



# Controlled synthesis of novel 3D CdS hierarchical microtremella for photocatalytic H<sub>2</sub> production

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## ARTICLE INFO

### Article history:

Received 22 August 2018  
Received in revised form 21 September 2018  
Accepted 1 October 2018  
Available online 3 October 2018

### Keywords:

Semiconductors  
Powder technology  
Structural  
Synthesis  
Photocatalytic activity

## ABSTRACT

In this paper, a novel three dimensional (3D) CdS hierarchical microtremella (MT) is fabricated by a facile solvothermal method at 60 °C with the assistance of EDA. Field emission scanning electron microscope (FESEM), UV-Vis diffuse reflectance spectroscopy (DRS), energy dispersive spectrometer (EDS) and X-ray diffraction (XRD) are used to investigate the crystal structure and optical properties of CdS MTs. The results indicated that the size of CdS MTs, in the form of nanosheets, is 0.5–1.5 μm and the samples are very pure. 0.6 wt% Pt is used as co-catalyst, the H<sub>2</sub> generation rate of CdS MTs under visible light illumination is 2.76 mmol h<sup>-1</sup> g<sup>-1</sup>, which is 2.2 times more than CdS nanoparticles without EDT. This work provides insight into the structure design of 3D photocatalysts and offers a new approach to broadband clean energy field.

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## 1. Introduction

Photocatalytic H<sub>2</sub> evolution (PHE) has received great attention as an effective pathway to convert sustainable and infinite solar energy into chemical energy for solving increasingly serious environmental pollution and energy shortage [1–3]. However, the photocatalyst suffers from a limited photocatalytic rate and lower quantum efficiency [4,5], which lead to significant losses to the actual application. Novel catalyst development is critical to address this challenge. As a consequence, the discovery and design of efficient photocatalysts is highly essential to visible-light photocatalytic degradation system.

In recent years, cadmium sulfide (CdS) has become one of the most popular materials for the design of excellent visible-light-driven photocatalysts [6,7]. Many attempts have been developed to control morphology, such as nanosheets [8], nanorods [9], quantum dots [10], and so on, for high photocatalytic activities and stability. However, the low efficiency caused by easy aggregation of CdS nanomaterials limits the practical application. Nowadays, three dimensional (3D) hierarchical materials, which can combine the advantages of ultrathin materials and hierarchical structures and improve the anti-aggregation behavior of ultrathin materials

[11], have been widely studied. The development of a facile and cost-effective synthesis method of 3D hierarchical CdS with high visible light photocatalytic activity remains a great challenge.

In this paper, a facile experimental procedure was designed to prepare novel 3D CdS hierarchical microtremella (MT) with the help ethylenediamine (EDA) via a hydrothermal method at very low temperature. The PHE activity of CdS has been greatly improved due to the novel 3D structure and high surface area.

## 2. Experimental

### 2.1. Synthesis of samples

1.14 g CdCl<sub>2</sub>·2.5H<sub>2</sub>O and 0.38 g thiourea ((NH<sub>2</sub>)<sub>2</sub>CS) were ultrasonically dissolved in the mixed solvents of 10 mL H<sub>2</sub>O and 20 mL EDA (C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>). Then the mixture was transferred to 50 mL autoclave and solvothermally treated at 60 °C for 12 h. Finally, the as-prepared sample was collected by washing thoroughly with water. As comparison, CdS nanoparticles (NPs) were also fabricated by changing 10 mL H<sub>2</sub>O and 20 mL EDA to 30 mL H<sub>2</sub>O.

### 2.2. Characterization

The crystal structure, morphology, element ingredient, Brunauer-Emmett-Teller (BET) specific surface area and optical

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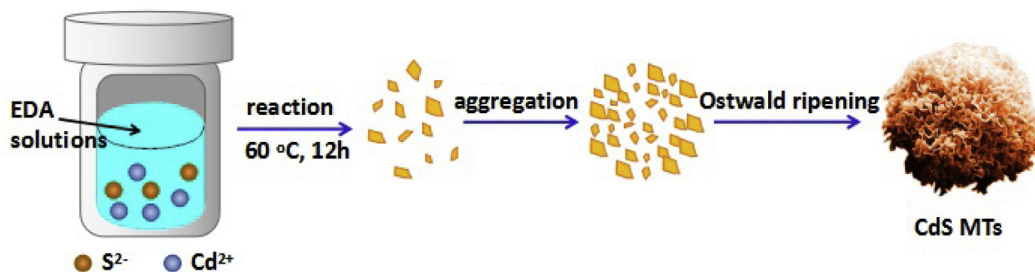


Fig. 1. Schematic illustration of the relevant preparation process of CdS MTs photocatalyst.

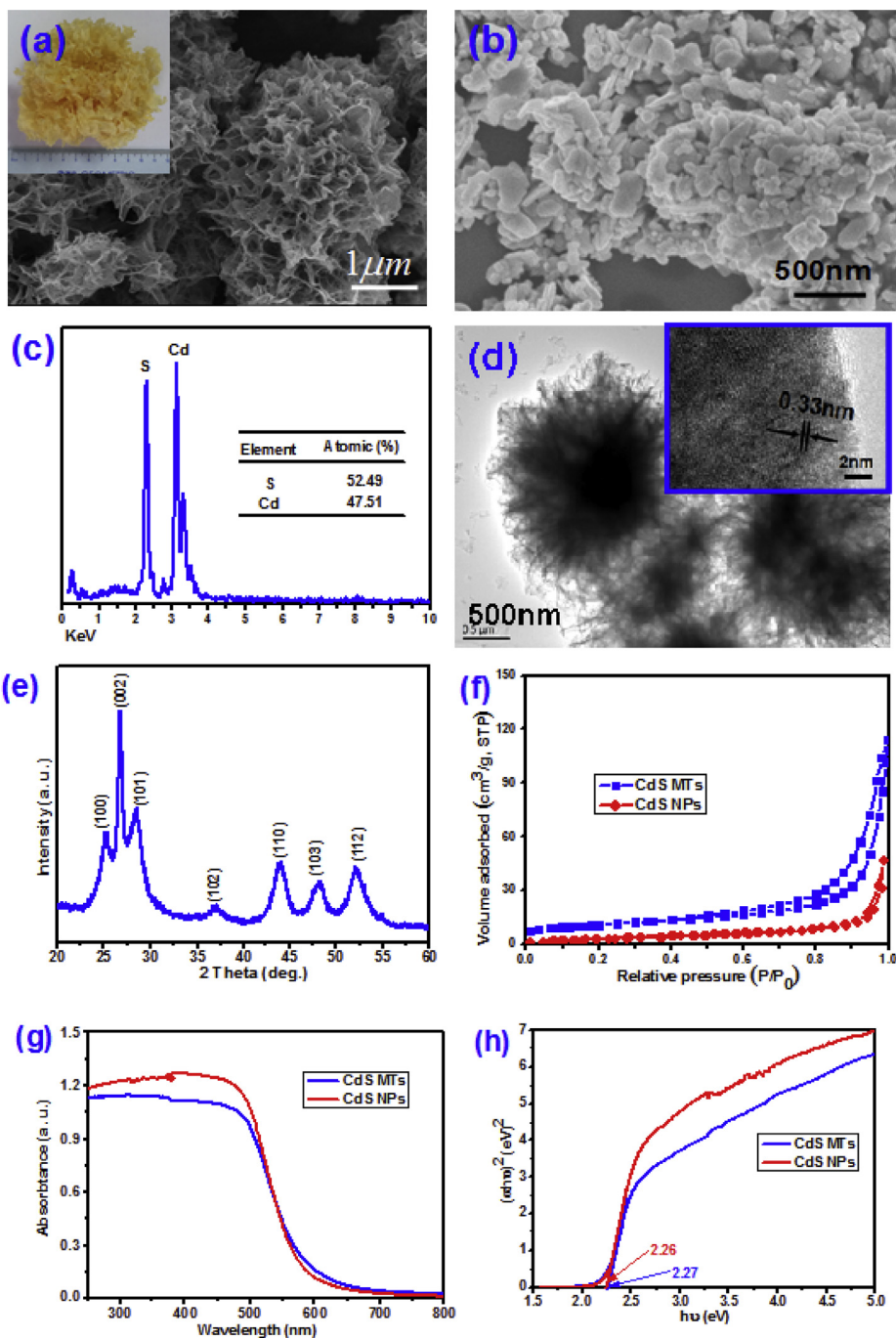


Fig. 2. SEM image of (a) CdS MTs and (b) CdS NPs, (c) EDS spectrum of CdS MTs and (d) TEM image of CdS MTs (the inserted images in 2a and 2d are photograph of tremella and HRTEM image of CdS MTs, respectively), (e) XRD pattern of CdS MTs and (f) Isotherms for N<sub>2</sub> adsorption-desorption of samples and (g) UV-Vis DRS spectra and (h) plots of  $(\alpha h\nu)^2$  versus energy ( $h\nu$ ) for CdS MTs and CdS NPs.

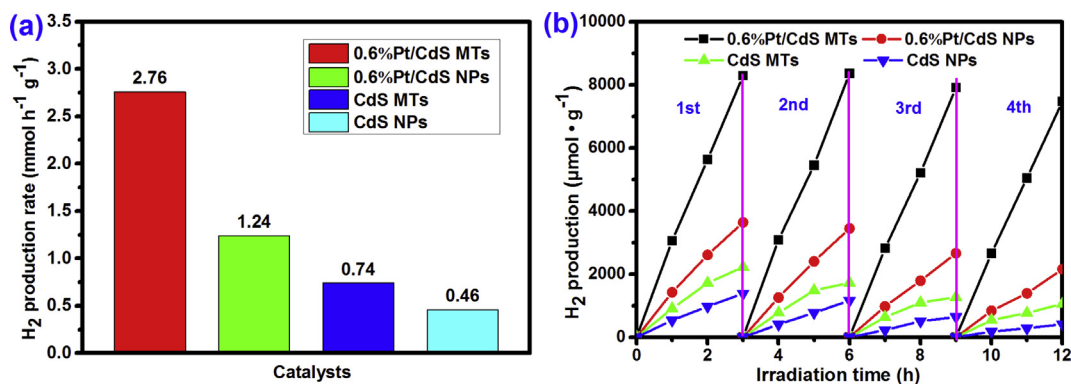


Fig. 3. (a) The comparison of pristine and 0.6%Pt-modified CdS composite in H<sub>2</sub> production and (b) cycling test of PHE over different photocatalysts.

performance of as-prepared samples were investigated by X-ray diffraction (XRD Panalytical Empyrean diffractometer), high-resolution transmission electron microscopy (HRTEM TecnaiG2 F20 S-Twin), scanning electron microscopy (FESEM JEOL 6300), N<sub>2</sub> gas adsorption system (Micromeritics ASAP 2010), energy-dispersive X-ray spectroscopy (EDS INCA) and UV-Vis diffuse reflectance spectroscopy (DRS PerkinElmer Lambda950).

### 2.2.1. PHE activity test

Catalyst (50.0 mg) was dispersed under constant stirring in a 100 mL mixed aqueous solution containing 0.35 M Na<sub>2</sub>S and 0.25 M Na<sub>2</sub>SO<sub>3</sub>. Pt (0.6 wt%) was photodeposited on the samples by directly dissolving H<sub>2</sub>PtCl<sub>6</sub> into the reactant suspension. 300 W Xe lamp equipped with a 420 nm-cut-off filter was used as light source. The amount of H<sub>2</sub> production was recorded by gas chromatography. As comparison, the PHE activity of CdS MTs and CdS NPs without Pt is also tested.

## 3. Results and discussion

The growth process of 3D hierarchical CdS MTs structure was illustrated in Fig. 1. Hierarchical CdS MTs were synthesized by a spontaneous Ostwald ripening process using solvothermal method, and EDA played an important role in this whole procedure. After thiourea dissolved in the water, S<sup>2-</sup> ions were slowly released from broken C=S chemical bonds. Nevertheless, because the Cd<sup>2+</sup> ions concentration was excess compared with concentration of S<sup>2-</sup> ions, the fractional Cd<sup>2+</sup> ions can react with EDA to form coordination complexes, which largely restricted the growth of generated CdS nanocrystals. Subsequently, in order to minimize the surface energy of CdS, the nanocrystals gradually aggregated into microtremella shapes. The special morphology and larger surface energy of inner nanocrystals led to the higher solubility than external CdS nanocrystals [12,13]. Thus, according to the Ostwald ripening effect [14], external CdS nanocrystals developed through unceasingly consuming of the inner nanocrystals.

Fig. 2a, b show the SEM image of CdS MTs and CdS NPs. The inserted in Fig. 2a is the photograph of real tremella. We can find that CdS has an obviously hierarchical MTs morphology with a clean and smooth surface. The EDS spectrum of CdS MTs is shown in Fig. 2c. It indicates that the samples are pure without other impurity elements. Fig. 2d shows the TEM image of CdS MTs. It turns out that the as-prepared samples were constituted with ultrathin nanosheets. Furthermore, the HRTEM image of CdS MTs is inserted in Fig. 2d, the lattice plane with spacing of 0.33 nm, corresponding to the (002) plane of hexagonal CdS. Fig. 2e shows XRD patterns of CdS MTs. The main peaks at 25.48°, 26.66°, 29.04°,

36.88°, 43.92°, 48.14° and 52.12° were observed and can be indexed to the (100), (002), (101), (102), (110), (103) and (112) of hexagonal CdS [JCPDS No. 41-1049] [15]. But the (002) diffraction peak of CdS MTs is very sharp, exhibiting that the crystal grows along the [001] preferred growth direction. Fig. 2f shows the N<sub>2</sub> adsorption-desorption isotherms for CdS MTs and CdS NPs at the same condition of 77 K. The surface area of CdS MTs (55.4 m<sup>2</sup>/g) is much higher than that of CdS NPs (13.7 m<sup>2</sup>/g). The UV-Vis absorption spectrum of the CdS MTs is shown in Fig. 2g. The fundamental absorption edge of CdS MTs is 546 nm, which means can be excited in the visible light region. As indicated in Fig. 2h, E<sub>g</sub> can be calculated according to the literature [16], and E<sub>g</sub> of CdS MTs is 2.27 eV.

Fig. 3a shows the PHE rates of pristine and 0.6%Pt-modified CdS composite under the irradiation of Xe lamp. CdS MTs with novel structure and large surface area show higher PHE performance (0.74 mmol h<sup>-1</sup> g<sup>-1</sup>) than that of CdS NPs (0.46 mmol h<sup>-1</sup> g<sup>-1</sup>). However, 0.6%Pt/CdS MTs exhibit much higher H<sub>2</sub>-production activity (2.76 mmol h<sup>-1</sup> g<sup>-1</sup>) than that of 0.6%Pt/CdS NPs (1.24 mmol h<sup>-1</sup> g<sup>-1</sup>) and CdS MTs. Fig. 3b shows the recycling PHE results of CdS MTs and CdS NPs. After 4 recycles, 0.6% Pt/CdS MTs still maintain 90% PHE performance, but the photocatalytic activity of 0.6% Pt/CdS NPs, CdS MTs and CdS NPs maintains 59%, 47% and 30%, respectively. Pt can be used as efficient co-catalyst not only for suppressing charge carrier recombination, but also for reducing the photocorrosion of CdS. Thus, the PHE performance of 0.6% Pt/CdS MTs dramatically increased.

## 4. Conclusions

In conclusion, we have successfully synthesized novel 3D CdS hierarchical MTs photocatalyst by a solvothermal treatment under very low temperature. The PHE performance of Pt-modified CdS hierarchical MTs is remarkably improved with the Pt co-catalyst, novel structure and large surface area. This novel structure will provide an importance strategy for designing and synthesizing economical and highly efficient visible-light-response photocatalysts.

## Acknowledgments

This work was supported by the National Natural Science Foundation of China (51572103 and 51502106), the Distinguished Young Scholar of Anhui Province (1808085J14), the Foundation for Young Talents in College of Anhui Province (gxyqZD2017051) and the Key Foundation of Educational Commission of Anhui Province (KJ2016SD53 and KJ2018A0394).

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