (0.1 M $NaNO_2$ aqueous solution) to cut off the light in the ultraviolet region. The amounts of H_2 evolution were measured by using a gas chromatography (QC-9101, 5Å-coloum) with thermal conductivity detector (TCD) and Ar as carrier gas.

3. Results and discussion

3.1. WPC photocatalysts structure and optical characterization

Fig. 1 shows the X-ray diffraction (XRD) patterns of the serial WPC samples. The main diffraction peak positions of the