

Effect of synthesis method on NS-TiO₂ photocatalytic performance

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Abstract

In this study, highly visible-light photoactive nitrogen and sulfur co-doped TiO₂ (N,S-TiO₂) nanoparticles and nanosheets were synthesized via two different methods, facile sol-gel and hydrothermal methods, respectively. The photocatalytic activity of N,S-TiO₂ photocatalysts were evaluated and compared by degradation of non-steroidal anti-inflammatory drugs, ibuprofen (IBP) and naproxen (NPX), under simulated solar irradiation. The sol-gel method developed a mesoporous structure N,S-TiO₂ nanoparticle which contains both anatase and rutile phases with large BET surface area (132 m²/g). However, N,S-TiO₂ nanosheets with pure anatase phase, with larger mesoporous structure and a smaller BET surface area (64 m²/g) was formed via hydrothermal method. NS-TiO₂ nanoparticles were coated on UVC-treated polycarbonate (PC) (NS-TiO₂@PC) by simple deposition method. The results showed that under identical condition, N,S-TiO₂ nanoparticles can degrade 85% and 99.3% of ibuprofen and naproxen while 71.6% of IBP and 99.1% of NPX were degraded by N,S-TiO₂ nanosheets. Optimization results showed that maximum degradation efficiency was achieved at the optimum conditions: irradiation intensity 8.36 mW/cm² (for ibuprofen) and 10 mW/cm² (for naproxen), initial drugs concentration 10 mg/L and reaction time 121 min. Under this condition, the maximum degradation efficiency of 83% and 100% were achieved for ibuprofen and naproxen, respectively. The results of this study elucidate co-doped NS-TiO₂ nanoparticles prepared by sol-gel methods are photocatalytically more effective and practically easier to reproduce for the practical application, both in terms of energy saving and cost reduction.

Keywords: NS co-doped TiO₂; photocatalyst; ibuprofen; naproxen; energy saving

1. Introduction

In recent years, pharmaceuticals and personal care products (PPCPs) have become an emerging issue which enters into the environment from a point and diffuse sources [1]. Due to the high resistance of PPCPs in the environment and continuous exposure with living beings, consequently, they turn into hazardous materials [2]. Non-steroidal anti-inflammatory drugs (NSAIDs) are frequently found in various water sources like surface water, sewer water, ground water and even in drinking water [4, 5]. Several studies have shown that advance oxidation processes using heterogeneous photocatalysts are an appropriate option for removing IBP and NPX from wastewater [1, 2]. Among various semiconductor materials, TiO₂ is by far the most common photocatalyst for environmental applications. It is suggested that a suitable photocatalyst should be nontoxic, cheap and highly effective to utilize light source. The simultaneous doping of nitrogen (N) and sulphur (S) atoms into TiO₂ has attracted considerable attention because the synergistic effect tuned the electronic structure increases the visible-light photocatalytic activity of TiO₂ [3-5]. In this study, we have prepared N,S co-doped TiO₂ nanoparticles and N,S co-doped TiO₂

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nanosheets through the facile sol-gel and hydrothermal methods, respectively. The photocatalysts were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), UV-vis diffuse reflectance spectroscopy (DRS), BET, and FT-IR. The photocatalytic activity of the N,S co-doped TiO₂ samples was examined via decomposition of ibuprofen (IBP) and naproxen (NPX) under simulated solar irradiation. The prepared N,S-TiO₂ nanoparticles, using a novel and easy coating method, were coated on a polycarbonate (PC) substrate and their photocatalytic activity were investigated.

Nomenclature

A
B
C

2. Material and methods

2.1 Synthesis

In a brief, for preparation of N,S co-doped TiO₂ nanoparticle by sol-gel method, 12 mL of Ti(OC₄H₉)₄ and 0.355 g of thiourea were mixed, under vigorous stirring, for 5 min and then 10 mL of deionized water was added. The solution was hydrolyzed under vigorous mixing at room temperature for 45 min, followed by 24 h thermal treatment at 80 °C in closed Erlenmeyer flask. The obtained precipitate was separated by centrifuge, washed with ethanol and then dried at 80 °C for 8 h. The prepared powder was calcinated at 450 °C for 2 h. For undoped TiO₂ the procedure was same, except that thiourea was not added. For synthesis of N,S co-doped TiO₂ nanosheets by hydrothermal method, in a dried Teflon-lined autoclave, 15 mL of Ti(OC₄H₉)₄ were mixed with 2 mL of hydrofluoric acid solution and this was kept at 180 °C for 24 h. The precipitate was separated by centrifuge and filtration, washed with ethanol, deionized water and 0.02 N NaOH and then dried at 80 °C for 8 h. The obtained powder was mixed mechanically with thiourea in 1:3 (Wt/Wt) ratio and then calcined at 450 °C for 2 h. The N,S-TiO₂ nanoparticles, N,S-TiO₂ nanosheets, TiO₂ nanoparticles and TiO₂ nanosheets thereafter denoted as S1, S2, S3 and S4, respectively.

The prepared N,S-TiO₂ nanoparticles were coated on PC sheet with a relatively novel and easy method. The following procedures were used for coating on PC: (1) The PC was washed with deionized (DI) water and detergent and dried at room temperature. (2) To enhance the binding between the PC and N,S-TiO₂ and also protect the PC from the photocatalytic degradation, a pre-coated peroxotitanium complex was used, (3) Subsequently, a highly concentrated suspension of N,S-TiO₂ in dichloromethane was coated on the PC surface.

2.2 Photocatalytic activity

All experiments for photocatalytic evaluation of the photocatalysts for the degradation of NSAIDs were carried out in a home-made tubular cylindrical Pyrex (with an internal diameter of 7 cm and 25 cm height) under visible light condition and at ambient temperature. The experiments of coating section were done in a rectangular photocatalytic reactor with the area of 4 cm × 30 cm. The solutions containing drugs were falling as a thin film on the top of the N,S-TiO₂ photocatalysts with a flow rate of 20 mL/min.

3. Result and discussion

3.1 Characterization of catalysts

TEM studies were used to observe the particle size, crystallinity, and morphology of the synthesized N,S-TiO₂ nanoparticles and N,S-TiO₂ nanosheets. Fig. 1a shows the relatively homogenous distribution of nanoparticles with spheroid morphology. The mean particle diameters were between 5 and 10 nm. The XRD pattern of the TiO₂

samples are shown in Fig. 2a. The diffraction pattern of hydrothermal TiO_2 nanosheets is almost similar with sol-gel TiO_2 nanoparticles. The XRD patterns of TiO_2 nanosheets (S2 and S4) demonstrate that all XRD peaks belong to the TiO_2 anatase phase. However, for the sol-gel samples (S1 and S3), the diffraction peaks at 2θ of 54.52° , 54.97° , and 62.8° match the characteristics peaks of the rutile pattern. A comparison of the UV-Vis adsorption spectra of the TiO_2 samples and Degussa P-25 is shown in Fig. 2b. Degussa P-25 represents adsorption at wavelength below 400 nm, and the beginning of the absorption edge for samples (S1-S4) is at ca. 400 nm, which is consistent with the intrinsic band gap absorption of pure anatase TiO_2 (3.2 eV). The band gap of the S2 sample (2.85 eV) is lower than that of the S4 (3.15 eV). Substitution of oxide centers by nitride centers and/or to the interstitial introduction of nitride into the oxide lattice narrows the band, and this can be attributed to the formation of intra gap states located above the valence band 35, 36. The enhanced absorbance at wavelength above 500nm is probably related to the synergistic effect of nitrogen and sulfur co-doping on the electronic structure of TiO_2 . The surface micrographs of N,S-TiO₂@PC are shown in Fig. 3a. TiO_2 film with a thickness of 481 μm was developed on the PC. The surface morphology of coating is shown in Fig. 3b. As seen, the coated surface contains high porosity, and no significant cracks were observed on the entire coated surface.

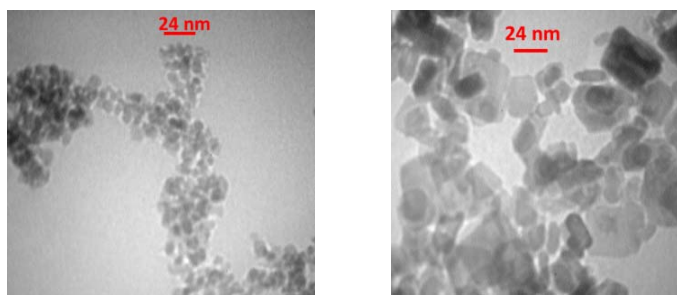


Fig 1. TEM images of (a) N,S co-doped TiO_2 nanoparticles (S1) (b) N,S co-doped TiO_2 nanosheets (S2).

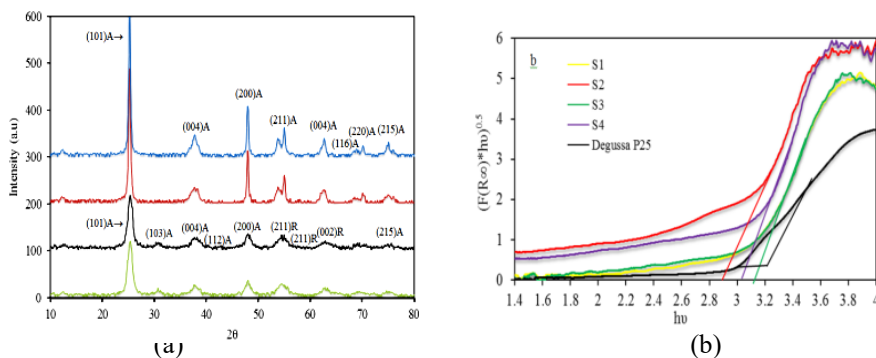
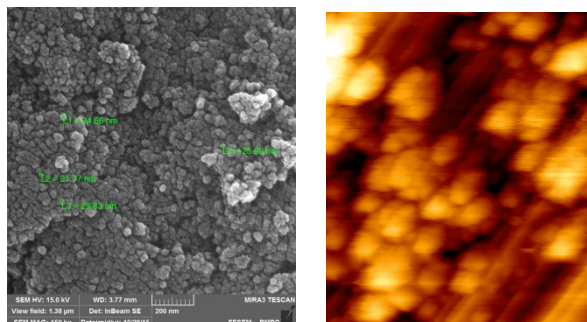


Fig. 2. XRD patterns and (b) UV-visible diffuse reflectance spectra of synthesized photocatalysts



(a) (b)

Fig. 3. FE-SEM images of the coatings prepared and (b) AFM micrographs of N,S-TiO₂ films coated on PC substrate

3.2 Photocatalyst screening

Screening experiments were performed to assess the relative photocatalytic activity of doped and un-doped TiO₂ samples prepared by two different methods under simulated solar light irradiation. The initial concentration of IBP and NPX was 5 mg/L. The strong effect of synthesis method on particle size and morphology was observed. The results are shown in Fig. 4. As clearly seen in the Fig. 4 (a and b), the N,S co-doped TiO₂ samples (S1 and S2) exhibit higher photoactivity than the un-doped samples (S3 and S4). The presence of N and S as dopants in the TiO₂ lattice created a mid-gap in the S1 sample and narrowed the band gap in the S2 sample; thus, photon absorption was increased and resulted in increased photocatalytic potential. Meanwhile, the localized N and S impurities in the TiO₂ lattice prevented the recombination of photoinduced electrons and holes which contributes to increased quantum efficiency [6].

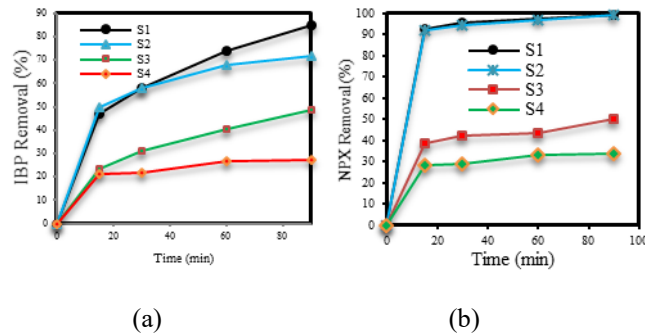
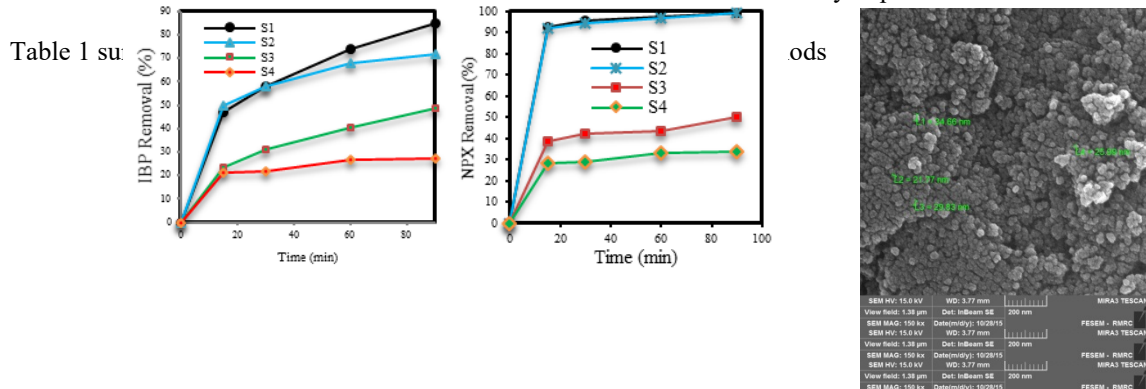


Fig 4. Photodegradation of (a) IBP (b) NPX over various photocatalysts under simulated solar light irradiation (pH 6, initial NSAID concentration = 5 mg/L, catalyst dose = 2 g/L)

The role of pH in the photocatalytic conversion was studied in the pH range 3–9 at a constant IBP concentration (5 mg/L). The final (i.e., after 90 min of irradiation) conversion levels of IBP for the S1 catalyst were 80%, 92%, and 82.5% at pH values of 3, 5, and 6, respectively. The conversion level decreased drastically, and no removal was observed at pH 9. However, for the S2 catalyst the final conversion level remains constant at about 64% regardless of pH value.

To identify reaction by-products of IBP and NPX degradation by N,S-TiO₂ under simulated solar light irradiation, a sample collected at the optimum condition for each drug and analyzed by electrospray ionization mass spectroscopy. In general, the concentration of by-products was too small to be detected. After photocatalytic treatment, the peak at m/z 209 was observed which could attribute to demethylation of IBP and then hydroxylation (dihydroxylated products) process. The degradation products such as aromatic ketones, carboxylic acids or phenols and also 4-ethylbenzaldehyde were detected. In the case of NPX, the concentration of ionized by-products was too low to be detected and nearly 100% NPX was removed during the photocatalytic process.



Synthesis method	Synthesis parameters			Characterization			Photocatalytic performance		
	Chemicals	Time required	Temp.	Morphology	Band gap	Crystal phase	Removal %	Time required	
Sol gel	Ti(OC ₄ H ₉) ₄ and thiourea	35h	80 (32h)-450 (2h)	Nanoparticle (5nm)	3.2 eV	Anatase and rutile	85 IBP NPX	99.3 NPX	90min
Hydrothermal	Ti(OC ₄ H ₉) ₄ , hydrofluoric acid and thiourea	34h	180 (24h)-80(8h), 450 (2h)	Nanosheet (10nm)	2.85 eV	Anatase	71.6 IBP NPX	99.1 NPX	90min

Table 1 summarizes the comparison between N,S-TiO₂ prepared by two different synthesis methods. From the results presented in this study, it could be concluded that co-doped N,S-TiO₂ nanoparticles synthesized by sol-gel method which uses less number of chemicals, lower temperature, time requirement and of course higher efficiency are easier to reproduce in industry, which can save the energy and is economical.

4. Conclusion

The photocatalytic activity of NS-codoped TiO₂, was evaluated through degradation and mineralization of IBP and NPX as model organic pollutants under simulated solar irradiation. The N,S-TiO₂ nanoparticles were synthesized by sol-gel method. The synthesis method had a great effect on particle size and surface area. The results of this study also elucidate that co-doped N,S-TiO₂ nanoparticles prepared by sol-gel methods are photocatalytically more effective and practically easier to reproduce for the practical application, both in terms of energy saving and cost reduction. Finally, this photocatalytic process is a promising alternative to conventional treatment for degradation and mineralization of recalcitrant pollutant such as pharmaceutical contaminants.

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