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Three-Dimensional MoS$_2$/CdS/$\gamma$-TaON Hollow Composites for Enhanced Visible-Light-Driven Hydrogen Evolution

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Three-dimensional MoS$_2$/CdS/$\gamma$-TaON hollow composites have been successfully synthesized by anchoring MoS$_2$/CdS nanostructures on the surfaces of $\gamma$-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/$\gamma$-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 $\mu$mol 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 oxynitrrides 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.$^{21}$ 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 photocatalysis 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 $\gamma$-TaON as MoS$_2$/CdS/$\gamma$-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/$\gamma$-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. Then the $\gamma$-TaON samples were prepared by nitridation via the controllable thermal time in our previous work.$^{22}$ Secondly, the layered MoS$_2$/CdS hybrid (denoted as MC) was prepared on the $\gamma$-TaON by the two-step ion-exchange reaction of Na$_2$S and Cd(AC)$_2$ with the Na$_2$MoO$_4$ and C$_2$H$_4$NS (see the Supporting Information for details). The formation of the MoS$_2$/CdS/$\gamma$-TaON composite (which contains 99 % $\gamma$-TaON and 1 % MoS$_2$/CdS cocatalyst) was demonstrated in Fig.1. The uniform hollow hierarchical nanostructures consist of well-organized independent 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 $\gamma$-TaON structures. The layered MoS$_2$ wrapped 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.

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_{3/2} line at 229.1 eV indicating molybdenum is in the formal 4+ state. Also, the Mo 3d_{5/2} and S 2s have a binding energy (BE) of 233.0 eV and 226.4 eV, respectively, assigning to the MoS₂ with good agreement with the previous results.

### Table 1. Effects of MoS₂ content on physicochemical properties of the MCT samples

<table>
<thead>
<tr>
<th>samples</th>
<th>MoS₂ Content in cocatalyst (wt %)</th>
<th>average pore size (nm)</th>
<th>S_{BET} (m² g⁻¹)</th>
<th>H₂ production rate (µmol h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCT0</td>
<td>0</td>
<td>18.5</td>
<td>67.2</td>
<td>45.1</td>
</tr>
<tr>
<td>MCT0.1</td>
<td>0.1</td>
<td>17.3</td>
<td>69.9</td>
<td>507.6</td>
</tr>
<tr>
<td>MCT0.2</td>
<td>0.2</td>
<td>17.2</td>
<td>69.5</td>
<td>628.5</td>
</tr>
<tr>
<td>MCT0.5</td>
<td>0.5</td>
<td>16.8</td>
<td>69.4</td>
<td>580.1</td>
</tr>
<tr>
<td>MCT1.0</td>
<td>1.0</td>
<td>16.4</td>
<td>69.1</td>
<td>345.6</td>
</tr>
<tr>
<td>Pt/T</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

All composite photocatalyst samples contain 1 wt% of cocatalyst. Pt/T: 1 wt% Pt loaded on TaON.

The photocatalytic H₂ production activity on MCT composite photocatalysts with different MoS₂ 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 H₂ production activity of γ-TaON, and the content of MoS₂ and CdS in this cocatalyst had a significant influence on the photocatalytic activity. Although CdS loading alone shows activity in photocatalytic H₂ evolution, the rate of H₂ 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 H₂. However, In the presence of a small amount of MoS₂ (0.1 %) in the hybrid cocatalyst, the activity of the sample (MCT0.1) in H₂ evolution is increased by up to ~11 times. With the increase of the amount of MoS₂ content, the rate of H₂ evolution on MCT is increased further and achieves a maximum when the loading amount of MoS₂ in composite cocatalyst reached about 0.2 % (sample MCT0.2). Further increases in the MoS₂ 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

![Fig. 1 TEM, SEM and HRTEM images of as-prepared MCT hollow composites.](image)

![Fig. 2 (a) The UV-vis diffuse reflectance spectra of the as-prepared MCT nanocomposites using different MoS₂ and CdS contents in MC hybrid as cocatalyst. (b) XPS spectra of MCT02.](image)

![Fig. 3 (a) H₂ production rates of the MCT composites with various content of MoS₂ 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 Na₂S and Na₂SO₃ as sacrificial agents.](image)
noble metal particles as cocatalysts. For comparison, the photocatalytic H\textsubscript{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 \mu mol h\textsuperscript{-1}) than the hollow heterojunction (sample MCT0.2), implying that heterogeneous junction between MoS\textsubscript{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.](image)

In summary, a high efficiency of the photocatalytic H\textsubscript{2} production without noble metal cocatalyst from water splitting under visible-light irradiation has been achieved over the MoS\textsubscript{2}/CdS/γ-TaON hollow composites photocatalyst synthesized by a two-step solvothermal method. The activity of the MCT heterojunction in H\textsubscript{2} evolution can be dramatically improved when a small amount of MoS\textsubscript{2} was introduced in the MC hybrid cocatalyst. The optimal weight percentage of MoS\textsubscript{2} was found to be 0.2 % in the cocatalyst resulting in a high visible-light photocatalytic H\textsubscript{2} production rate of 628.5 \mu mol h\textsuperscript{-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 photoelectron-hole recombination as well as the unique features of MoS\textsubscript{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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† Electronic Supplementary Information (ESI) available: Experimental details, XRD pattern, PL spectra, etc. See DOI: 10.1039/b000000x/