



Photocatalytic properties of free and oxide-supported MoS₂ and WS₂ nanoparticles synthesized without surfactants

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ABSTRACT

MoS₂ and WS₂ are narrow bandgap semiconductors that become photocatalytically active when dispersed on the nanometer scale. Surfactant-free nanoparticles of MoS₂ and WS₂ were synthesized by thermally decomposing the metal hexacarbonyls in the presence of co-dissolved sulfur. The nanoparticles exhibit a size-dependent shift in their threshold UV–visible absorption. A significant fraction of the nanoparticles is 10–20 nm in diameter. Free unsupported MoS₂ and WS₂ nanoparticles catalyzed the photodegradation of acetone in an aqueous solution under visible light of wavelength ≥ 400 nm. These nanoparticles did not disperse in the solutions due to hydrophobicity. Water dispersible MoS₂ and WS₂ were prepared by synthesizing them in the presence of high surface silica or titania (anatase) to produce oxide-supported nanoparticles (1 wt%). These silica- and titania-supported MoS₂ and WS₂ nanoparticles catalyzed the photodegradation of methylene blue under irradiation of wavelength ≥ 400 nm.

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1. Introduction

Atomically layered metal sulfides such as MoS₂ and WS₂ have a graphite-like structure. Each layer has the 1:2 stoichiometry and consists of a plane of metal atoms sandwiched between two close-packed planes of sulfur atoms. This anisotropic arrangement produces two types of surface sites: sulfur-terminated basal planes and the layer edges where metal atoms are partly exposed. The two types of sites exhibit distinctly different chemical properties. For example, in the catalytic hydrogenation, hydrodesulfurization and hydrodenitrogenation of petroleum products on MoS₂ and WS₂ [1,2], the layer edge sites are highly catalytically active while the basal planes are inert [3–7]. Various molecules preferentially adsorb on the layer edge even it is fully sulfided, i.e. when all edge metal atoms are fully coordinated, as observed experimentally [2,8,9] and theoretically [10,11]. Calculations show that for the edge metal atoms *d*-states protrude outward between and beyond the terminal sulfur atoms [12] thus enabling coordination of extra-neous molecules.

MoS₂ and WS₂ are also promising as tunable band gap semiconductor photocatalysts that may be more active than TiO₂, an archetypal photocatalytic material. In the TiO₂-mediated

photocatalysis such as photocatalytic oxidation in aqueous media, absorption of light induces electron–hole separation across the band gap; then the hole transfers onto a water molecule triggering its dissociation into H⁺ and •OH, hydroxyl radical [13]. Reactions of the very reactive hydroxyl radical with organic compounds lead to their photooxidative degradation. This is the basis of numerous environmental applications such as air purification, water and waste treatment, decontamination, self-cleaning and bactericidal surfaces [14,15]. Bulk MoS₂ and WS₂ are narrow band semiconductors, which are photocatalytically inactive. With band gaps of 1.20 eV and 1.35 eV respectively [16–18], redox potentials of the photoproduct electrons and holes are not sufficient for the interfacial charge transfer onto adsorbed molecules. In the nanoparticles, however, the band gap widens due to quantum confinement. For the MoS₂ nanoparticles, strong quantum confinement was observed at or below 4.5 nm when the particle radius (2.2 nm) approaches the bulk exciton Bohr radius (2.0 nm) [19–23]. With enough energy separation between the valence and conduction bands, the transfer of electrons and holes onto adsorbates becomes possible. This marks the onset of photocatalysis.

Studies of photocatalysis on MoS₂ have been pioneered by Tributsch and Bennett [24]. However, most of the well-controlled fundamental studies were done by Wilcoxon et al. [19–23] using size-selected MoS₂ nanoparticles synthesized in inverse micelles. These works have shown that small MoS₂ clusters (3.0–4.5 nm) catalyze photooxidation of phenol, chlorinated aromatics, and methylene blue under visible light [21,22]. This is superior to TiO₂, which requires UV light for the initial electron–hole excitation. The larger MoS₂ clusters (8–10 nm) did not photodegrade phenol by

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Table 1
Reactant quantities for synthesis of free or oxide-supported metal sulfide nanoparticles.

Product	Metal carbonyl (mg \pm 0.1 mg)	Sulfur (mg \pm 0.1 mg)	Solvent (mL)	Oxide support (g)	Sulfide to support mass ratio
MoS ₂	60.0	14.8	200	–	–
WS ₂	81.0	15.0	200	–	–
MoS ₂ /SiO ₂	61.0	14.8	200	3.60	1:97.3
WS ₂ /SiO ₂	80.6	15.0	200	5.70	1:100
MoS ₂ /TiO ₂	60.4	14.8	200	3.68	1:100
WS ₂ /TiO ₂	80.4	15.0	200	5.70	1:100

themselves; however, they were able to sensitize TiO₂ for this process [19]. When attached to TiO₂, MoS₂ acts as a co-catalyst by assisting the electron–hole separation and thus minimizing their recombination in favor of redox chemistry. Similarly, Ho et al. [18] observed that MoS₂ and WS₂ deposited on TiO₂ accelerate the photodegradation of 4-chlorophenol and methylene blue under visible light. MoS₂ deposited on CdS enhances photo splitting of water [25]. Importantly, MoS₂ (and likely WS₂) is photostable: the energy levels adjacent to the band gap on both sides are composed primarily of Mo *d*-orbitals, therefore most photoexcitations do not cause Mo–S bond weakening and lattice disintegration [26,27].

In order to uncover the details of the photocatalytic surface chemistry on pure MoS₂ or WS₂, the surfaces of the nanoparticles need to be free of surfactants or capping agents. The synthesis of the size-selected MoS₂ nanoparticles by Wilcoxon et al. involved inverse micelles with long-chain polyalcohol surfactants [19]. Their presence on the surface did not preclude the photocatalysis but it would complicate the mechanistic studies. Duphil et al. reported a fairly simple surfactant-free synthesis of the MoS₂ and WS₂ nanoparticles by thermal decomposition of the metal carbonyls in *p*-xylene in presence of dissolved sulfur [28,29]. The concern is that the nanoparticles are produced with a wide size distribution reaching the diameters of up to 30 nm. The goal of this study was to verify whether the MoS₂ and WS₂ nanopowders produced by this method (1) exhibit size sensitive widening of the band gap, and (2) are photocatalytically active under visible light. The results of the photooxidative degradation of methylene blue and acetone on these nanoparticles, both free and deposited on SiO₂ and TiO₂, confirmed that this is the case.

2. Experimental

2.1. Synthesis of unsupported MoS₂ and WS₂ nanoparticles in *p*-xylene and in decalin

MoS₂ and WS₂ nanoparticles were synthesized similarly to the method described by Duphil et al. [29], which involves thermal decomposition of metal carbonyls in high boiling solvents at 140–143 °C in presence of co-dissolved sulfur. Metal carbonyls Mo(CO)₆ (Sigma–Aldrich 98%) or W(CO)₆ (Strem Chemicals 99%) and sulfur (Fisher Scientific, sublimed) were used without further purification. Solvents, *p*-xylene (EM Science 98%) or decalin (Aldrich 99%, anhydrous), were outgassed before syntheses by refluxing under argon flow. All synthesis steps were carried out under argon atmosphere. Molar ratio of a metal carbonyl to sulfur was kept at 1:2. Typical proportions are listed in Table 1. The reaction times ~20 h in the case of MoS₂ or over four days for WS₂ based on the original procedure [29]. Synthesized nanoparticles were washed by cycles of centrifugation and redispersion in cyclohexane.

The original procedure by Duphil et al. calls for *p*-xylene as a solvent. By this procedure, we prepared the MoS₂ nanoparticles. However, this method failed to produce any significant amount of the WS₂ nanoparticles and instead lead to a side product, likely a π -complex such as a “piano stool” (η^6 -C₈H₁₀)W(CO)₃, reported

in literature [30–33]. Decalin was chosen as a non-coordinating replacement for *p*-xylene due to its lack of aromaticity and high boiling point (192–194 °C). The proportions and the rest of the procedure were kept the same. Both MoS₂ and WS₂ nanoparticles were successfully produced. Washed and dried MoS₂ is orange-brown and WS₂ is reddish-brown (see photographic images in Supporting information). These synthesized unsupported MoS₂ and WS₂ nanoparticles were found to be very hydrophobic; they dispersed in chloroform or benzene but did not disperse in water or acetone.

2.2. Synthesis of the MoS₂ and WS₂ nanoparticles supported on SiO₂ and TiO₂

In order to make the sulfide nanopowders dispersible in water, we prepared the MoS₂ and WS₂ nanoparticles supported on SiO₂ or TiO₂. Synthesis of both metal sulfides in decalin was carried out in the presence of silica (nanopowder, 10–20 nm particles, 99.5% Aldrich) or titania (anatase, nanopowder, <25 nm particles, 99.7% Aldrich). SiO₂ or TiO₂ was added in the amount that would yield ~1.0 wt% deposited sulfide catalysts (see Table 1). The oxide was added to the reaction mixture from the very beginning and the rest of the procedure was the same. Washed and dried MoS₂/SiO₂, MoS₂/TiO₂, WS₂/SiO₂, and WS₂/TiO₂ are light brown powders.

2.3. Characterization of the synthesized nanomaterials

Transmission electron microscopy (TEM) imaging was performed on Hitachi H-600 electron microscope using 75 kV accelerating voltage. Magnification was calibrated using a catalase standard (Electron Microscopy Sciences, part No. 80014). The support grids had a carbon film suspended on the copper mesh (Electron Microscopy Sciences, CF400-Cu). The samples were deposited dropwise from liquid suspensions, followed by drying in ambient atmosphere.

Ultraviolet–visible (UV–vis) absorption spectra were acquired on the HP 8452A diode-array spectrophotometer using a 10-mm path quartz cuvette and the slit width of 1 nm. The integration time was 25 s for the nanoparticle characterization or 5 s during photocatalytic tests.

2.4. Photocatalytic tests

Photodegradation of methylene blue (methylene blue hydrate, 95% pure, Riedel-deHaën) or acetone (\geq 99.5%, A.C.S. reagent, Sigma–Aldrich) was used to test the photocatalytic activity of the synthesized catalysts. The light source was a 300 W ozone-free xenon arc bulb (Newport, model 6258) in a fan-cooled, universal housing (Newport Oriel, model SP66902-4000, 2 in. beam output) equipped with a shutter, a water filter, and a 400 nm long-pass color glass cut-off filter (Edmund Industrial Optics, NT47 series, 2 in.²). Then a mirror (Newport, model 66225) reflects the beam straight down into a beaker containing the solution with a photocatalyst. The reaction beaker was positioned entirely within the light beam and placed in the water bath to prevent temperature fluctuations. The mixture was stirred rapidly by a magnetic stirrer.

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