Supporting Information

Three-Dimensional MoS₂/CdS/γ-TaON Hollow Composites for Enhanced Visible-Light-Driven Hydrogen Evolution

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EXPERIMENTAL SECTION

Synthesis

Ethanol, hydrogen peroxide and hydrofluoric acid (Caution! Hydrofluoric acid is highly corrosive and it must be handled carefully.) were supplied by Sinopharm Chemical Reagent Beijing Co., Ltd (SCRB). Tantalum powders (99.9%) were supplied from Aladdin. Ammonia gas was supplied by Haipu Gas Co., Ltd. All materials were used as supplied. Deionized (DI) water was used in all experiments. At first, tantalum oxide three-dimensional nanostructures are prepared by a hydrothermal process. In a typical synthesis procedure, stoichiometric tantalum powder was added to a certain amount of hydrofluoric acid and hydrogen peroxide aqueous solution, which was loaded into a Teflon-lined cylindrical autoclave. Then the sealed autoclave was heated at 240°C for several hours in a box furnace. After that, the γ -TaON samples were prepared by nitridation at 850 °C for 5 h under the flow of ammonia gas (20 mL min⁻¹) through a conical flask containing 100 mL deionized water at 30 °C. Secondly, an aqueous solution of Na₂S•9H₂O and a pre-determined amount of γ -TaON nanoparticles was added slowly to $Cd(Ac)_2 \cdot 2H_2O$ solution under vigorous stirring for 24 h and then loaded into autoclave heated at 180°C. And then as prepared powder was added into the sodium molybdate $(Na_2MoO_4 \cdot 2H_2O)$ and thioacetamide (C_2H_5NS) aqueous solution and stirred to form the suspension. The solution was transferred to a Teflon-lined stainless steel autoclave and then heated in an electric oven at 200 °C for 24 h. The final precipitates were separated, washed with ethanol and DI water for three times and then dried in oven at 60 °C for 12 h to obtain the final products of composite powders. Conventional TaON samples was prepared by nitridation of amorphous Ta_2O_5 powders at 850 °C for 2 h in flowing ammonia with a flow rate of 20 cm³min⁻¹.

Characterization

The obtained products were characterized with powder X-ray diffraction (XRD, MAC Science Co. Ltd Japan) using Cu K α (λ = 0.1546 nm) and XRD patterns were obtained for 10-90° 20 by step scanning with a step size of 0.02°. The morphology and size of the resultant powders were characterized by a Zeiss Ultra 55 field-emission scanning electron microscope (SEM) associated with X-ray energy-dispersive spectrometer (EDX). Transmission electron microscopy (TEM) images were captured on the transmission electron microscopy (TEM, JEM-2010) at an acceleration voltage of 200 kV. The optical properties of the samples were analyzed by UV-vis diffuse reflectance spectroscopy (UV-vis DRS) using a UV-vis spectrophotometer (UV-2550, Shimadzu). Fine BaSO₄ powder is used as a standard for baseline and the spectra are recorded in a range 190-900 nm. The chemical states of the sample were determined by X-ray photoelectron spectroscopy (XPS) in a VG Multilab 2009 system (UK) with a monochromatic Al K α source and charge neutralizer. The surface area of the samples was measured by TriStar 3000-BET/BJH surface area. The photoluminescence (PL) spectra were recorded at room temperature by using a SpectraPro-500i spectrometer.

Photocatalytic Tests

Photocatalytic hydrogen production was carried out in an air free closed gas circulation system reaction cell made of quartz. The total cylindrical volume of the cell was 250 mL.

In a typical photocatalytic experiment, 0.2 g of the prepared MCT composite photocatalysts were dispersed under constant stirring in an 200 mL mixed aqueous solution containing 0.35 M Na₂S and 0.25 M Na₂SO₃. An optically polished piece of quartz glass was fused on top of the cell to minimize light scattering. Hydrogen evolution was detected using a gas chromatograph (Beijing, GC-3240, TCD, Ar carrier), which was connected to a gas-circulation line. The reaction was initiated by irradiation with a 300 W xenon lamp fitted with a cut off filter ($\lambda > 420$ nm). The whole system, including the photocatalyst, was flushed with Ar at 100 mL min⁻¹ for 1 h to remove any trace of air (including nitrogen and oxygen) before any photocatalytic reaction was carried out. During the process, agitation of the solution ensured uniform irradiation of the suspensions.

Additional Results



Fig. S1 XRD of as-prepared γ -TaON and MCT composites samples. All the diffraction peaks of the composites are well indexed according to γ -TaON phase, and no characteristic diffraction peaks for MoS₂ and CdS species are observed because of the low amount and relatively low diffraction intensity of MoS₂ and CdS.



Fig. S2 SEM images of γ -TaON (a) and MCT0.2 (b). It is evident that there is nearly no change in the morphology of γ -TaON after the coating of MC cocatalyst. The as-obtained MCT products are uniform hollow hierarchical nanostructures consisting of nanoneedles with a length of 100–200 nm.



Fig. S3 HRTEM images of MCT0.2. The HRTEM image in Fig. S3 for the MCT0.2 sample shows that the size of the CdS nanocrystals in the composites is about 3-5 nm. The lattice fringes of individual CdS nanocrystals with a *d* spacing of ca.0.21 nm can be assigned to the (110) lattice plane of the CdS. The fringes with a lattice spacing of 0.27 nm correspond to the (100) plane of MoS_2 is also observed.



Fig. S4 Photocatalytic water splitting activity on MoS_2/γ -TaON (MT)、 CdS/ γ -TaON (CT equal to MCT0), MoS_2/CdS (MC) and MCT. Although the MoS_2 could reduce over potential in hydrogen evolution on catalysts surface, sample MT showed a very low photocatalytic activity because of the rapid recombination of electrons and holes. When the CdS was introduced in γ -TaON, the activity of CT was increased due to the separation of photoelectrons and holes between the CdS and γ -TaON. However, the MC hybrid can significant enhance the property, which is ascribed to combined effect of MoS_2 and CdS.



Fig. S5 Photoluminescence spectra of γ -TaON and MCT0.2 composites. For semiconductors, the photoluminescence (PL) spectrum is related to the transfer behavior of the photoinduced electrons and holes, so that it can reflect the separation and recombination of photoinduced charge carriers. The excitation wavelength is determined as 325 nm, and the γ -TaON has a strong emission peak at about 630 nm. The PL intensities of MCT composites decreased with an addition of MoS₂ and CdS nanocrystals. This is ascribed to the fact that the electrons are excited from the valence band to the conduction band of CdS migrate to γ -TaON nanocrystals and then to MoS₂ nanosheets, which prevent the direct recombination of electrons and holes.



Fig. S6. Cyclic H_2 evolution curve for the MCT0.2 photocatalyst. The recycling experiment shows that the MCT0.2 sample does not exhibit any significant loss of activity, indicating that the catalysts are stabile during photocatalytic H_2 production.