INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–9

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Hybridizing MoS_2 and C_{60} via a van der Waals heterostructure toward synergistically enhanced visible light photocatalytic hydrogen production activity

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ARTICLE INFO

Article history:
Received 2 December 2017
Received in revised form
12 February 2018
Accepted 5 March 2018
Available online xxx

Keywords:
Molybdenum disulfide (MoS_2)
Fullerene
Photocatalyst
Hydrogen production
Photoinduced electron transfer

ABSTRACT

Molybdenum disulfide (MoS_2) as a representative transition-metal dichalcogenide (TMD) has been extensively used as a noble-metal-free cocatalyst for photocatalytic hydrogen (H_2) production, but suffers from poor photocatalytic activity due to the catalytic inactivity of its basal plane. Herein, by bounding another metal-free cocatalyst, C_{60}, with MoS_2, we report the first MoS_2-C_{60} hybrid featuring a van der Waals heterostructure prepared via a facile and eco-friendly solid-state mechanochemical route. C_{60} bounding onto the edge of MoS_2 nanosheets leads to the decreases of both the number of layers and the size of MoS_2 nanosheets, as well as a negative shift of the conduction band minimum along with a positive shift of valance band maximum relative to the bulk MoS_2 and MoS_2 ball-milled without C_{60} (MoS_2-BM). Under the optimized weight ratio of MoS_2:C_{60} (1:1) in the raw mixture subject to ball-milling, MoS_2-C_{60} hybrid containing 2.8 wt% C_{60} shows an exceptional visible light photocatalytic H_2 production rate of 6.89 mmol h^{-1} g^{-1} in the presence of a photosensitizer Eosin Y (EY), which is significantly enhanced relative to the bulk MoS_2 and pristine C_{60}, both of which show almost no photocatalytic H_2 activity. Thus, the synergistic enhancement of photocatalytic activities of both MoS_2 and C_{60} is revealed.

Introduction

Atomically thin transition-metal dichalcogenides (TMDs) as emerging two-dimensional (2D) layered nanomaterials have recently attracted considerable interest owing to their unique structures and properties as well as promising applications in energy, catalysis, electronics and photonics [1–5]. The existence of weak van der Waals forces in the

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https://doi.org/10.1016/j.ijhydene.2018.03.148
0360-3199/

bulk structure of TMD enables the feasibility of making single- or few-layer TMD nanosheets with in-plane stability resulted from the strong covalent bonds between the transition metal and chalcogen atoms [1–7]. In particular, as one of the most representative TMDs, molybdenum disulfide (MoS_2) has been extensively used as a noble-metal-free catalyst since the first report of applying MoS_2 nanoparticles as an active electrocatalyst for hydrogen (H_2) production by Nørskov et al., in 2005 [8], and shows advantages of low cost, nontoxicity, high reactivity and excellent chemical stability [9]. In recent years special attention has been paid on the application of MoS_2 in photocatalytic H_2 production via water splitting which is regarded as a promising solution for tackling worldwide energy crisis [10–15]. According to the theoretical and experimental results on the electronic structure of MoS_2, the bandgap of MoS_2 increases from ~1.2 eV for bulk MoS_2 to ~1.9 eV for single-layer MoS_2 [16]. Such an increase of bandgap leads to a change in the redox potential, and thus improves the photocatalytic property of MoS_2 [10–17]. As a result, although bulk MoS_2 cannot reduce H^+ to H_2 because the energy level of its conduction band is lower than the redox potential of H^+/H_2, the single-layer MoS_2 with more negative conduction band energy level enables its ability to produce H_2 more efficiently [16]. However, because only the edges of MoS_2 has the high catalytic activity for H_2 production whereas its basal plane is inactive, even the single-layer MoS_2 shows low photocatalytic activity resulted from the facile recombination of photoexcited electron-hole pairs before migrating to the surface for reactions. Therefore, MoS_2 is typically applied as a cocatalyst which is loaded on the conventional metal-based semiconductor photocatalysts such as TiO_2, CdS, ZnO, playing the role as a promoter to reduce the energy barrier of water splitting and to increase the stability of photocatalysts [18–24]. Without using metal-based semiconductor photocatalysts, how to enhance the photocatalytic H_2 production activity of MoS_2 itself remains challenging but crucial for understanding the underlying reasons for its poor photocatalytic activity.

As another type of metal-free cocatalyst, nanocarbons have been also widely employed in photocatalytic H_2 production with the advantages of simple composition with earth-abundant element, high electrical conductivity, large surface area and high chemical stability [25,26]. Compared to graphenes with the 2D layered structure analogous to MoS_2 [13,27,28], much less attention has been paid on the applications of zero-dimensional (0D) fullerenes in photocatalysis. Limited reports reveal that the exotic closed-cage structure with strong electron-accepting ability of fullerene is actually beneficial for improving the efficiency of photoinduced electron transfer and consequently enhancing the photocatalytic activities of metal-based semiconductor photocatalysts [29–34]. For instance, Oh et al. prepared a C_{60}/TiO_2 composite by a modified oxidation method, which exhibited enhanced photocatalytic activity in terms of the decomposition of methylene blue under UV light irradiation [29]. Likewise, a C_{60}-coated ZnO photocatalyst prepared by blending physically C_{60} and ZnO nanoparticles by Zhu et al. showed enhanced photocatalytic activity for the degradation of the organic dye MB and inhibited photocorrosion of ZnO due to the high migration efficiency of photoinduced electrons on the interface of C_{60} and ZnO [32]. Xu et al. prepared different TiO_2-nanocarbon composites via a combination of sol-gel and hydrothermal methods, and found no much difference on improving the photocatalytic performance of TiO_2 toward selective oxidation of benzyl alcohol to benzaldehyde among C_{60} and other two nanocarbons, namely graphene and carbon nanotube [34]. More recently, C_{60} was incorporated into the pore wall of mesoporous CdS/TiO_2, affording enhanced photostability and photocatalytic H_2 production activity under visible light irradiation since C_{60} layers effectively enhanced the light absorption capability of the photocatalysts and greatly accelerated the photogenerated electron transfer velocity [30]. Noteworthy, most of these experimental studies are focused on applying fullerenes (mainly C_{60}) as cocatalyst in enhancing the photocatalytic activities of metal-based photocatalysts via physically blending fullerene and photocatalyst, and the interactions between C_{60} molecules and semiconductor photocatalysts are relatively weak. In this regard, for 2D layered nanomaterials such as MoS_2, the existence of the interlayer van der Waals interactions makes it possible to construct the so-called van der Waals (vdW) heterostructures, by integrating 2D layered nanomaterials with another material of different dimensionality, toward enhanced intermolecular interactions [35]. In particular, recently a MoS_2/C_{60} vdW heterostructure featuring the strong non-covalent interactions between MoS_2 and C_{60} was proposed theoretically by Luo et al., showing significantly reduced charge recombination and thus enhanced photocatalytic H_2 production activity [36]. However, experimental reports on MoS_2/C_{60} composites are very rare. In 2005 Remskar et al. prepared MoS_2/C_{60} composite crystals via a high-temperature (1030 K) catalyzed transport reaction, featuring a layered structure composed of alternating MoS_2 and C_{60} molecular layers [37]. Without using such a harsh condition, recently Chen et al. prepared C_{60}-MoS_2 nanocomposites via a combined solvent transfer and surface deposition method, and the as-formed hybrid *p-n* heterojunctions showed unique electrical property which was not possessed by the C_{60} and MoS_2 components [38]. Note that in this report the solubility difference of MoS_2 and C_{60} in solvents had to be considered, and the prepared C_{60}-MoS_2 nanocomposites were largely based on a physical blend with limited intermolecular interactions [38]. Hence, it is highly desired to develop more facile methods to prepare MoS_2-C_{60} hybrid vdW heterostructures with enhanced intermolecular interactions and then to investigate their mutual influence on the photocatalytic properties.

Herein, we report the first MoS_2-C_{60} hybrid vdW heterostructure prepared via a facile and eco-friendly solid-state mechanochemical route. Upon simply ball-milling MoS_2 and C_{60} powders, both the number of layers and the size of MoS_2 are dramatically decreased, and C_{60} bounding is found to greatly affect the band structures of MoS_2. MoS_2-C_{60} hybrid shows a significantly enhanced visible light photocatalytic H_2 production activity relative to the bulk MoS_2 and pristine C_{60}, revealing the synergistic enhancement of photocatalytic activities of both MoS_2 and C_{60}.

Please cite this article in press as: Guan J, et al., Hybridizing MoS_2 and C_{60} via a van der Waals heterostructure toward synergistically enhanced visible light photocatalytic hydrogen production activity, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.03.148