



# Sulfanilic acid-modified P25 TiO<sub>2</sub> nanoparticles with improved photocatalytic degradation on Congo red under visible light

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## ABSTRACT

Visible-light-induced titania/sulfanilic acid nano-composite photocatalysts were prepared and characterized by FTIR, XPS, UV-vis, XRD, and SEM. The results indicate that the formation of Ti–O–S bonds after the modification of P25 TiO<sub>2</sub> nanoparticles with sulfanilic acid ligands extends the photoresponse of the photocatalyst from the UV to the visible range. The photocatalytic activity of the nano-composite photocatalyst was examined by degrading Congo red under visible light, in which its effecting factors such as irradiation time, catalyst dosage, solution pH and the addition of H<sub>2</sub>O<sub>2</sub>, were investigated in detail. The possible mechanism of photocatalytic degradation under visible irradiation has been also presented.

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## 1. Introduction

In the last decade, much attention has been paid to the eradication of various environmental pollutants such as dyes, pesticides, detergents, and volatile organic compounds from wastewater [1–4]. Traditional physical techniques, which include adsorption on activated carbon, reverse osmosis, coagulation by chemical agents, and ion exchange on synthetic adsorbent resins, have been used for the removal of dye pollutants [5,6]. However, these methods only succeed in transferring organic pollutants from water to the other phase. Further, secondary pollution is created, which entails additional and costly solid-waste treatment and regeneration of the adsorbent. Therefore, an alternative to conventional methods is needed. In this regard, a typical alternative method is semiconductor photocatalyst-assisted advance oxidation processes. These are based on the generation of reactive species such as hydroxyl radicals (<sup>•</sup>OH) that can oxidize a broad range of organic pollutants quickly and non-selectively [7]. Due to its high chemical stability, non-toxicity, high photocatalytic activity to oxidize pollutants in air and water, and relative low price, TiO<sub>2</sub> has been widely used as a photocatalyst in recent decades [8]. However, its

application is limited because of its narrow photocatalytic region (near-ultraviolet region) and small fraction (<5%) absorption of incident solar irradiation and indoor light, which results from its relatively large band gap (3.2 eV). In the enhancement of the photoresponse of TiO<sub>2</sub> from the UV to the visible range without decreasing photocatalytic activity, surface modification and dye sensitization have been proven as effective methods as demonstrated by a number of studies [9–12].

The modification of the TiO<sub>2</sub> surface with noble metals such as Ag [13], Pd [14], Au [15], and Pt [16], as well as anion-doping with N [17,18] is well established and is in fact one of the most effective ways to improve TiO<sub>2</sub> photocatalytic activity in the photocatalytic degradation of organic pollution under visible light irradiation. However, the use of noble metals is costly, thereby hindering its practical application. Therefore, there is a need for the development of efficient and cheap co-catalysts as alternatives to noble metals.

Recently, the modification of TiO<sub>2</sub> nanoparticles with organic chelating ligands has been a key research interest because it not only induces dramatic changes in the electrical and optical properties of the nanoparticles, but it also results in the formation of other desirable properties. For example, Cozzoli et al. prepared organic-capped anatase TiO<sub>2</sub> nanorods at 80 °C, which can be dispersed in organic solvents to form optically clear concentrated solutions because of oleic acid surface modification [19]. The Niederberger group developed a nonaqueous sol–gel method to synthesize water-soluble

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dopamine-functionalized anatase TiO<sub>2</sub> nanoparticles [20]. Tahir et al. also prepared dopamine-functionalized rutile TiO<sub>2</sub> nanorods via a hydrothermal method [21]. Wang et al. developed an *in situ* chemical oxidative polymerization method in hydrochloric acid solutions to synthesize TiO<sub>2</sub> nanoparticles modified by polyaniline. These nanoparticles exhibit significantly higher photocatalytic activity than neat TiO<sub>2</sub> on the degradation of phenol aqueous solution under visible light irradiation [22]. Zhang et al. synthesized TiO<sub>2</sub> nanorods with enhanced photocatalytic activity *in situ* functionalized with L-hydroxyproline [23]. The Mu group recently prepared a new C<sub>60</sub>(CHCOOH)<sub>2</sub>-modified P25 TiO<sub>2</sub> photocatalyst, in which C<sub>60</sub> is bound chemically to the surface of P25. The photocatalytic reduction activity of the modified P25 for Cr(VI) ions in an aqueous solution can be enhanced significantly [24].

Degussa P25 is a commonly used formulation of TiO<sub>2</sub>, which consists of a mixture of anatase (70%) and rutile (30%) mineral phases. This chemical has been proven to be particularly active in oxidizing organic compounds and is frequently used as a representative mixed-phase titanium catalyst, as it displays greater photoactivity compared with single-phase catalysts [25,26]. In addition, commercially available, light sensitive sulfanilic acid (SA) is widely used as small molecular catalysts in the asymmetric synthesis of organic compounds [27,28]. On the other hand, hydrothermal synthesis is a very important and promising method for the fabrication of nanoscale materials. It has been well-proven to be suitable for large-scale production and can yield fine particles with a uniform distribution and high dispersion either in polar or non-polar solvents [29,30]. Further, the aqueous solvents used in the process are environmentally acceptable.

In this study, based on the viewpoints mentioned above, a simple and scalable method to prepare novel SA-modified TiO<sub>2</sub> nanoparticles was developed using hydrothermal treatment under 160 °C. The photocatalytic degradation property of Congo red (CR) using TiO<sub>2</sub>/SA nanoparticles as the photocatalysts under visible light irradiation was also examined. The photocatalytic activity of the nano-composite photocatalyst was examined by degrading Congo red under visible light, in which its effecting factors such as irradiation time, catalyst dosage, solution pH and the addition of H<sub>2</sub>O<sub>2</sub>, were investigated in detail. The possible mechanism of photocatalytic degradation under visible irradiation was also presented.

## 2. Experimental procedure

### 2.1. Materials and preparation of the TiO<sub>2</sub>/SA nanoparticles

Degussa P25 was purchased from Degussa: Huls Corporation. Sulfanilic acid (AR.) and Congo red (AR.) were obtained from Sigma Chemical Co.(St. Louis, Missouri). All other reagents were used as received and without further purification. Distilled deionized water was used with a resistivity of 18 MΩ cm. The modified TiO<sub>2</sub> nanoparticles with SA (labeled as TiO<sub>2</sub>/SA) were prepared from typical hydrothermal treatment as follows. A mixture of TiO<sub>2</sub> (1.598 g, 20 mmol), SA (0.866 g, 5 mmol), cetyltrimethylammonium bromide (CTAB, 0.911 g, 2.5 mmol), and distilled deionized water (65 mL) was sealed in a 100 mL Teflon-lined reactor and heated in an oven at 160 °C for 10 h and then slowly cooled to room temperature. After filtering, the resulting powder was washed with water and ethanol several times to remove the unreacted SA and surfactant CTAB, then dried at 70 °C in a dust-proof environment to obtain a grayish powder of the TiO<sub>2</sub>/SA photocatalyst.

### 2.2. Characterization of the photocatalyst

The infrared spectra on the pellets of the samples mixed with KBr were recorded on a Perkin Elmer Spectrum 2000 FTIR

spectrophotometer at a resolution of 4 cm<sup>-1</sup>. The TiO<sub>2</sub>/SA samples were ultrasonically and fully cleaned to remove the SA ligands physically attached to the TiO<sub>2</sub> surfaces before characterization. The concentration of the TiO<sub>2</sub>/SA was kept at about 0.25–0.30 wt.%.

A PerkinElmer Lambda 35 UV/vis spectrometer equipped with a labsphere diffuse reflectance accessory was used to characterize the reflectance spectra of the catalysts over a range of 200–700 nm. Labsphere RSA-PE-20 was used as reflectance standard.

The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-RB diffractometer with monochromatized CuKα radiation (λ = 1.5418 Å). The generator was operated at 40 kV and 25 mA. The samples were scanned at diffraction angles from 10 to 80° at a scanning rate of 0.068°/s; The C, N and S elemental analyses were carried out on a Perkin–Elmer elemental analyzer.

Morphological observations were performed on a field emission scanning electron microscope (FESEM, S-4800, Hitachi, Japan) and linked with an Oxford Instruments X-ray analysis system.

XPS experiments were carried out in an ultrahigh vacuum using ESCALAB Mark II X-ray photoelectron spectroscopy (XPS, VG Scientific, UK) with Mg Kα radiation (1253.6 eV) from the Mg anode source. The high-resolution scans of core-level spectra were recorded with an energy step of 0.05 eV and set to 15 eV pass energy. The binding energy was referenced at 284.6 eV to the C1s peak. Experimental data were deconvolved by Gaussian–Lorentzian mixture peak-fitting software.

The measurements of surface charge density of TiO<sub>2</sub>/SA catalyst as a function of pH were performed by a potentiometric titration process with 100.0 mL of a 20.0 g L<sup>-1</sup> TiO<sub>2</sub>/SA aqueous suspension. The TiO<sub>2</sub>/SA was protonated by addition of 0.4 mL of a 1.0 mol/L HCl solution firstly. Then this sample was titrated with NaOH diluted. The pH values were obtained with pH meter (Philips PW 9422).

### 2.3. Evaluation of photocatalytic properties

To examine the photocatalytic degradation of CR, a solution containing a known concentration of dye and TiO<sub>2</sub>/SA nanoparticles was prepared and allowed to equilibrate for 30 min in the darkness. The reactor was open to air to ensure enough oxygen in the reaction solution. The suspension pH values were adjusted to the desired level using dilute NaOH and HCl, and then the pH values were measured with pH meter.

The lamp was switched on to initiate the reaction. A 300 W halogen-tungsten lamp with a cutoff filter (λ > 400 nm) was used as visible-light irradiation source. During irradiation, agitation was maintained to keep the suspension homogeneous, and then this was sampled after an appropriate illumination time. The concentration of the dye in each degraded sample was determined with a spectrophotometer (UV/vis Spectrophotometer, WZJUV-2000) at λ<sub>max</sub> = 502 nm and a calibration curve. Using this method, the conversion percentage of CR can be obtained at different intervals. The degree of degradation rate (DR, %) as a function of time is given as follows: DR/% = (C<sub>0</sub> – C<sub>t</sub>)/C<sub>0</sub> × 100%, where C<sub>0</sub> is the initial concentration of CR, and C<sub>t</sub> is the instant concentration in the sample.

## 3. Results and discussion

### 3.1. SEM image

Fig. 1 shows the SEM images of the neat TiO<sub>2</sub> and the prepared TiO<sub>2</sub>/SA nanoparticles. From the SEM images, we find that the SA-modified TiO<sub>2</sub> does not change significantly the size compared with the neat TiO<sub>2</sub>, but obvious aggregation has been observed after hydrothermal treatment. Clearly, the synthesized TiO<sub>2</sub>/SA nanoparticle powders were 30–40 nm in size and spherical-like in

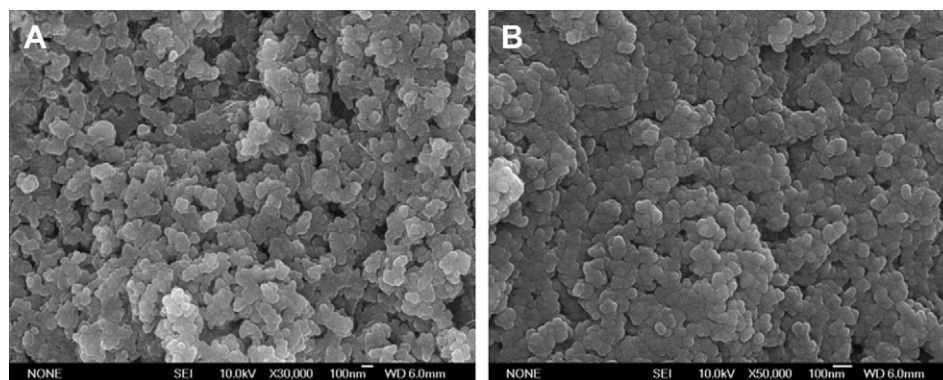


Fig. 1. SEM images of (A) neat  $\text{TiO}_2$  and (B) the  $\text{TiO}_2/\text{SA}$  nanoparticles.

shape with a uniform distribution. A higher dispersion increases the specific surface area, which ultimately enhances the photocatalytic performance on the  $\text{TiO}_2/\text{SA}$  nanopowders.

### 3.2. XRD patterns

Fig. 2 shows the XRD patterns of the neat  $\text{TiO}_2$  and  $\text{TiO}_2/\text{SA}$  samples. These patterns can be well indexed to the mixed phases of anatase and rutile. The modification of the  $\text{TiO}_2$  particles by SA does not cause any change in their peak positions and shapes compared with the neat  $\text{TiO}_2$ . This indicates that SA modification through hydrothermal treatment at  $160^\circ\text{C}$  does not change the crystalline structure of  $\text{TiO}_2$ . Additionally, the amount of grafted SA in the  $\text{TiO}_2/\text{SA}$  measured by elemental analyses (Found C: 5.06, N: 1.03, S: 2.29%) is about 12% (wt.). In the view of the fact that no new diffraction peak appears in the pattern of the  $\text{TiO}_2/\text{SA}$  sample and the content of the SA, it can be concluded that the SA is amorphous in the composite.

The diffraction peaks of the  $\text{TiO}_2/\text{SA}$  sample were slightly sharper than those of neat  $\text{TiO}_2$ . The mean size of neat  $\text{TiO}_2$  and the SA modified particles calculated from Scherrer's formula was 30 and 35 nm, respectively, which agrees well with the SEM image. These results may be attributed to the bonding with SA under the hydrothermal treatment.

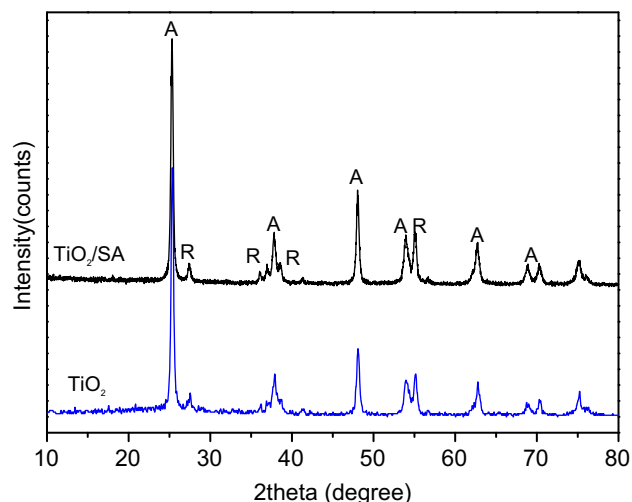


Fig. 2. XRD powder patterns of  $\text{TiO}_2$  and  $\text{TiO}_2/\text{SA}$ . A: anatase, R: rutile.

### 3.3. FT-IR analysis

The IR spectroscopy of modified  $\text{TiO}_2$  ( $\text{TiO}_2/\text{SA}$ ) and neat  $\text{TiO}_2$  and SA is shown in Fig. 3. Clearly, the spectrum of the modified  $\text{TiO}_2$  nanoparticles ( $\text{TiO}_2/\text{SA}$ ) consists of the characteristic peaks of neat  $\text{TiO}_2$  and SA ligand. In the spectrum of the  $\text{TiO}_2/\text{SA}$  sample (Fig. 3c), the band at  $1633\text{ cm}^{-1}$  is attributed to the stretching mode of O–H bonds on the surface of the  $\text{TiO}_2$  nanoparticles, and the bands at  $1548$ ,  $1423$ , and  $1319\text{ cm}^{-1}$  are the characteristic peaks of the benzene ring which came from organic SA. The wide adsorption band below  $950\text{ cm}^{-1}$  is attributed to the vibrations of the inorganic Ti–O and Ti–O–Ti framework bonds in  $\text{TiO}_2$ . Meanwhile, the peaks at  $1035$  and  $1005\text{ cm}^{-1}$  in the modified  $\text{TiO}_2$  sample can be assigned to the S=O asymmetric and symmetric stretching vibrations, respectively. Notably, the band at  $708\text{ cm}^{-1}$  can be assigned to the stretching vibration of the S–O bond in the  $\text{TiO}_2/\text{SA}$  spectra, which is larger than that ( $681\text{ cm}^{-1}$ ) of the neat SA sample (Fig. 3b). This indicates that SA can be modified onto the surface of  $\text{TiO}_2$  nano-particles through Ti–O–S bonds, which was further confirmed by the XPS results (Fig. 4). The possible graft mechanism of the SA-modified  $\text{TiO}_2$  is represented in Scheme 1.

### 3.4. XPS spectra

XPS characterization of the samples ( $\text{TiO}_2/\text{SA}$  nanoparticles) was also performed to identify the chemical bonding nature of SA on the

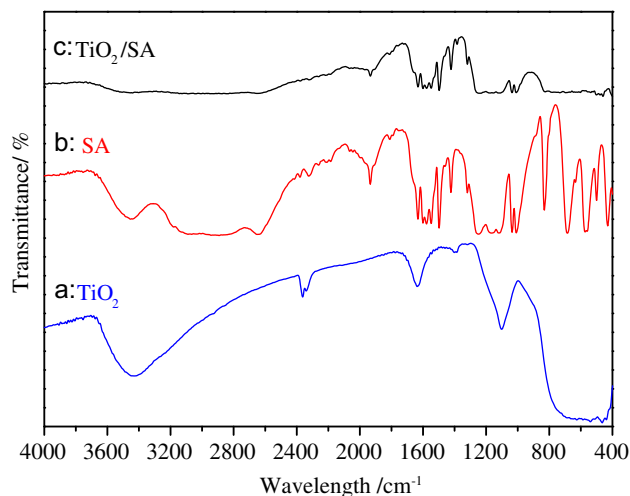


Fig. 3. FTIR spectra of neat  $\text{TiO}_2$  (a), SA (b) and modified  $\text{TiO}_2/\text{SA}$  (c).

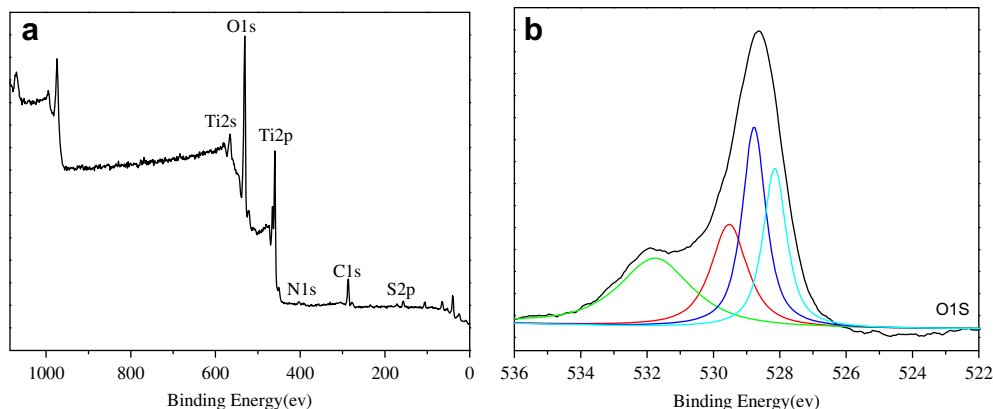


Fig. 4. XPS spectra of survey spectrum (a), and O1s (b) for  $\text{TiO}_2$  nanoparticles modified by SA.

$\text{TiO}_2$  nanoparticle surface, as shown in Fig. 4. The typical XPS survey spectrum of the  $\text{TiO}_2$  modified by SA reveals that the sample is composed of five elements: Ti, O, C, N, and S (Fig. 4(a)). The XPS Ti 2p core level was observed at binding energies of around 457 eV (Ti 2p<sub>3/2</sub>) and 463 eV (Ti 2p<sub>1/2</sub>), which is in good agreement with the finding on neat  $\text{TiO}_2$ . Curve-fitting result suggested that there should exist four kinds of oxygen in SA modified  $\text{TiO}_2$ , as shown in Fig. 4(b). The peaks at around 528.1, 528.8 and 529.5 eV can be attributed to the oxygen in S=O, Ti–O–Ti and Ti–O–S, respectively [31,32], while the peak at around 531.8 eV can be assigned to surface hydroxyl [33]. The IR and XPS results all confirmed that SA has been successfully bonded to the surface of the  $\text{TiO}_2$  nanoparticles by covalent interactions and formed a Ti–O–S bond via esterification, which make a strong adsorption as chemical adsorption.

### 3.5. UV–vis diffuse reflectance spectra

Fig. 5 shows the UV–vis diffuse reflectance spectra of SA and the neat  $\text{TiO}_2$  and modified  $\text{TiO}_2/\text{SA}$  nanoparticles. Clearly, there is no absorption above 400 nm for neat  $\text{TiO}_2$ . However, the modified  $\text{TiO}_2/\text{SA}$  nanoparticle exhibits strong absorption from 400 to 800 nm, which conforms to the grayish color of the powder. Notably, the absorption edge of the  $\text{TiO}_2$  modified by SA also red-shifts about 15 nm compared with that of the neat  $\text{TiO}_2$  sample. The UV–vis result indicates that some electron interactions between SA and the  $\text{TiO}_2$  nanoparticles exist in  $\text{TiO}_2/\text{SA}$ , which might be favorable for the improvement of the photocatalytic activity of  $\text{TiO}_2$ .

The band gap energies ( $E_g$ ) of the neat  $\text{TiO}_2$  and modified  $\text{TiO}_2/\text{SA}$  nanoparticles were 3.02 and 2.91 eV, respectively, which were obtained from the wavelength values corresponding to the intersection point of the vertical and horizontal parts of the spectra using the following equation:  $hc/\lambda = E_g$ .  $E_g$  is the band gap energy (eV),  $h$  is Planck's constant,  $c$  is the light velocity (m/s), and  $\lambda$  is the wavelength (nm). The results show that the band gap energy of the  $\text{TiO}_2/\text{SA}$  nanocomposites is apparently lower than that of the neat  $\text{TiO}_2$  nanoparticles. Therefore, the  $\text{TiO}_2/\text{SA}$  nanocomposites can be

excited to produce much more electron–hole pairs under visible light illumination, resulting in higher photocatalytic activities. This also indicates that SA modification provides an effective approach to extend the absorption of  $\text{TiO}_2$  to the visible light range.

### 3.6. Studies of photocatalytic factors

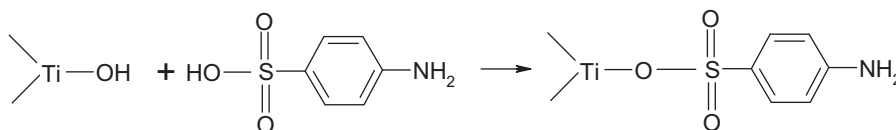
#### 3.6.1. Effect of irradiation time

Shown in Fig. 6 is the effect of irradiation time on CR degradation. Color of the sample changed to colorless with increasing irradiation time. The experiments showed that absorbance value corresponding to 502 nm increases as irradiation time was increased from 30 to 210 min, concluding that degradation was completed nearly within 210 min. It was observed that decolorization and photodegradation increased with increase in the irradiation time. In order to determine the kinetics of photodegradation, the relationship between  $\ln C_t/C_0$  and irradiation time was plotted (as inset in Fig. 6). It was found that the degradation reaction of CR under the catalysis of  $\text{TiO}_2/\text{SA}$  basically obeys to the first order reaction kinetics. For comparison, we also carried out degradation of the CR dye in solution over the neat  $\text{TiO}_2$  reference photocatalyst under the same condition, in which only about 12% degradation of CR was observed within 210 min. So the modified  $\text{TiO}_2$  nanoparticles show higher photocatalytic activity than that of the neat  $\text{TiO}_2$  under visible light irradiation.

#### 3.6.2. Effect of solution pH

The effect of initial solution pH on photocatalytic degradation is generally complex. The solution's initial pH value can directly affect the nature of the charge carried by the catalyst surface and the adsorption behavior of the pollutant in the catalyst surface. In addition, the initial solution pH also further affects the aggregation of the semiconductor catalyst and the band position of the catalyst in the solution.

In order to obtain the pH of the point of zero charge (pzc) for the  $\text{TiO}_2/\text{SA}$  catalyst in the solution, the surface charge density as a function of pH for the photocatalyst was studied, as shown in Fig. 7. The surface charge density  $\sigma_0$  ( $\text{C m}^{-2}$ ) was calculated from the



Scheme 1. Schematic of the SA grafted onto the  $\text{TiO}_2$  surface by monodentate binding mode.



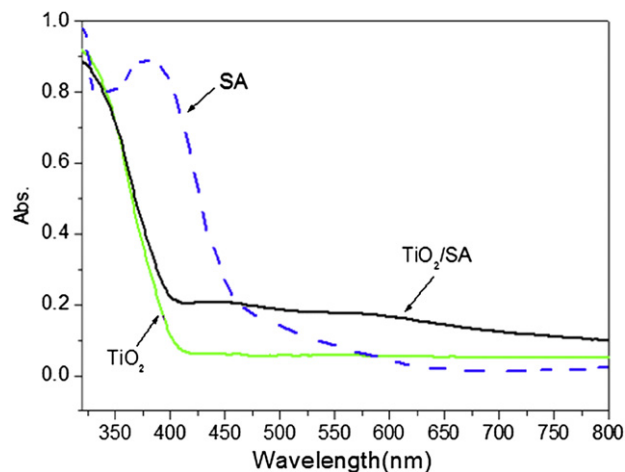


Fig. 5. UV-vis absorbance spectra of the SA, neat  $\text{TiO}_2$  and modified  $\text{TiO}_2/\text{SA}$  nanoparticles.

concentration of  $\text{H}^+$  and  $\text{OH}^-$  ions ( $\text{mol L}^{-1}$ ) adsorbed onto the surface, using the following equation:  $\sigma_0 = FAm ([\text{H}^+] - [\text{OH}^-])$ , where  $F$  is the Faraday constant,  $A$  the surface area ( $\text{m}^2 \text{g}^{-1}$ ) and  $m$  is the concentration of the  $\text{TiO}_2/\text{SA}$  catalyst ( $\text{g L}^{-1}$ ). The  $\text{pH}_{\text{pzc}}$  calculated from the results falls at a pH of about 6.3.

The photocatalytic degradation of CR was carried out at different pH values in the range of 2.0–10.0 (Fig. 7 inset) shows that the pH of the solution has a direct effect on the heterogeneous photocatalysis process. High degradation ratios were achieved in acidic and neutral pH regions. This result can be explained that CR molecule with two sulfonic groups ionizes easily in strong acidic media and becomes a soluble CR anion, which can be easily adsorbed to  $\text{TiO}_2/\text{SA}$  particles with positive surface charge. About 75% degradation of CR was observed at pH 6.3 after 100 min. On the contrary, when the solution is in the acidic (pH: 2–4) or alkaline media (pH: 8–10), the degradation rate of CR is lower than that in the optimum pH value. Therefore, the optimum pH for the removal of CR was about pH 6.3.

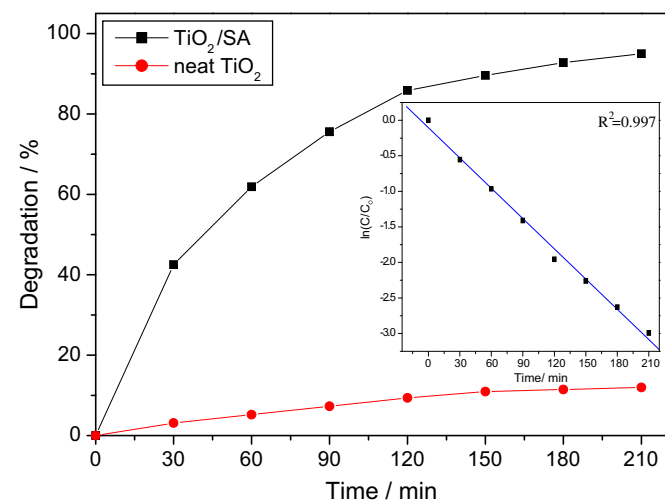


Fig. 6. Photocatalytic degradation curves of CR by  $\text{TiO}_2/\text{SA}$  and neat  $\text{TiO}_2$ . Inset presents the degradation kinetics of CR using  $\text{TiO}_2/\text{SA}$  by means of plotting  $\ln(C/C_0)$  vs. time. Volume = 100 ml; initial concentration of CR =  $40 \text{ mg L}^{-1}$ ; amount of  $\text{TiO}_2/\text{SA}$  =  $1.5 \text{ g L}^{-1}$ ; initial pH was used.

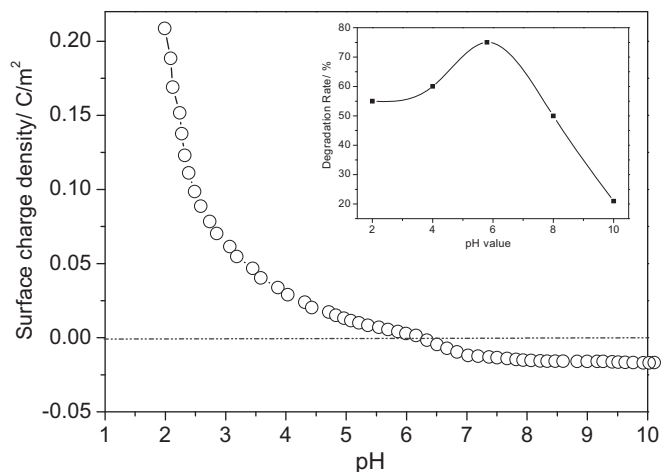


Fig. 7. The variation of surface charge density as function of pH for  $\text{TiO}_2/\text{SA}$  photocatalysts. Inset: Effect of pH value on degradation of CR after 100 min with the  $\text{TiO}_2/\text{SA}$  under visible light. Volume = 100 ml; initial concentration of CR =  $40 \text{ mg L}^{-1}$ ; amount of  $\text{TiO}_2/\text{SA}$  =  $1.5 \text{ g L}^{-1}$ .

### 3.6.3. Effect of catalyst dosage

Fig. 8 shows the effect of  $\text{TiO}_2/\text{SA}$  dosage on the degradation rate of CR at a fixed initial CR concentration ( $40 \text{ mg/L}$ , initial pH value was used) and the same irradiation time (150 min). With an increase in the dosage from 0.5 to  $1.0 \text{ g/L}$ , the degradation rate apparently increased. A further increase in the dosage resulted in a remarkable decrease in the degradation rate. The optimum weight of catalyst loading was about  $1.0 \text{ g/L}$  under the given experimental condition. The enhancement in degradation rate as a result of photocatalyst loading is due to the ready availability of total surface area and active sites of the photocatalyst. A reduction in degradation rate was obviously observed at photocatalyst overdose due to the opacity caused by excess photocatalyst clusters. The presence of these clusters then reduces visible light penetration and increases the scattering effect.

### 3.6.4. Effect of $\text{H}_2\text{O}_2$

Hydrogen peroxide, an electron scavenger accepts a photo-generated electron from the conduction band and thus prevents

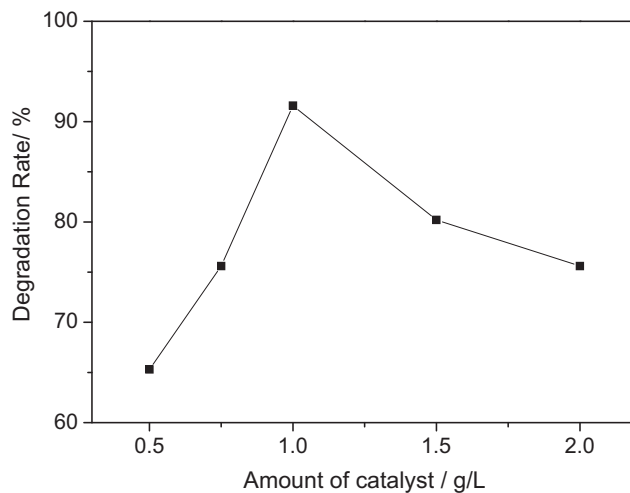
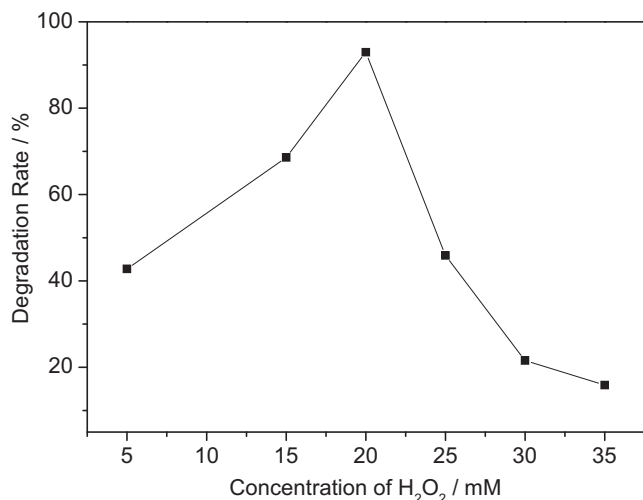


Fig. 8. Relation between amount of catalyst and degradation efficiency of CR; initial concentration of CR =  $40 \text{ mg L}^{-1}$ , Volume = 100 ml; initial pH value was used; irradiation time = 150 min.

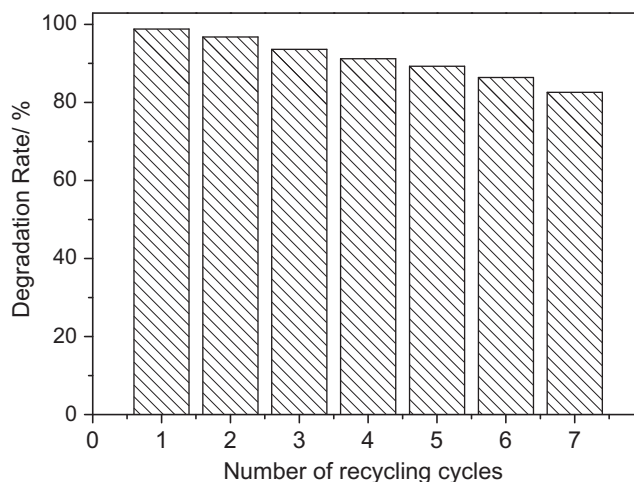


**Fig. 9.** Effect of dosage of H<sub>2</sub>O<sub>2</sub> on degradation of CR after 100 min with the TiO<sub>2</sub>/SA under visible light initial concentration of CR = 40 mg L<sup>-1</sup>; Volume = 100 ml; initial pH was used; amount of TiO<sub>2</sub>/SA = 1.5 g/L<sup>-1</sup>.

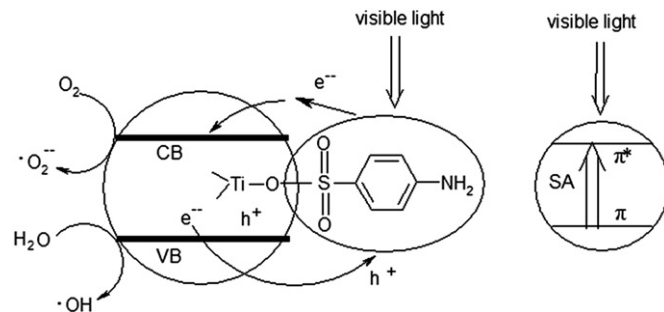
electron–hole recombination forming OH<sup>•</sup> radicals [34]. The effect of H<sub>2</sub>O<sub>2</sub> dosage, from 5 to 35 mM, on photodegradation of CR on the TiO<sub>2</sub>/SA under visible light was investigated. As shown in Fig. 9, there was an optimal dosage of H<sub>2</sub>O<sub>2</sub>, 20 mM, at which the degradation efficiency of CR on the TiO<sub>2</sub>/SA attained the height. Below the optimal dosage, the enhancement of degradation by addition of H<sub>2</sub>O<sub>2</sub> could be attributed to the increase of reactive hydroxyl radical concentration [35]. While when H<sub>2</sub>O<sub>2</sub> presented at higher dosage, the degradation efficiency of CR decreased. This was because the very reactive <sup>•</sup>OH radicals and valence band holes could be consumed by H<sub>2</sub>O<sub>2</sub> itself [36,37].

### 3.7. Study on the reuse of the photocatalyst

The reuse of the photocatalyst was also studied. The photocatalyst used once under the given condition was dried at 80 °C for 5 h. Then the recovered photocatalyst was reused in the next cycle. As shown in Fig. 10, there is no significant reduction in photoactivity observed when the photocatalyst is used six times for the



**Fig. 10.** Effect of number of recycling cycles on the degradation of CR. Initial concentration of CR = 40 mg L<sup>-1</sup>; Volume = 100 ml; initial pH was used; amount of TiO<sub>2</sub>/SA = 1.5 g/L<sup>-1</sup>; irradiation time = 210 min.



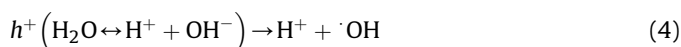
**Scheme 2.** Mechanism of SA-modified P25 TiO<sub>2</sub> nanoparticles to enhance photocatalytic activity under visible light irradiation.

degradation ignoring the factor of the reduction in quality, indicating that the photocatalytic activity has a good reproducibility and the considerable stability of the photocatalyst under the present conditions.

### 3.8. Possible visible light-induced photocatalytic mechanism

SA has a maximum absorption at 382 nm and shows strong absorption in the visible light region, whereas TiO<sub>2</sub> itself has an upper absorption edge at about 400 nm, as seen from Fig. 5. The absorption of TiO<sub>2</sub>/SA greatly extended to the visible region may be attributed to the synergistic effect between the inorganic and organic composites [38].

The relative energy level of SA ( $\pi$ -orbital and  $\pi^*$ -orbital), TiO<sub>2</sub> (conduction band (CB), and valence band (VB)) is shown in Scheme 2. According to the results of the photocatalytic degradation on CR, the mechanism of photocatalytic degradation under visible light irradiation may be interpreted as follows. As a semiconductive material, SA absorbs visible light to induce electron  $\pi \rightarrow \pi^*$  transition. Afterward, the excited-state electrons are transported from the  $\pi$ -orbital to the  $\pi^*$ -orbital. The d-orbital (CB) of TiO<sub>2</sub> and the  $\pi^*$ -orbital of SA match well in terms of energy level for the charge transfer [22,24]. With this, the excited-state electrons can be readily injected into the d-orbital (CB) of TiO<sub>2</sub> and transferred to the nanocomposite surface to react with oxygen, thus yielding superoxide radicals <sup>•</sup>O<sub>2</sub><sup>-</sup> subsequently. At the same time, a positive charged hole ( $h^+$ ) might be formed by electron migration from the TiO<sub>2</sub> valence band to the SA  $\pi$ -orbital, which can react with H<sub>2</sub>O in the solution to generate <sup>•</sup>OH. The superoxide radical ion <sup>•</sup>O<sub>2</sub><sup>-</sup> and hydroxyl radical <sup>•</sup>OH are responsible for the degradation of organic compounds. The whole process is shown and described in Scheme 2. Therefore, the whole visible light-induced photocatalytic process of TiO<sub>2</sub>/SA can be summarized briefly as follows:



## 4. Conclusion

SA-modified P25 TiO<sub>2</sub> visible light photocatalysts have been successfully prepared through hydrothermal treatment. The as-prepared nanoparticles show higher photocatalytic activity than the neat TiO<sub>2</sub> nanoparticles. The active range of the prepared

catalyst is extended from the UV to the visible region, with the formation of Ti–O–S bonds. The photocatalytic activity of TiO<sub>2</sub>/SA was examined by degrading CR under visible light, in which its effecting factors (irradiation time, catalyst dosage, solution pH and the addition of H<sub>2</sub>O<sub>2</sub>) were investigated in detail.

It can be concluded that from the experimental results: (1) The degradation reaction of CR basically obeys to the first order reaction kinetics; (2) The optimum pH for the removal of CR was about 6.3; (3) The optimum weight of catalyst loading was about 1.0 g/L; (4) The optimal dosage of H<sub>2</sub>O<sub>2</sub> was 20 mM; (5) The photocatalyst show a good reproducibility and the considerable stability.

Furthermore, the possible visible light-induced photocatalytic mechanism has been proposed. Overall, this study provides an alternative functionalization approach for the effective improvement of the photocatalytic activity of P25 TiO<sub>2</sub> under visible light.

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