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Coconut shell carbon nanosheets facilitating electron transfer for highly efficient visible-light-driven photocatalytic hydrogen production from water

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ABSTRACT

Coconut shell carbon (CSC) nanosheets were applied to support CdS quantum dots (≤5 nm) and Pt nanoparticles to form a composite Pt/CdS/CSC catalyst for the visible-light-driven photocatalytic H_2 production from water. The H_2 evolution rate on Pt/CdS/CSC is as high as 1679.5 μmol h^{-1}, which is significantly enhanced as compared with that on Pt/CdS without CSC (636.2 μmol h^{-1}). Electrocatalytic experiments indicate a highly efficient electron transfer on the CSC nanosheets, which may be due to the presence of the abundant nanopores (<4 nm) and surface oxygen-containing groups behaving as the charge capture traps. The unique electron transfer flexibility of CSC facilitates the separation of the photoinduced electron–hole pairs on CdS/Pt/CSC in the photocatalytic process. This is the main origin for the significantly enhanced photocatalytic performance of CdS/Pt/CSC. It is believed that the findings from this study will provide useful clues for designing efficient biochar-based catalysts for visible-light-driven photocatalysis.

Introduction

Photocatalysis under the irradiation of visible light, which is the main part of the solar light (44%), holds promise to address the current and future global energy demands [1–9]. Incorporating active catalysts onto certain support materials has been proposed to be a good strategy for promoting the efficiency of the visible-light-driven photocatalysis [1–5,10–17]. Strong interactions can be formed between the catalyst nanoparticles and the support materials, thus suppressing the aggregation of the catalyst nanoparticles [11,12,16,18]. Dispersion of the catalyst nanoparticles on the support materials help to obtain optimum catalyst utilization, and to reduce the amount of precious metal used, thus reducing the catalyst costs. The support materials with large surface areas can promote the interaction of the reactants with the active catalysts, leading to more efficient adsorption and activation of the reactants [4,5,10–12]. The support materials with high conductivity can suppress the recombination of the photoinduced electron–hole pairs, improve the separation efficiency of the photoinduced electron–hole pairs, thus finally

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achieving improved efficiency of the visible-light-driven photocatalysis [2,6,8,17,18].

Carbon nanostructured materials have been commonly used as supports in visible-light-driven photocatalysis, due to their high stability, high surface area and high conductivity [1–5,10–13]. Peng et al. prepared a carbon-coated Ni (Ni@C)/CdS nanocomposite photocatalyst, which resulted in an average H_2-production rate of 622.7 μmol h^{-1} during 5-h visible-light irradiation and an apparent quantum yield up to ca. 20.5% under 420 nm monochromatic light irradiation [3]. Li et al. reported that, on the graphene nanosheets decorated with CdS and Pt nanoparticles (NPs), the visible-light-driven H_2 production can reach a rate of 1120 μmol h^{-1}, with an apparent quantum efficiency (QE) of 22.5% [10]. Kim et al. utilized multi-walled carbon nanotubes as a support of CdS and Pt NPs to generate hydrogen at a rate of about 820 μmol h^{-1} g^{-1} under visible-light irradiation [13]. Despite many encouraging developments, the efficiency of visible-light driven H_2 production requires further significant improvements for large-scale applications.

Biochar materials, which are prepared from biomasses such as tea, grass, coffee, olive stone and peach stone, have been widely used as catalyst supports in the field of traditional thermal catalysis [19,20]. The particular textures and surface chemical characteristics of the biochars can effectively affect the activity of catalysts [20]. However, the biochar materials are relatively little studied in the field of photocatalysis. In the present work, coconut shell carbon (CSC) nanosheets were prepared and used as a support of CdS quantum dots (QDs) with size ≤5 nm and Pt NPs for visible-light-driven production of H_2 from water. Under the action of the catalyst Pt/CdS/CSC, hydrogen can be generated at a rate as high as 1679.5 μmol h^{-1}, with a highest quantum efficiency of 39.4% under 460 nm light irradiation. The fast electron transfer kinetics across the CSC surface should be responsible for the excellent photocatalytic performance of Pt/CdS/CSC.

Experimental

Sample preparation

The coconut shells from Hainan China were crushed and sieved to a size of less than 2 mm. The crushed shells were cleaned with deionized water and dried in a vacuum oven at 90 °C for 24 h. The dried shells were carbonized under N_2 atmosphere up to 600 °C at a ramp rate of 20 °C min^{-1} and then held for 2 h. The carbonized coconut shells were mixed with 50 wt% KOH aqueous solution in a stainless steel reactor with amass ratio of KOH/C equal to 4:1. The mixtures were kept at 130 °C for 5 h to evaporate water, and then were heated under N_2 atmosphere at a ramp rate of 5 °C min^{-1} to 800 °C, and kept at this temperature for 1 h. The sample was cooled to room temperature and washed with hydrochloric acid and deionized water until no more chloride ions can be detected in the wash solution. Finally, the resulting sample was dried at 110 °C for 12 h, leading to the formation of CSC.

CSC was mixed with spectro grade paraffin wax (molten at about 60 °C) to prepare a coconut shell carbon paste electrode (CSCPE, Φ3.0 mm). The commercial graphite powder (320 mesh, spectro grade) was also used to prepare a graphite paste electrode (GPE, Φ3.0 mm) for comparison. The mass ratios of powder to wax were 0.64:1 and 2.7:1 in CSCPE and GPE, respectively. Increasing CSC content in the paste can improve the electrical conductivity and active area of the electrode, but it is difficult to obtain a well-blended paste with a higher CSC content due to its low density. The preparation procedures for CSCPE and GPE were the same and reported in our previous paper [21].

Water-soluble CdS QDs capped with mercaptopropionic acid (MPA) were prepared using the same method described in our previous work [12,15]. Fig. S1 in the Supplementary data shows the TEM image of the CdS QDs. Loading of CdS QDs and Pt NPs on the CSC support to form the Pt/CdS/CSC catalyst proceeded in a 200 mL, 20 vol% lactic acid solution after adding CdS QDs solution (10 mL, 20 mg mL^{-1}), CSC (typically 2.4 mg) and an aqueous solution of H_2PtCl_6 (typically 2 mL, 2.4 mg Pt). The mixture was stirred for 2 h under light irradiation for reducing the Pt ions to Pt NPs, and then divided into two equal parts. One part was centrifuged to collect the solid sample, which was washed with deionized water and dried in a vacuum freeze-drier for further characterization. The other part was used for the visible-light-driven photocatalytic H_2 evolution from water. The Pt/CdS catalyst was prepared through the same procedures as those of Pt/CdS/CSC, except that CSC was not used. For comparison, commercial CdS (Sigma–Aldrich, purity: 99.999%) was also used to prepare a Pt/CdS(C)/CSC catalyst.

Characterization

The crystallographic properties of the samples were analyzed by X-ray diffraction (XRD) patterns from an X'Pert PRO MPD diffractometer (Panalytical, Netherlands) under operation conditions of 40 kV and 40 mA with Cu Kα radiation. Raman spectra were obtained on a LabRAM HR confocal laser micro-Raman spectrometer (Horiba Jobin-Yvon, France) with an excitation wavelength of 532 nm. The Fourier transformation infrared (FTIR) spectra were recorded on a Nicolet 67 FTIR spectrometer (Thermo Nicolet, USA) using a standard KBr disk technique. X-ray photoelectron spectra (XPS) were collected on an EscaLab 250Xi spectrometer (Thermo Fisher, USA) fitted with a monochromatic Al Kα X-ray source ($h\upsilon = 1486.6$ eV). The morphological features of the samples were observed on a SU8020 field-emission scanning electron microscope (FE-SEM, Hitachi, Japan). Transmission electron microscope (TEM) observations of the samples, including elemental mapping, were performed on a JEM-2100F field emission transmission electron microscope (JEOL, Japan) with a beam energy of 200 kV. The DFT pore size distribution and the Brunauer–Emmett–Teller (BET) surface area of the CSC samples were measured on an ASAP 2020 HD88 physisorption analyzer (Micromeritics, USA). UV–visible diffuse reflectance spectra (UV–vis DRS) were obtained on an UV-2450 UV–visible spectrophotometer (Shimadzu, Japan). PL spectra were collected on a Fluorolog 3-TAU luminescence spectrometer (Horiba Jobin Yvon, France). The Pt concentration in the catalysts was determined by inductively-coupled plasma (ICP) optical emission spectrometer on a Perkin–Elmer ICP Optima 2000DV.

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