



# Solar light driven photoelectrocatalytic hydrogen evolution and dye degradation by metal-free few-layer MoS<sub>2</sub> nanoflower/TiO<sub>2</sub>(B) nanobelts heterostructure



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## ARTICLE INFO

### Keywords:

MoS<sub>2</sub>/TiO<sub>2</sub> nanobelt  
Heterostructure  
Photocatalysis  
Dye degradation  
Photoelectrocatalysis  
Hydrogen evolution reaction

## ABSTRACT

A rational design of metal-free hierarchical nanostructures is critical for achieving next-generation photo-catalytic system. Transition metal dichalcogenide, e.g., MoS<sub>2</sub> based heterostructures (HSs) with shape-controlled TiO<sub>2</sub> have attracted great attention in visible light electrocatalysis owing to their unique crystal structure, morphology and chemical properties. Herein, we demonstrate a low temperature solvothermal growth of few layer MoS<sub>2</sub> nanoflowers (NFs) over the porous TiO<sub>2</sub>(B) nanobelts (NBs) for enhanced hydrogen evolution reaction (HER) in acidic media as well as improved photocatalytic degradation of organic dye rhodamine-B (RhB) under visible light. Few-layer MoS<sub>2</sub> NFs with lateral sizes 130–350 nm were successfully grown on TiO<sub>2</sub> NBs, as revealed from the high resolution TEM imaging. EDS mapping confirms the elemental composition and their spatial distribution in the HS sample. MoS<sub>2</sub>/TiO<sub>2</sub> NBs HS exhibits extremely high adsorption ability (66% after 40 min) under dark as well as enhanced photocatalytic degradation efficiency (80% after 60 min) of RhB under visible light irradiation. A systematic photoelectrochemical measurements demonstrate that the MoS<sub>2</sub>/TiO<sub>2</sub> NBs HS exhibits excellent HER activity in acidic electrolyte with an overpotential and estimated Tafel slope to be –320 mV at 10 mA/cm<sup>2</sup> and 95 mV/dec, respectively, which is much lower than that of the pristine TiO<sub>2</sub> NBs measured to be –792 mV and 135 mV/dec, respectively, under visible light. It is shown that the Volmer-Heyrovsky mechanism leads to the extremely high hydrogen generation at the working electrode made with edge-defect enriched few layer MoS<sub>2</sub> on porous TiO<sub>2</sub> NBs.

## 1. Introduction

Ever increasing energy crisis and environmental pollution have necessitated the research efforts on the development of pollution free energy sources and practical solution to the everyday pollutions to the environment. Hydrogen is believed to be one of the most promising alternatives to fossil fuels and a source of renewable green energy having potential ability to replace the conventional energy sources in future. Solar light driven photocatalysis using semiconductor heterostructures (HSs) is one of the most promising green technologies for the generation of hydrogen by water splitting as well as remediation of environmental pollution [1–3]. After the pioneering work by Fujishima and Honda on the water splitting at the TiO<sub>2</sub> electrode in an electrochemical cell under the irradiation of UV light, hydrogen production using photoelectrocatalytic method by solar energy harvesting has

become a clean, economical and environment friendly approach [4]. Simultaneously TiO<sub>2</sub> and TiO<sub>2</sub> based nanostructures are being used for the decontamination of toxic and hazardous organic pollutants for the environmental protection [5–12]. To make the system commercially viable, the photocatalyst should be solar light active and efficient enough with high stability. To broaden the light harvesting window from UV to visible/NIR and uplift the catalytic activity, numerous strategies have been explored including impurity doping [13–15], staggered type HSs [1,5,16] and TiO<sub>2</sub> based plasmonic HSs with noble metal nanoparticles (NPs) [17–20] etc. Carbon nanotube coated with Cu<sub>2</sub>O [21], Fe-Pd alloy [22] can be a good photocatalyst. Synthesis of Fe<sub>3</sub>O<sub>4</sub>/ polyaniline by self-assembly approach, cobalt-based mixed oxide nanocrystals, edge-enriched graphene quantum dots and various core-shell nanostructures have recently been introduced for the efficient photocatalytic dye degradation, heavy metal removal, water oxidation

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and supercapacitance [23–28]. In a suitable heterostructured system, the presence of heterojunction modifies the band positions as well as their inclination at the interface that accelerates the migration of photogenerated charge carriers through the heterojunctions, which eventually makes a photocatalyst highly efficient [29]. Therefore, incorporation of suitable co-catalysts like Pt, Pd, Ag, Au, Ru etc. and their oxide on the surfaces of TiO<sub>2</sub> can serve as catalytically active centers for the enhanced degradation of toxic pollutants as well as H<sub>2</sub> or O<sub>2</sub> generation [16,30,31]. However, extremely high cost and limited resources hinder their widespread use in commercial applications. To overcome these challenges, enormous effort has been paid towards the development of metal-free systems to achieve the enhanced catalytic performance. Discovery of graphene-based nanosheets [32–34] motivates more intense research on single/few-layer 2D transition metal chalcogenides. Among them, MoS<sub>2</sub> has now been recognized as an efficient co-catalyst [35] due to its structural anisotropy, chemical inertness and good electroconductivity [36]. The HER activity by MoS<sub>2</sub> nanosheets is limited on the edge-sites and vacancy sites, while the basal surface remains inert [37,38]. Thus, vacancy rich and maximally edge-exposed MoS<sub>2</sub> nanostructures are promising to grow in order to maximize the catalytic activity. When few-layer MoS<sub>2</sub> nanoflowers (NFs) are incorporated with the porous TiO<sub>2</sub> NBs, edge-rich MoS<sub>2</sub> with higher vacancy concentration is expected to be formed, with enhanced visible light absorption. Another way, MoS<sub>2</sub> and TiO<sub>2</sub> may form type-II heterojunction at their interfaces, facilitating easy and efficient migration of the photogenerated charge carriers from one semiconductor to another through the interface, which eventually boost the photocatalytic activity.

Recently, several studies have been reported on the photocatalytic hydrogen evolution and dye degradation using the MoS<sub>2</sub>/TiO<sub>2</sub> composites. Pourabbas et al. [39] have reported the photo-oxidation of phenol by MoS<sub>2</sub> NPs incorporated with ultrafine P25 TiO<sub>2</sub> from aqueous solution, while Xiang et al. [40] have demonstrated the hydrogen generation by TiO<sub>2</sub> NPs integrated with layered graphene and MoS<sub>2</sub> nanosheets under UV irradiation. Though the above mentioned systems exhibit superior photocatalytic activity, the ultra-small size of the nanocomposites (5–8 nm) suffers from the high collection cost after each cycle. Zhou et al. [1] and Li et al. [2] have modified the morphology of TiO<sub>2</sub> from its ultra-small spherical NPs to long nanobelts (NBs) and employed few layer MoS<sub>2</sub> nanosheets on them with high catalytic surface area, which in turn enhanced the hydrogen generation efficiency synergistically. Thus, a rational design of hierarchical nanostructures is crucial for achieving high efficiency photocatalytic and photoelectrocatalytic systems.

Herein, we report on the successful growth of pure TiO<sub>2</sub>(B) NBs via a solvothermal method and its in-situ surface decoration with few layer MoS<sub>2</sub> NFs by a 2nd stage hydrothermal method. The presence of edge-rich MoS<sub>2</sub> NFs on the porous TiO<sub>2</sub> NBs enhances the HER activity by photoelectrocatalytic water splitting as well as dye degradation efficiency under visible light. We demonstrate strong adsorption ability (66% after 40 min) as well as enhanced photocatalytic performance (80% after 60 min irradiation) in the decomposition of organic dye (RhB) by MoS<sub>2</sub>/TiO<sub>2</sub> HS under visible light irradiation. Additionally, HER activity of TiO<sub>2</sub> NBs greatly enhances after its integration with few layer MoS<sub>2</sub> NFs, which further increases after the irradiation with visible light. We show that the overpotential for TiO<sub>2</sub> is reduced considerably after the incorporation of MoS<sub>2</sub> under dark. Upon illumination with visible light, the charge transfer at the type-II heterojunction of MoS<sub>2</sub>/TiO<sub>2</sub> enhances, increasing the carrier density in the system which may be realized by the reduced charge transfer resistance. It is shown that the overpotential is substantially reduced in MoS<sub>2</sub>/TiO<sub>2</sub> under light irradiation. The mechanism of improved photoelectrocatalysis is discussed in details.

## 2. Experimental details

### 2.1. Materials

All the chemicals were used as-received without further purification. The purchased reagents are anatase TiO<sub>2</sub> powder (99%, Merck, India), ethylene glycol (99%, Merck, India), sodium hydroxide pellets (NaOH, 97%, Merck, India), sodium molybdate dihydrate (Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, 99%, Sigma-Aldrich, USA) and thioacetamide (C<sub>2</sub>H<sub>5</sub>NS, 99%, Titan Biotech Limited, India).

### 2.2. Preparation of TiO<sub>2</sub> NBs

Anatase TiO<sub>2</sub> nanopowder (average particle size ~ 80 nm), ethylene glycol and sodium hydroxide (NaOH) pellets were used in our experiments as received from Merck without any further purification. In a typical synthesis, 0.2 g of anatase TiO<sub>2</sub> powder was dispersed in a 50 ml of 10 M NaOH solvent prepared by mixing DI water and ethylene glycol in 1:1 volume ratio. Afterwards, the mixed TiO<sub>2</sub> solution was transferred into a Teflon-lined autoclave (Berghof, BR-100) and the inside temperature was maintained and monitored at 220 °C for 16 h with a constant magnetic stirring at 500 rpm. The treated precipitates were washed thoroughly with DI water and 0.1 N HCl until the pH reduces to 7, which confirms the complete exchange of Na<sup>+</sup> by H<sup>+</sup> ions. Then, the obtained H-titanate NBs were calcined at 500 °C for 5 h in ambient atmosphere to grow porous TiO<sub>2</sub>(B) NBs.

### 2.3. Growth of MoS<sub>2</sub>/TiO<sub>2</sub> NBs heterostructures

Typically, 20 mg of TiO<sub>2</sub>(B) NBs were dispersed into a 40 ml of MQ water in an ultrasonic bath for 30 min. Then, 60 mg sodium molybdate (Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O) and 120 mg thioacetamide (C<sub>2</sub>H<sub>5</sub>NS) were dissolved in the above solution. The mixture was transferred to a Teflon-lined stainless steel autoclave and heated at 240 °C for 24 h with a constant magnetic stirring at 250 rpm. The amount of reagent was chosen and optimized based on the initial report by Zhou et al. [1]. The obtained black precipitates were washed several times with DI water for removing the additional salts and impurities followed by a centrifugation and drying process at 50 °C for 12 h to obtain few-layer MoS<sub>2</sub> NFs decorated on TiO<sub>2</sub> NBs (MoS<sub>2</sub>/TiO<sub>2</sub> HSs) with 1:1 weight of MoS<sub>2</sub> and TiO<sub>2</sub>. For comparison, pure MoS<sub>2</sub> NFs were synthesized under identical conditions without the presence of TiO<sub>2</sub> NB platform.

### 2.4. Characterization techniques

Morphology and size of the as-synthesized TiO<sub>2</sub> NBs and MoS<sub>2</sub> NFs on the TiO<sub>2</sub> NBs have been studied by a field emission scanning electron microscope (FESEM) (Sigma, Zeiss) equipped with an energy dispersive X-ray (EDX) spectrometer. The high magnification surface morphologies and structures of the as-grown samples have been studied by a field emission transmission electron microscope (FETEM) (JEOL-JEM 2100 F operated at 200 kV). Samples for TEM analysis have been prepared on a carbon coated Cu grid of 400 mesh size (Pacific Grid, USA). The crystal structure of the as-grown catalysts has been obtained from X-ray powder diffraction (XRD) pattern (Rigaku RINT 2500 TTRAX-III, Cu K $\alpha$  radiation). Crystallinity and phase composition of the as-synthesized NBs and the number of layers in MoS<sub>2</sub> NFs have been confirmed from the micro-Raman measurement (LabRam HR800, Jobin Yvon). The Fourier transform infrared (FTIR) spectra were measured for each of the catalysts in the range 400–4000 cm<sup>-1</sup> with a FTIR spectrometer (Perkin Elmer, Spectrum BX) using KBr wafer. X-ray photoelectron spectroscopy (XPS) has been carried out using a PHI X-tool automated photoelectron spectrometer (ULVAC-PHI, Japan) with an Al K $\alpha$  X-ray beam (1486.6 eV) at a beam current of 20 mA. The shift in the binding energy of various catalysts has been corrected using the C1s spectrum at 284.8 eV as a standard value [5]. Nitrogen adsorption-desorption

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