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Preparation of a TiO₂–MoS₂ nanoparticle-based composite by solvothermal method with enhanced photoactivity for the degradation of organic molecules in water under UV light

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Abstract: The MoS₂ nanocrystals coupled with anatase nanoparticles were prepared by the solvothermal method at relatively low temperatures. It was determined that the materials consisted of 15–20 nm diameter anatase nanoparticles with highly dispersed MoS₂ nanocrystals of approximately 3–7 nm in size. Visible light absorption in the MoS₂–TiO₂ samples increased with the MoS₂ content. However, their lambda edges (ledge) remained almost identical at approximately 390 nm, meaning that MoS₂ did not cause a red shift in the anatase bandgap energy. The hybrid MoS₂-anatase materials had higher surface area (70–124 m² g⁻¹) than commercial TiO₂ (P25) (50 m² g⁻¹). The MoS₂-anatase hybrid nanocrystals showed enhanced activity in the oxidation of methylene blue in water under UV light irradiation. A photomechanism able to elucidate the observed dye decolourisation was suggested.

1. Introduction

Titanium dioxide nanoparticles (TiO₂-NPs) are interesting photoactive nanostructure materials with a promising future owing to their potential application for photovoltaic cells [1], hydrogen production by water splitting [2], environmental photocatalysis [3] and self-cleaning surfaces [4].

It has been demonstrated [5] that several structural parameters such as morphology, particle size, crystallinity and surface features strongly influence the properties of TiO₂-NPs. Such parameters are determined by the synthesis method and the post-treatments (e.g. thermal post-treatment to improve crystallinity). The most popular synthesis techniques are sol-gel processes [6], hydrothermal and solvothermal methods [7]. Absorption of a photon with sufficient energy by a TiO₂ crystal leads to a charge separation owing to an electron promotion to the conduction band and a resulting hole in the valence band [8]. This hole can be used to oxidise organic compounds onto the surface of the TiO₂ crystal. Nevertheless, the photocatalytic efficiency of TiO₂ towards organic compounds degradation can substantially decrease as a result of the high recombination ratio of photo-induced electron-hole pairs generated under UV radiation. The modification of TiO₂-NPs with inorganic substances, such as noble metals [9], transition metals [10], non-metals [11] and semi- conductors [12], has been considered for maximising its photocatalytic efficiency. These dopers work by favouring the electron-hole separation and promoting the interfacial electron transfer [13], decreasing TiO₂ bandgap (which benefits the electron transfer from valence band to conduction band [14]) or increasing the activity of TiO₂ by extending the wavelength range response of TiO₂ to the visible region [15]. Unfortunately, dopers can also operate as electron-hole recombination centres that are detrimental to photocatalytic activity [16].

On the other hand, coupling on the crystal surface with metals [16], non-metals [17] or semiconductors [12] has positive effects, with a heterostructure being generated on the interface between TiO₂ and semiconductor NPs that is beneficial to enhancing the separation efficiency of the photogenerated electron-hole pair.

In this respect, combining semiconductors with a small bandgap, such as CdS [12] or Bi₂S₃ [18], with TiO₂ helps the photogenerated electron in the small bandgap semiconductor transfer to the TiO₂ particles, while the holes remain in the particles of the

other coupling materials. Owing to the values of energy in the conduction and valence band of MoS₂ [19] compared to anatase, MoS₂ works in a way that is different from CdS or Bi₂S₃. MoS₂ could accept the photogenerated electron from TiO₂ while keeping the hole separated from the electron. Additionally, MoS₂ shows several particular advantages over CdS and Bi₂S₃ that should be considered. First of all, the electronic states of the conduction and valence bands in bulk MoS₂ are derived from the electronic structure of Mo (4d orbital), so photoexcitation of electrons should not weaken Mo–S bonds, which are responsible for the photostability of MoS₂ during photo-oxidation of water [20]. Moreover, if the size of MoS₂ is reduced to the nanoscale, edge-site Mo atoms are not protected by the inert basal planes of MoS₂. As a result, the bandgap of the MoS₂ nanocrystals becomes small enough to allow a wider range of the solar spectrum to be collected [21].

In contrast to CdS, MoS₂ nanoparticles are considerably stable in water. The lattice dissolution process via the oxidation of sulphur to a sulphate ion is slower in a covalent material such as MoS₂, compared to an ionic semiconductor such as CdS [22]. Thus, it would be possible for MoS₂ nanoparticles to be employed in wastewater treatments.

This Letter describes a simple method for coupling MoS₂ nanocrystals with TiO₂–NPs we have developed to obtain a hybrid nanostructured material with enhanced activity for the degradation of organic molecules in water under UV light.

2. Materials and methods

TiO₂–NPs were prepared by a combination of sol–gel and solvothermal methods. In a typical experiment, 5 ml of titanium isopropoxide (Aldrich) were diluted in 45 ml of 2-propanol. The solution was added drop-wise into a mixture consisting of 26 ml of 2-propanol with 26 ml of water. In contact with aqueous medium, titanium isopropoxide decomposes to form non-crystalline TiO₂–NPs. The resulting powders were aged overnight in the reaction mixture, then filtered and washed with distilled water, and dried at 105°C for 24 h.

For the synthesis of hybrid materials, the previously prepared TiO₂–NPs were mixed with different quantities (0, 2, 5, 7.5 and 10 weight%) of MoS₂ (Aldrich) in 20 ml of a 1/1 (volumetric ratio) water/2-propanol solution and strongly stirred for 2 h. The mixtures were then thermally treated in a 25 ml autoclave (200°C, 35 bar) for 24 h in order to

convert amorphous TiO₂-NPs into crystal anatase-NPs. The obtained materials were filtered, rinsed with distilled water and dried at 105°C for 24 h. MoS₂ content in the hybrid materials were confirmed by scanning electron microscopy–energy-dispersive X-ray spectroscopy (SEM-EDX) measures (0, 2.3, 5.6, 7.1 and 12 weight%).

The nanostructures were characterised by transmission electron microscopy (TEM, JEOL-200FXII), SEM-EDX (Hitachi S3400N- Roñtech) X-ray diffraction (XRD) (Bruker AXS D8 advance diffractometer), nitrogen adsorption (Micromeritics ASAP 2020) and UV–vis absorption (UV–VIS Spectrometer Shimadzu UV-3600 equipped with a labsphere diffuse reflectance accessory) and elemental analysis (Carlo Erba 1108).

3. Results and discussions

3.1. Characterisation

XRD spectra (Fig. 1) revealed a pattern of broad peaks, characteristic of small particle sizes. Two small and broad peaks were found at 13.58 and 33–35.8 in the XRD spectra for all the samples containing MoS₂. According to the literature, such peaks are related to the (002) and (100) crystallographic planes [23] in the hexagonal structure of MoS₂. Furthermore, the diffractogram of all the samples showed the characteristic peaks of anatase (the most photoactive crystalline form of TiO₂ [24]), which were found at 25.58, 37.38, 38.8, 39.88, 48.258, 54.2, 55.48, 62.98, corresponding to its (101), (103), (004), (112), (200), (105), (211), (204) crystallographic planes [25].

Crystal size was calculated by using the Scherrer formula. The average crystal size (Table 1) obtained for anatase from XRD data was around 20 nm for anatase-NPs and 5 nm for MoS₂-NPs. Brunauer–Emmett–Teller (BET) surface area results for MoS₂–TiO₂-NPs are listed in Table 1. The highest value is related to samples with the highest MoS₂ concentration. It can be concluded from the TEM images analysis of the MoS₂–TiO₂-NPs samples that the anatase-NPs were agglomerated and covered with MoS₂ nanocrystals. An image from a 7.1% MoS₂ sample is shown in Fig. 2.

Diffuse reflectance UV–vis absorption spectra for the MoS₂–TiO₂-NPs are shown in Fig. 3. All the samples exhibited absorption bands in the visible region owing to MoS₂ and in the UV region owing to anatase. The absorption onsets were determined by linear extrapolation from the inflection point of the curve to the baseline. The edges of the absorption of the MoS₂–TiO₂-NPs samples were measured at approximately 390 nm,

corresponding to bandgap energy of 3.2 eV [26]. There was no red shift when compared with anatase.

3.2. Photodecolouration activity

The photocatalytic activity of TiO₂ systems is usually evaluated by measuring the time dependence of the concentration loss of a degraded compound, commonly, dyes such as methylene blue (MB) which predicts an exponential decay of concentration as a function of time. The enhancement achieved in the MoS₂–TiO₂ composite may be evaluated by comparison with the activity relative to a standard (which is usually P25).

Nevertheless, the comparison among different series of experiments could be a complex task due to the variety of different equipments (lamps, reactors, etc.) and testing methods used in different laboratories. Although the relative activity can be well quantified for a given set of experiments, it is inaccurate using it as an independent standard for the comparison with results obtained from other studies because the way in which the kinetic parameters are obtained is inherently linked to experimental details [27].

Alternatively, the beneficial effects can be quantified in terms of a synergy factor R (1) defined by Matos et al. [28]

$$R = k_{app}(\text{TiO}_2 - \text{MoS}_2) / k_{app}(\text{TiO}_2) \quad (1)$$

where k_{app} is taken as the apparent first-order rate constant. Photodecolouration activity measurements were carried out in a photocatalytic reactor consisting of a 1-litre quartz vessel (diameter 1/4 12 cm) with two valves (air entrance and purge), a sample collector and two UV lamps (Philips TL8W (Hg), maximum emission at 360 nm). The lamps are cylindrical (30 × 15 cm) and the separation between their centres is 7 cm. Given its environmentally harmful character and widespread use in the textile industry, MB was chosen as our model molecule in order to test the ability of the prepared MoS₂–TiO₂–NPs to decompose organic molecules.

After checking there was no MB degradation under UV radiation without TiO₂ and in the presence of TiO₂ without UV radiation, 300 ml of a 5 ppm MB aqueous solution was introduced into the reactor together with 100 mg of the tested reactant (the different produced MoS₂–TiO₂–NPs samples and the commercial TiO₂ (P25), respectively). Prior to the measurement, the mixture was stirred in darkness at 250 rpm for 30 min to assure reactant surface saturation with the MB (**Fig. 4**). The solutions were subsequently aerated

and illuminated by the UV lamps. 3 ml samples were regularly extracted and filtered. The MB degradation was followed by UV–vis absorption spectroscopy at 662 nm.

The reaction followed apparent first-order kinetics, in agreement with the generally observed Langmuir–Hinshelwood kinetics model:

$$r = dc / dt = kKc / (1 + KC) \quad (2)$$

This equation can be simplified to an apparent first-order equation

$$\ln (c/c)_0 = kKt = k_{app}t \quad (3)$$

with k_{app} being the first-order rate constant. The results of these experiments are plotted in Fig. 5 and the apparent first-order rate constants, k_{app} [min⁻¹], are shown in Table 1. To confirm that the loss of colour observed during the photocatalysis experiments was due to the mineralisation of the MB instead of the photoreduction of the MB to leuco-MB (which is also colourless), the purged gases from the photoreactor were blown through a H₂O adsorber and CO₂ adsorber consecutively. The powders resulting from the CO₂ adsorption (containing the adsorbing material and the adsorbed CO₂) were characterised using the previously mentioned elemental analysis equipment. The increase in carbon content with respect to the raw adsorber allowed us to calculate the mineralisation percentage obtained with each tested photocatalyst material after 100 min operation. These results are listed in Table 1 where the percentage of mineralisation can be compared with the degradation percentages. A mineralisation level of 43% was obtained after 100 min with the 7.1% MoS₂, compared with the 7% reached by the Degussa P-25 reaching under the same experimental conditions.

The synergy R factors calculated using expression (1) for the different tested samples are also listed in Table 1. It was observed that the R factors corresponding to the MoS₂–TiO₂–NPs samples are always higher than the R factor of P25 (equal to the unit), reaching the highest value (R = 2.125) for the sample containing 7.1% MoS₂.

By comparison with the commercial TiO₂ (P25), the hybrid MoS₂–TiO₂ materials always showed an increase in the reaction rate, doubling its value with the optimum content of MoS₂ (7.1%).

Since no red shift was detected in the anatase bandgap, we assumed that the improvement in the photocatalytic activity of the MoS₂–TiO₂–NPs could be explained by the inter-particle electron transfer from irradiated anatase crystal to the MoS₂ conduction band

(CB) [29], as has been schematically represented in Fig. 6. In the MoS₂ conduction band (CB), electrons are scavenged by molecular oxygen O₂ (from air gas) to yield the superoxide radical anion ($\cdot\text{O}_2^-$) and the hole remaining in the TiO₂-NPs. This newly formed intermediate (O_2^-) can react to produce ($\text{OH}\cdot$) (hydroxyl radical ion) [5]. These types of radicals are powerful oxidising agents capable of degrading most pollutants [30]. Therefore, this charge transfer enhances the photo-oxidation of the adsorbed organic substrate by isolating electrons and holes in two distinct particles.

Increased content of MoS₂ improves photocatalysis of anatase because MoS₂-NPs allow more electrons to remain separate. However, there is an optimum concentration of MoS₂ after which the reaction rate begins to decrease, since anatase-NPs are responsible for the generation of electron-hole pairs. Excess MoS₂ might compete with TiO₂ for the UV light [31].

4. Conclusions

We have developed an easy method to synthesise hybrid MoS₂-TiO₂ nanomaterials at low temperatures with improved catalytic properties with a significant potential for the photodegradation of organic molecules. MoS₂ nanoparticles anchored on the surface of anatase nanoparticles do not have a reductive effect on the bandgap energy of the hybrid material but are able to remove electrons from the surface of anatase. Thus, the isolation of electron-hole pairs on both crystal surfaces seems to be prolonged, what might explain the enhanced photoreaction of the hybrid material with pollutant organic molecules. The highest photocatalytic activity for the degradation of MB was reached for the MoS₂-TiO₂ sample containing 7.1 wt% of MoS₂. By comparison with the commercial TiO₂ (P25), the hybrid MoS₂-TiO₂ materials always showed an increase in the reaction rate, doubling its value with the optimum content of MoS₂ (7.1%).

5. Acknowledgments

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Figures

Figure 1 XRD spectra of the TiO₂-NPs samples a Doped with 12% MoS₂ b Doped with 7.1% c Doped with 5.6% d Doped with 2.3% e TiO₂-NPs

Figure 2 TEM micrograph corresponding to the TiO₂-NPs doped with 7.1% MoS₂

Figure 3 Diffuse reflectance UV-vis absorption spectra of the TiO₂-NPs samples a Doped with 12% MoS₂ b Doped with 7.1% MoS₂ c Doped with 5.6% MoS₂ d Doped with 2.3% MoS₂

Figure 4 (A) Rates of photocatalysed degradation of the MB aqueous solutions under a simulated solar irradiation and (B) adsorption in darkness of MB a Doped with 12% MoS₂ b Doped with 7.1% c Doped with 5.6% d Doped with 2.3% e Doped with 0%

Figure 5 Schematic representation for the redox potential of the valence (VB) and conduction bands (CB) of the TiO₂-NP and the MoS₂-NP for the prepared hybrid nanomaterials

Tables

Table 1 Crystal sizes (calculated from XRD measurements using the Scherrer formula), specific surface areas calculated by the BET method and kinetic parameters (apparent first-order rate constant with R²) for the commercial TiO₂ (P25) and the TiO₂-MoS₂-NPs with different contents of MoS₂, synergy factor R based on P25 and TiO₂ NP as growth and % of degradation and mineralisation

Figure 1

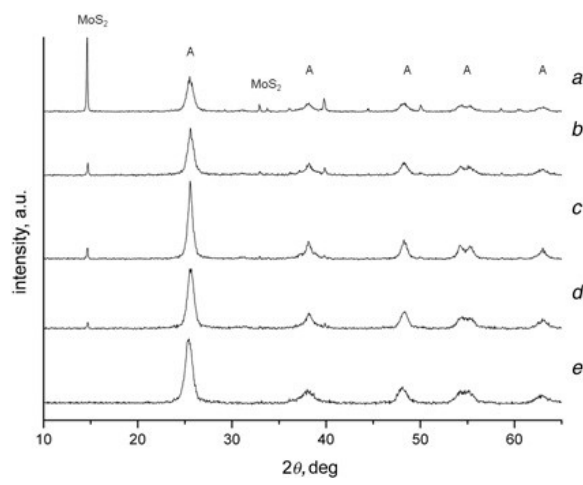


Figure 2

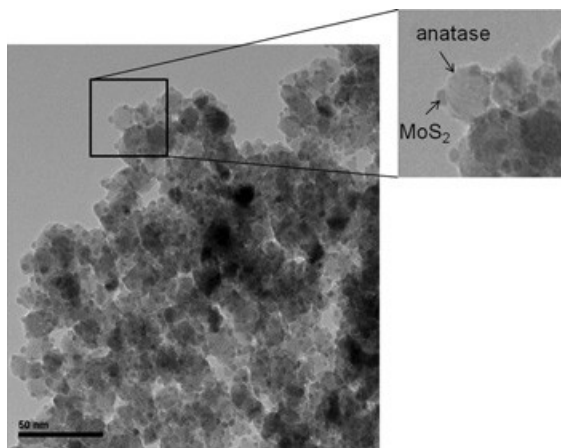


Figure 3

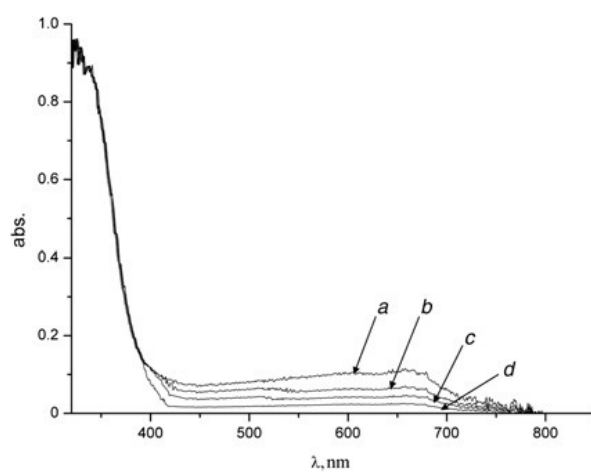


Figure 4

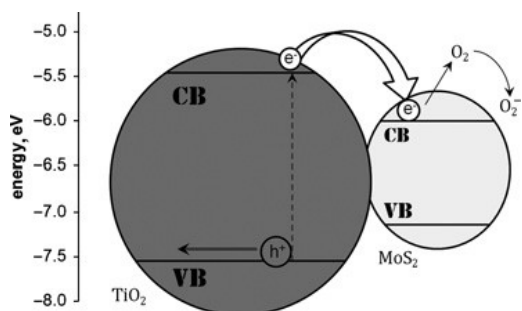


Figure 5

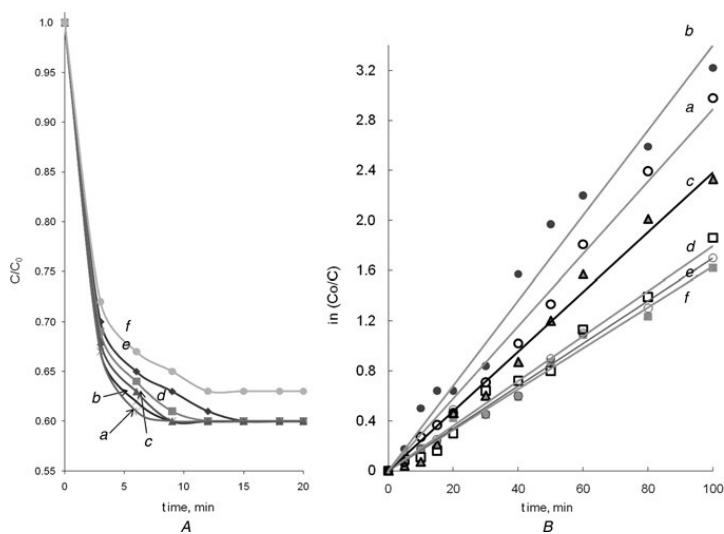


Table 1

Sample	Cristal size, nm		Specific surface, m ² /g	Photodecomposition				
	Anatase	MoS ^a		k_{app}, min^{-1}	R^2	$R = \frac{k_{app}(\text{TiO}_2\text{-MoS}_2)}{k_{app}(\text{P25})}$	Degradation, %	Mineralisation, %
P25	32	52	50	0.016	0.989	1.000	15	7
TiO ₂ Np ^b	21	0	70	0.017	0.987	1.063	22	13
2.3% MoS ₂	20	7	100	0.018	0.987	1.125	31	23
5.6% MoS ₂	15	7	116	0.021	0.987	1.313	41	31
7.1% MoS ₂	15	5	118	0.034	0.976	2.125	65	43
12% MoS ₂	15	3	124	0.024	0.984	1.500	41	35

^aIn case of P25 MoS₂ crystal size means rutile crystal size

^bSample of TiO₂ nanoparticles as growth without MoS₂