Surface modification—a novel way of attaching cocatalysts on CdS semiconductors for photocatalytic hydrogen evolution

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Abstract. Noble metals as cocatalysts for hydrogen evolution are widely investigated for semiconductor photocatalytic water splitting. In this paper, we present a novel way to attach not only noble metals, but also transitional metals onto CdS nanocrystals as cocatalysts for hydrogen evolution. The hydrogen evolution performances for each metal were compared and result shows that Pd attached CdS gives the highest hydrogen evolution rate of 250 \( \mu \)mol/h. The amounts of metal ions attached on the surface were measured by inductively coupled plasma optical emission spectrometry (ICP-OES). This work confirms that surface modification is a promising way of attaching cocatalysts onto semiconductor photocatalysts.

1. Introduction
Photocatalytic hydrogen evolution using semiconductor powder materials has gained considerable attention because of the importance of utilizing solar energy as renewal energy to form green fuel [1]. Nanocrystals (NCs) in particular have seen significant growth as the photocatalyst to generate hydrogen due to superior photostability, larger absorption spectral range and properties that deliver multiple electrons with minimal structural perturbations compared to organic or organometallic molecules. For semiconductor photocatalyst system, cocatalysts play an extremely important role as it helps to promote charge separation, which in return reduces bulk and surface electron/hole recombination [2]. In general, there are two main ways to deposit cocatalyst on semiconductors, i.e. photodeposition and impregnation. However, both processes inherit the following disadvantages. For example, both ways always result in nonuniform distribution of the cocatalysts on the surface. Second, the size distribution of cocatalyst is hard to be controlled hence results are difficult to be reproduced. Third, noble metals are still widely used which hindered the wide application due to the high cost of these materials. Therefore, alternative methods and low-cost cocatalyst materials are still much needed for the synthesis of low-cost, highly stable and effective water splitting photocatalyst systems.

Semiconductor CdS has been reported as effective photocatalyst for \( \text{H}_2 \) evolution in literatures, and effective cocatalys are always needed for this photocatalyst to produce hydrogen, thus CdS nanocrystals was chosen as photocatalyst for testing our surface modification approach [3,4] and materials. Here, by modifying the CdS NCs’ surface with organic molecules, i.e. 1,2-Ethanedithiol

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(EDT), we achieved a stable, reproducible and efficient way of depositing various of cocatalysts on CdS surface.

2. Materials and methods

2.1. Materials

Sodium sulfide nonahydrate (Na$_2$S·9H$_2$O, ≥98%) and cadmium(II) acetate nonahydrate (Cd(OAc)$_2$·9H$_2$O, ≥98%) were purchased from Acros Organics. 1,2-Ethanedithiol (EDT), triethanolamine (TEOA), ascorbic acid (AA), copper(II) sulfate pentahydrate, ferric nitric acid nonahydrate, cobalt chloride, gold(III) chloride trihydrate, palladium(II) chloride, trisodium rhodium(III) hexachloride were all purchased from Sigma-Aldrich.

2.2. Methods

2.2.1. Synthesis of CdS. CdS nanocrystals was synthesized according to a previous report [5]. In detail, 400 ml of a Na$_2$S (0.14 M) aqueous solution and 500 ml of a Cd(OAc)$_2$ (0.14 M) aqueous solution were mixed together under vigorous stirring. After being continuously stirred for 24 h, the solution was filtered and the solid was washed several times with deionized water. The yellow solid was then dispersed in 100 ml of deionized water and transferred to a Teflon-lined stainless autoclave for hydrothermal processing. After being heated at 453 K for 3 days, the yellow solid was filtered again and kept under vacuum until dry.

2.2.2. Attaching metals ions as cocatalysts on CdS. A solution of CdS (100 mg) in toluene (50 ml, >99.9%, Sigma-Aldrich) was sonicated at room temperature, 1 ml of 1% (v/v) EDT solution in ethanol (absolute grade, Sigma-Aldrich) were added. The resulting mixtures were stirred for 6 h and centrifuged. The precipitates were washed with ethanol (20 ml) 3 times and redispersed in ethanol (40 ml). Then, 0.1 mol/l M (M=Cu, Fe, Mn, Co, Au, Pd, Rh) ions in ethanol (10 ml) was added to this suspension. The suspension was stirred for 1 h and then centrifuged. The resulting precipitates were washed with ethanol (20 ml) 3 times, centrifuged, and dried under vacuum at 50°C to obtain a greenish-yellow solid in quantitative yield.

2.2.3. Characterization. Photocatalytic testing was conducted using a recirculating batch reactor and top-irradiated photocatalytic reactor. The accumulated gaseous products were analyzed with a Bruker 450 gas chromatograph equipped with a TCD and a molecular sieve 5A column. The light source was an Asahi Spectra MAX-303 (300 W Xe lamp) with a cold mirror and various band-pass filters. The photon irradiance was measured using an EKO LS-100 spectroradiometer. 50 mg of photocatalyst was immersed by sonication in 25 ml of a solution of 0.5 M Na$_2$S and 0.5 M Na$_2$SO$_3$. The reactor was connected to a recirculation system, and the dissolved air in the solution was evacuated before the photocatalytic test.

3. Results and discussion

We used 1,2-ethanedithiol (EDT) as a molecular linker to attach various metal ions to CdS NCs surfaces through exceptionally stable metal-thiol bond. Since the metal ions are only attached to the surface with SH group, the position of the metals can be confirmed and The amounts (0.1~0.3 wt%, ICP results) that required to obtain an optimal H$_2$ evaluation rate are significantly lower than that of the metal deposited by photo-deposition (normally around 1 wt%), as shown in Table 1. Not only noble metals, but also transitional metals can be attached to the surface of CdS NCs (Figure 1). For the transitional metals, Ni shows the highest H$_2$ evolution rate of 110 μmol/h. Mn and Co are also effective cocatalysts for H$_2$ evolution. Figure 2 shows the H$_2$ evolution rate when noble metals are attached. All the noble metals improved H$_2$ evolution rate compare to bare CdS NCs, among which,
the highest hydrogen evaluation rate of 255 (µmol/h) was achieved by Pd which is around 30% higher than that of photo deposited Pd. These results confirm that surface modification is an effective way of attaching various metals as cocatalysts on semiconductor surface. Interestingly, some metals (such as Cu^{2+}, Fe^{3+}) had negative effect, while others improved the hydrogen evolution rate. One has to see that almost any metal ions can be attached to semiconductor surface through this surface modification approach while photo deposition only works for certain metals.

Figure 1. The H₂ evolution amount vs. time for transitional metals. Amount of catalysts: 50 mg; Electrolyte solution: 25 ml, Na₂S (0.5 M) / Na₂SO₃ (0.5 M). Light source: ASAHI Xe lamp, 300 W.

Figure 2. The H₂ evolution amount vs. time for noble metals. Amount of catalysts: 50 mg; Electrolyte solution: 25 ml, Na₂S (0.5 M) / Na₂SO₃ (0.5 M). Light source: ASAHI Xe lamp, 300 W.

In our recent research work [6], we have proved that only 0.01 ml of 1% EDT solution (in ethanol) was enough to fully cover 100 mg CdS NCs surface. Here, we used 1 ml 1% EDT solution in order to make sure that the complete surface of CdS NCs (100 mg) was saturated with EDT molecules. The metals ions were then added into the solution, which will be linked onto the CdS surface via
coordination bond between the metal ions and EDT molecules. The exact amounts of metal ions that attached onto the surface of CdS NCs were measured by ICP, as shown in Table 1.

| Metal ions | Metal (wt%) | $\text{H}_2$ ($\mu$mol/h)$^a$ |
|------------|-------------|-------------------------------|
| Fe         | 0.07        | 0.2                           |
| Mn         | 0.28        | 25                            |
| Co         | 0.10        | 32                            |
| Ni         | 0.14        | 110                           |
| Rh         | 0.24        | 40                            |
| Pd         | 0.36        | 255                           |
| Pt         | 0.33        | 18                            |

$^a$Conditions: 50 mg-cat, 20°C, 0.5 M Na$_2$S, 0.5 M Na$_2$SO$_3$, 25 ml, 300 W Xe lamp.

The effect of various sacrificial reagents such as Na$_2$S/Na$_2$SO$_3$, TEOA and AA was also studied and the corresponding hydrogen evaluation rates are shown in Figure 3. The results show that the highest $\text{H}_2$ evolution rate was obtained when Na$_2$S/Na$_2$SO$_3$ was used as sacrificial reagent. The enhancement of $\text{H}_2$ evolution rate was attributed to improved S oxidation rate assisted by the sacrificial reagents [7].

4. Conclusion
We demonstrated EDT as a highly efficient molecular linker to attach various metal ions onto CdS NCs surfaces through stable metal-thiol bonds. The performance of different metals as cocatalyst are fully investigated, among which Ni and Pd show $\text{H}_2$ evolution rate 110 and 255 $\mu$mol/h, respectively. The effect of sacrificial reagents was also investigated and Na$_2$S/Na$_2$SO$_3$ sacrificial reagent show
better performance than TEOA and AA. This approach also can be used as a universal method to load metal ions or semiconductor nanocrystals onto photocatalysts for hydrogen evolution.

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