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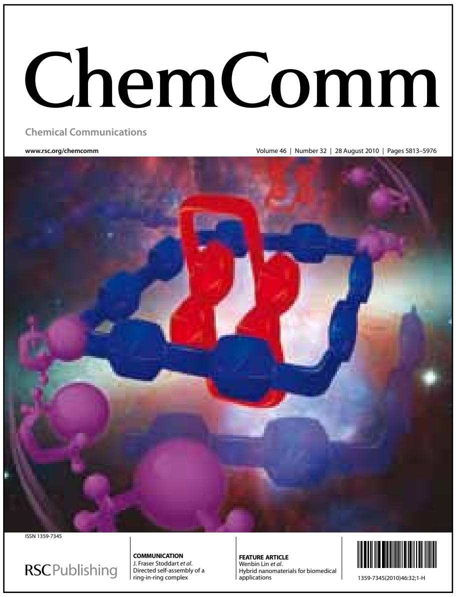

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COMMUNICATION

Three-Dimensional MoS_2/CdS/γ-TaON Hollow Composites for Enhanced Visible-Light-Driven Hydrogen Evolution

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Three-dimensional MoS_2/CdS/γ-TaON hollow composites have been successfully synthesized by anchoring MoS_2/CdS nanocrystals on the surfaces of γ-TaON hollow spheres via a two-step ion-exchange route with assistance from a hydrothermal process. Even without the noble-metal cocatalyst, the as-prepared MoS_2/CdS/γ-TaON hollow structure with the decoration of 1 wt% MoS_2/CdS cocatalysts (0.2wt% MoS_2) reaches a high photocatalytic hydrogen production rate of 628.5 μmol h^{-1}.

Due to the global energy crisis and demand for environmental protection, the development of clean chemical energy produced by solar energy conversion has attracted great attention recently.[1] The water-splitting for hydrogen production using solar energy, a clean, economical and environment friendly approach, has become promising.[2] Among various semiconductor photocatalysts, tantalum oxynitrides have drawn considerable interest and proven to be a suitable candidate for photocatalytic water splitting because of their narrow band gap and the more negative potential of the nitrogen 2p orbital than oxygen 2p orbital inducing the photocatalytic reactions can be conducted under visible light irradiation.[3-7] However, the hydrogen evolution from water splitting on tantalum oxynitride is found to be relatively very low. It is therefore highly desirable to develop a new modification and/or preparation method that can enhance the photocatalytic performance of oxynitride nanostructures.[8-11]

To improve the performance of semiconductor photocatalysts, there is increasing interest in tailoring the structure of semiconductors on the nanoscale. Three-dimensional (3D) hierarchically nanostructured materials have the apparent advantages of improving absorbance, promoting the transport and separation of photoexcited charge carriers, and providing abundant surface reaction sites, which are crucial for obtaining high solar energy conversion efficiency.[12-15] The use of heterojunction structures is another important strategy because it allows for the combination of properties from each element. The heterojunction built not only can expand the spectral range of light absorption, but also may promote photoexcited electron-hole separation which can minimize electron-hole recombination, thus significantly enhancing energy efficiency.[16-26]

Although photocatalytic activity can be much improved by loading noble metal particles as cocatalysts, the whole replacement of noble metals by other materials is an important direction in the future developments of photocatalysis. Recently, molybdenum disulfide (MoS_2) with a layered structure has been extensively investigated as a promising cocatalyst for H_2 evolution. For example, Jaramillo et al.[27] reported that the MoS_2 nanoparticles could enhance H_2 evolution as the active sites. MoS_2/TiO_2 heterostructure photocatalyst exhibited wide light response and high photocatalytic performance for pollutant degradation. Nguyen et al.[28] reported that $MoS_2/Zn_{0.2}Cd_{0.8}S$ hybrid photocatalysts showed much faster H_2 evolution rate compared with pristine $Zn_{0.2}Cd_{0.8}S$. Min et al.[29] reported that limited-layered MoS_2 confinedly grown on RGO sheets can act as a high active cocatalyst for hydrogen evolution reaction in a dye sensitized photocatalytic system under visible light irradiation. Yu et al.[30] demonstrated MoS_2/Graphene/TiO_2 have high apparent QE even without a noble-metal cocatalyst. MoS_2/CdS system has been reported for much enhanced photocatalsis by Li et al.[31] It is considered that the junction formed between MoS_2 and CdS was responsible for the unexpectedly enhanced photocatalytic activity, and MoS_2 was used as a possible substitute for noble metals and as a cocatalyst in the MoS_2/CdS system.

Here we report the first time the fabrication of MoS_2/CdS hybrid coupled on γ-TaON as MoS_2/CdS/γ-TaON three-dimensional hollow spheres. We have looked at using this strategy in synergy to improve photocatalysis for hydrogen production without noble metals loaded.

The MoS_2/CdS/γ-TaON composite (denoted as MCT) hollow composite photocatalyst is synthesized by the two-step ion-exchange route with assistance from a hydrothermal process. At first, tantalum oxide three-dimensional nanostructures are prepared by a hydrothermal process. And then the γ-TaON samples were prepared by nitridation via the controllable thermal time in our previous work.[32] Secondly, the layered MoS_2/CdS hybrid (denoted as MC) was prepared on the γ-TaON by the two-step ion-exchange reaction of Na_2S and $Cd(Ac)_2$ with the Na_2MoO_4 and C_2H_5NS (see the Supporting Information for details). The formation of the MoS_2/CdS/γ-TaON composite (which contains 99 % γ-TaON and 1 % MoS_2/CdS cocatalyst) was demonstrated in Fig.1. The uniform hollow hierarchical nanostructures consist of well-organized idependent nanoneedles with the length of 100~200 nm (Fig. 1a and b). As shown in Fig. 1c, the as-prepared products are composed of the MC cocatalyst decorated on the surface of hollow γ-TaON structures. The layered MoS_2 wraped around the tiny CdS nanocrystals with the diameter of 5 nm spread uniformly and tightly on the γ-TaON as the perfect MCT core–shell hierarchical composites, indicating that γ-TaON is essentially interacting with MC hybrid. The crystal structures of pristine γ-TaON and MCT composites were analyzed by XRD patterns shown in Fig. S1. The diffraction peaks match those of the crystalline monoclinic phase of γ-TaON (ICCD card no. 01-076-3258). It is evident that there is nearly no change in the crystal structure of γ-TaON after the coating of MC cocatalyst. Also no evident shift in the peak positions is observed in the as-prepared MCT samples, suggesting that the deposited MC nanocrystals do not incorporate into the lattice of γ-TaON. Thus, it was clear that the coating of 1 wt% MC nanocrystals had a negligible effect on the crystal structure of γ-TaON due to the low amount of MC and relatively strong diffraction intensity of γ-TaON.

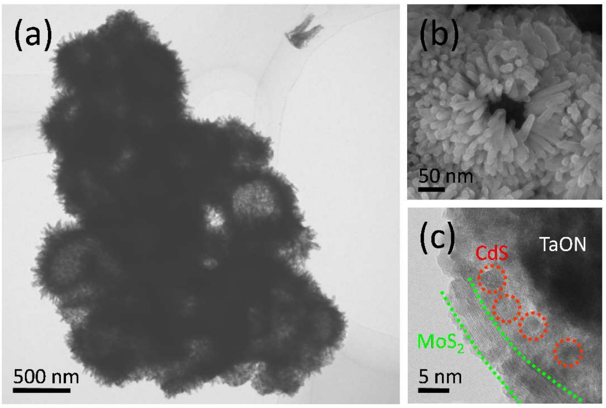

Fig. 1 TEM, SEM and HRTEM images of as-prepared MCT hollow composites.

UV-vis diffuse reflectance spectra of the samples, γ-TaON and MCT, are shown in Fig. 2. Compared with pristine γ-TaON, the MC modified samples exhibit a significant increase in photoabsorption over the whole range of the spectrum and a shift of the absorption edge to longer wavelength. The direct band gaps of the samples loaded MC hybrid were determined according to the Kubelka-Munk method and their values are mainly distributed in the range of 2.6-2.7 eV. The γ-TaON sample modified by MC can be excited to produce more electron-hole pairs, resulting in high potential ability for photodecomposition of contaminants under visible light irradiation. Furthermore, the appropriate modification in the energy levels of the conduction band edges is an evidence for MC nanocrystals to be acting as sensitizers making MCT composites active under visible light irradiation.[33]

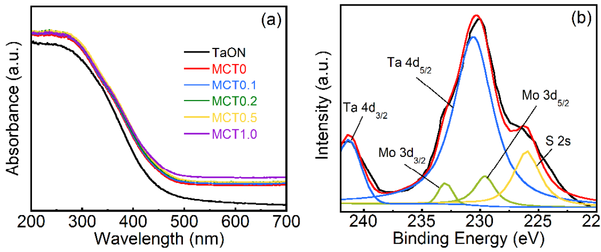

Fig. 2 (a) The UV-vis diffuse reflectance spectra of the as-prepared MCT nanocomposites using different MoS_2 and CdS contents in MC hybrid as cocatalyst. (b) XPS spectra of MCT02.

The chemical states of Mo in the MCT composites at the surfaces were examined using X-ray photoelectron spectroscopy (XPS). The high-resolution XPS spectra show that the Mo $3d_{5/2}$ line at 229.1 eV indicating molybdenum is in the formal 4+ state. Also, the Mo $3d_{3/2}$ and S 2s have a binding energy (BE) of 233.0 eV and 226.4 eV, respectively, assigning to the MoS_2 with good agreement with the previous results.[34]

Table 1. Effectes of MoS_2 content on physicochemical properties of the MCT samples

samples[a]	MoS_2 Content in cocatalyst (wt %)	average pore size (nm)	S_{BET} (m^2 g^{-1})	H_2 production rate (μmol h^{-1})
MCT0	0	18.5	67.2	45.1
MCT0.1	0.1	17.3	68.9	507.6
MCT0.2	0.2	17.2	69.5	628.5
MCT0.5	0.5	16.8	69.4	580.1
MCT1.0	1.0	16.6	69.9	345.6
Pt/T[b]	-	-	-	9.0

[a]All composite photocatalyst samples contain 1 wt% of cocatalyst.
[b]Pt/T: 1 wt% Pt loaded onTaON.

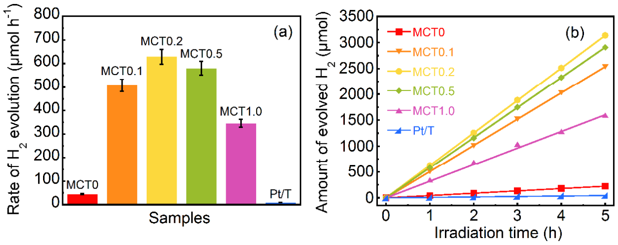

Fig. 3 (a) H_2 production rates of the MCT composites with various content of MoS_2 in cocatalyst; (b) Comparison of the photocatalytic hydrogen production activities of different samples under the illumination with the same lighting source in the mixed aqueous solution containing Na_2S and Na_2SO_3 as sacrificial agents.

The photocatalytic H_2 production activity on MCT composite photocatalysts with different MoS_2 and CdS contents in the MC cocatalyst (denoted as MCT0, MCT0.1, MCT0.2, MCT0.5, and MCT1.0 as shown in Table 1) was evaluated under xenon arc lamp irradiation, together with those on Pt/T for a comparison (Fig. 3). The introduction of the MC cocatalyst resulted in a significant improvement in the photocatalytic H_2 production activity of γ-TaON, and the content of MoS_2 and CdS in this cocatalyst had a significant influence on the photocatalytic activity. Although CdS loading alone shows activity in photocatalytic H_2 evolution, the rate of H_2 evolution is very low (ca. 45.1 μmol h^{-1}) because of the rapid recombination between CB electrons and VB holes in composites and the presence of a large over potential in the production of H_2. However, In the presence of a small amount of MoS_2 (0.1 %) in the hybrid cocatalyst, the activity of the sample (MCT0.1) in H_2 evolution is increased by up to ~11 times. With the increase of the amount of MoS_2 content, the rate of H_2 evolution on MCT is increased further and achieves a maximum when the loading amount of MoS_2 in composite cocatalyst reached about 0.2 % (sample MCT0.2). Further increases in the MoS_2 content in the cocatalyst led to a gradual reduction of the photocatalytic activity. It is well-known that photocatalytic activity can be improved by loading noble metal particles as cocatalysts. For comparison, the photocatalytic H_2 production activity of Pt loaded TaON nanoparticle (sample Pt/T) has also been tested and analyzed. As shown in Fig. 3, the sample Pt/CT shows a relatively lower activity (ca. 9 μmol h^{-1}) than the hollow heterojunction (sample MCT0.2), implying that heterogeneous junction between MoS_2, CdS and γ-TaON play an important role in the enhancement of photocatalytic activity for MCT composites by facilitating the separation of electron and hole pairs between the three components.

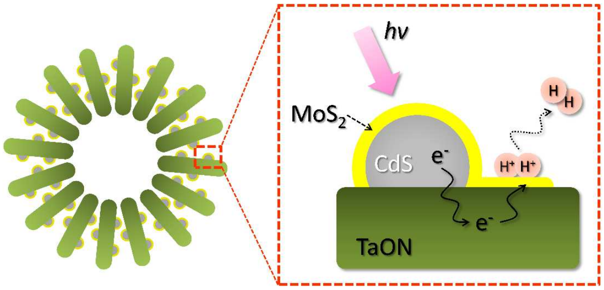

Fig. 4 Schematic illustration of the charge transfer in MCT composites. The enhanced electron transfer in the MCT system under irradiation ascribed that the photoexcited electrons are transferred from the CB of CdS to the γ-TaON and then to the MoS_2 nanostructure, which can effectively reduce H^+ to produce H_2.

To give further evidence to support the above-suggested, photocatalytic water splitting activity on MoS_2/γ-TaON (MT), CdS/γ-TaON (CT equal to MCT0) and MoS_2/CdS (MC) was evaluated in Fig. S4. 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. The high H_2 production activity of the samples MCT0.1, MCT0.2, MCT0.5 and MCT1.0 under visible-light irradiation can be understood as illustrated in Fig. 4. Under visible-light irradiation, the photogenerated electrons are excited from the valence band (VB) to the conduction band (CB) of CdS, creating positive holes in the VB of CdS. Normally, these charge carriers quickly recombine and only a fraction of the electrons and holes participate in the photocatalytic reaction, resulting in low reactivity.[35] However, in the sample of MCT, because the CB edge potential of CdS is more negative than that of TaON, The photo-excited electrons in the CB of CdS can migrate and be injected into TaON, followed by transfer to the MoS_2 nanosheets to generate hydrogen.[36] Hence, the MCT composites can increase photoactivity as a result of the efficient separation of the photogenerated electron–hole pairs, for which there is evidence in the photoluminescence spectra (Fig. S5). Moreover, in the heterojunction, the MoS_2 materials can be a substitute for Pt in photocatalytic H_2 production. Additionally, The MoS_2 in MCT heterojunction not only transfers the photoelectrons excited by visible light but also inhibits the photocorrosion of CdS. The existence MoS_2 on the CdS surface can effectively restrain the oxidation of CdS, thus no obvious deactivation occurs in the process of the photocatalytic reaction, indicating that the as prepared MCT photocatalyst has good anti-photocorrosion property (Fig. S6).

In summary, a high efficiency of the photocatalytic H_2 production without noble metal cocatalyst from water splitting under visible-light irradiation has been achieved over the MoS_2/CdS/γ-TaON hollow composites photocatalyst synthesized by a two-step solvothermal method. The activity of the MCT heterojunction in H_2 evolution can be dramatically improved when a small amount of MoS_2 was introduced in the MC hybrid cocatalyst. The optimal weight percentage of MoS_2 was found to be 0.2 % in the cocatalyst resulting in a high visible-light photocatalytic H_2 production rate of 628.5 μmol h^{-1} which was ~70 times higher than that of Pt loaded pristine TaON under the same reaction conditions. It is believed that the matched energy band of MCT heterostructure favors the charge transfer and suppresses the photoelectronhole recombination as well as the unique features of MoS_2 make it a substitute for noble metals, leading to the enhanced photocatalytic hydrogen production. This work shows that the development of three-dimensional hierarchical composites constructed by combination of 1D and 2D nanostructures containing an inexpensive and environmentally noble metal free cocatalyst is feasible and has a great potential in the field of energy conversion.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, XRD pattern, PL spectra, etc. See DOI: 10.1039/b000000x/

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