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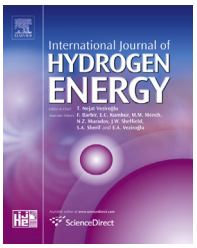

Insights into photo-activated electrode for boosting electrocatalytic methanol oxidation based on ultrathin MoS_2 nanosheets enwrapped CdS nanowires

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ABSTRACT

In this paper, a new and high-performance visible-light-activated electrode is designed in terms of two dimensional (2D) MoS_2 nanosheets enwrapped 1D CdS nanowires as photo-activated support for depositing Pt nanoclusters. Compare to traditional ambient electrocatalytic process, the as-prepared photo-activated electrode shows evidently improved electrocatalytic activity and stability of methanol oxidation reaction (MOR) under visible light illumination. The efficient interfacial electron transfer from the excited CdS moieties to the decorated ultrathin MoS_2 shell contributes to the synergistic effect of photocatalytic and electrocatalytic process for the boosting of catalytic efficiency.

Introduction

Fuel cell, as a technology for direct conversion of the chemical energy of a fuel into electrical energy, has been recognized as a promising future power source [1]. Recently, traditional noble metal anode electrocatalysts hybridized with optically active semiconductors have been certified as the promising photo-electrocatalysts for the improvement of fuel cell anodic reactions [2–12]. With assistance of light illumination, those of noble metal/semiconductor modified electrodes displayed evidently boosted catalytic performance and stability for the anodic oxidation of small organic molecules (SOMs). Despite some efforts have been devoted to the study of photoassisted fuel cell, most of optically active semiconductors have localized in UV-light-activated TiO_2, which might hinder their broad applications.

Multifarious nanostructures with different dimensions including zero-, one-, two-, and three-dimensional (0D, 1D, 2D and 3D), have received wide recognition for their unique size– and shape–dependent physicochemical properties [13–16]. Among these nanostructures, well-defined 1D nanoarchitectures such as wires, rods, belts, *etc.* have become the focus of intensive research owing to their unique large aspect

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ratio, which is beneficial to a directional charge transfer with a reduced grain boundary scattering, since the discovery of carbon nanotubes by Iijima [14–20]. Nowadays, the 1D nanomaterials play important roles as key units into nanoscale optic, electronic, electrochemical and particular interest to photo-/electro-catalytic fields [14,15,19,20].

1D CdS nanomaterials are fascinating and promising optoelectronical material for the energy conversion [19,20]. This is because of its unique and versatile fundamental properties including desired band-gap width (2.4 eV), relative low work function, high refraction index, excellent transport properties, high electronic mobility, *etc.* However, the pure CdS suffers from the rapid recombination of photogenerated electrons and holes, and also severe photocorrosion effect. Recently, molybdenum sulfide (MoS_2) nanosheet, a 2D chalcogenide nanomaterial with the same hexagonal crystalline structure as CdS nanoparticles (NPs), is often used to improve the photocatalytic performance of CdS nanostructures [21–31]. Exhibiting p-type properties, the 2D MoS_2 nanosheets with large surface area can be integrated with an n-type CdS semiconductor to improve the separation of photoinduced electrons and holes. For example, Li's group had reported that MoS_2 as a cocatalyst loaded on CdS NPs for the enhancement of photocatalytic H_2 evolution under visible light irradiation [22,23]. Zhang et al. synthesized 2D MoS_2/CdS p–n nanohybrids through a one-pot solvothermal process for photocatalytic H_2 production [25]. However, the above investigations limited CdS NPs modified MoS_2 sheets, we expect that it is necessary to construct a core/shell nanoarchitecture with 1D CdS as core and 2D MoS_2 sheets as shell for the investigation of charge separation and interfacial electron transfer of CdS/MoS_2. Moreover, compared to massive studies of high-efficiency photocatalytic H_2 evolution on the CdS/MoS_2 heterostructure, comparatively few reports have been published on this hybrid for other applications.

Herein, we reported the fabrication of a novel and high-performance visible-light-activated electrode in terms of 2D MoS_2 nanosheets enwrapped 1D CdS nanowires. Firstly, by means of a one-pot solvothermal method, core/shell heterostructures with ultrathin 2D MoS_2 sheets coated 1D CdS nanowires were easily obtained (Scheme 1). Then, the as-prepared heterostructures can be served as support for depositing Pt nanoclusters. Interestingly, compared to traditional methanol oxidation reaction (MOR), the ternary as-prepared Pt-CdS/MoS_2 photoanode showed evidently improved electrocatalytic activity and stability of MOR under visible-light illumination. The highly efficient interfacial charger transfer from excited CdS moieties to decorated ultrathin MoS_2 shell contributes to the synergistic effect of photocatalytic and electrocatalytic process for the boosting of catalytic methanol oxidation. The outstanding catalytic performance suggests that the CdS nanowire/MoS_2 nanosheet core/shell heterarchitecture could act as a promising photo-activated material in solar and chemical energy conversion.

Experimental

Materials

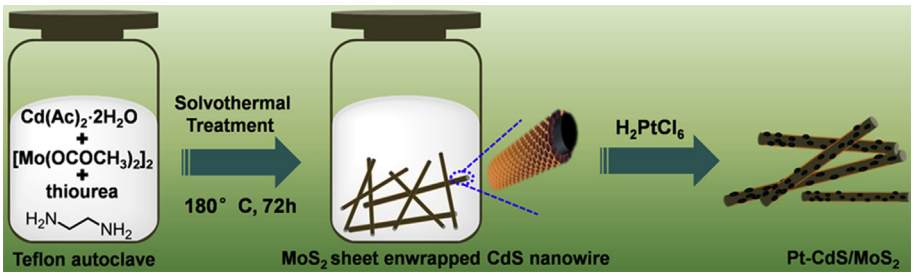
Thiourea (CH_4N_2S), cadmium acetate dihydrate ($C_4H_6CdO_4 \cdot 2H_2O$), molybdenum (II) acetate dimer ($C_8H_{12}Mo_2O_8$), $H_2PtCl_6 \cdot 6H_2O$, and ethylenediamine ($C_2H_8N_2$) were purchased from Sinopharm Chemical Reagent Co., Ltd. All materials were used directly without purification in advance.

Synthesis of CdS nanowires and CdS/MoS_2 nanocomposites

The CdS nanowires and CdS/MoS_2 nanocomposites were prepared through a modified solvothermal method [32,33] (Scheme 1). Firstly, $C_4H_6CdO_4 \cdot 2H_2O$ (1.1994 g), $C_8H_{12}Mo_2O_8$ (0.0087 g) and thiourea (1.1276 g) was dispersed in 80 mL $C_2H_8N_2$ under ultrasonic for 1 h. After that, the mixture solution was transferred into Teflon autoclave (100 mL) and held at 180 °C for 72 h. Then, the powders were obtained by using high-speed centrifugation and washed with ethanol and water thoroughly. After that, the powders were dried in vacuum oven at 40 °C for 12 h. The weight ratio of MoS_2 to CdS was 1:100. The different samples with the weight ratio of MoS_2 to CdS were prepared by adding different amount of Mo precursor. On the other hand, the pure CdS nanowires and MoS_2 were prepared by similar procedure except that the $C_8H_{12}Mo_2O_8$ and $C_4H_6CdO_4 \cdot 2H_2O$ were not used, respectively.

Preparation of Pt-CdS and Pt-CdS/MoS_2 modified electrodes

The CdS and CdS/MoS_2 coated on F-doped tin oxide (FTO) electrodes were prepared. Before coating, the FTO electrodes were cleaned by sonication for 10 min under acetone, ethanol, and water, respectively. 10 mg as-synthesized samples were added into 1 mL water-ethanol mixtures (V_{water}:$V_{ethanol}$ = 1:1). Then, 10 μL Nafion was added into above dispersion and placed under ultrasound for 30 min to obtain yellow



Scheme 1 – The schematic illustration of the formation process of ultrathin MoS_2 sheets enwrapped CdS nanowires and corresponding Pt nanoparticles decorated on CdS/MoS_2 composites.

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