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# Effects of Ag<sup>0</sup>-modification and Fe<sup>3+</sup>-doping on the structural, optical and photocatalytic properties of TiO<sub>2</sub>

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Pure TiO<sub>2</sub>, Ag<sup>0</sup>-modified TiO<sub>2</sub>, Fe<sup>3+</sup>-doped TiO<sub>2</sub>, and Ag<sup>0</sup>-modified/Fe<sup>3+</sup>-doped TiO<sub>2</sub> photocatalysts were synthesized *via* sol-gel technology. The crystal structure, element composition and surface morphology of the obtained photocatalysts were characterized *via* XRD, XPS, SEM and TEM, respectively. The results indicate that Ag-TiO<sub>2</sub> samples show higher photocatalytic activity than pure TiO<sub>2</sub>. Unexpectedly, the photocatalytic activities of Fe-TiO<sub>2</sub> and 1% Ag/1% Fe-TiO<sub>2</sub> are lower than pure TiO<sub>2</sub>. To analyze the main factors affecting photocatalytic performance, the samples were further investigated by PL, DRS and BET. The results prove that the additions of Ag and Fe are advantageous for inhibiting the recombination of photoinduced pairs and improving the utilization of light. Fe-TiO<sub>2</sub> and 1% Ag/1% Fe-TiO<sub>2</sub> exhibit smaller specific surface areas than pure TiO<sub>2</sub>, which is the primary reason for their reduced photocatalytic performances.

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## Introduction

In the last few years, titanium dioxide (TiO<sub>2</sub>) has been widely used in the degradation of organic pollutants due to its strong photocatalytic ability, low cost, non-toxicity and chemical stability.<sup>1-4</sup> However, two main drawbacks limit its practical application. Firstly, with a wide energy gap of 3.2 eV, TiO<sub>2</sub> only absorbs ultraviolet light with a wavelength of less than 387 nm, therefore, the utilization rate of sunlight is limited.<sup>5-9</sup> Secondly, the high recombination rate of photogenerated electrons and holes results in low quantum yield.<sup>10-12</sup>

Precious metal deposition is able to improve the utilization of sunlight and promote the separation of photogenerated pairs, which are in favor of photocatalytic activity.<sup>13-16</sup> Zhou *et al.*<sup>17</sup> prepared Au-deposited TiO<sub>2</sub> films on indium-tin oxide glass by magnetron sputtering. Compared with pure TiO<sub>2</sub> film, Au/TiO<sub>2</sub> films show better photocatalytic activity because of their higher separation rate of photogenerated pairs and narrower band gaps. In the research of noble metal modifying, Ag-modified TiO<sub>2</sub> has attracted much attention owing to its cheapness and effectiveness.<sup>18</sup> Wang *et al.*<sup>19</sup> prepared Ag/TiO<sub>2</sub> nanotubes by electrospinning method and the photocatalytic performance is improved after Ag modification.

Besides, TiO<sub>2</sub> modification by metal ion doping has also been extensively studied.<sup>20-24</sup> Wu *et al.*<sup>25</sup> synthesized Cu-doped

TiO<sub>2</sub> by hydrothermal synthesis and air heat treatment. 0.5 mol%-Cu/TiO<sub>2</sub> shows better photocatalytic activity than pure TiO<sub>2</sub> because it enlarges the visible light absorbance due to the presence of Cu 3d orbitals. However, the photocatalytic performance declines when the concentration of Cu is more than 1 mol%. They believe that the high content of Cu forms new recombination centers, reducing the separation of photoinduced pairs. Moradi *et al.*<sup>26</sup> reported that Fe-doped TiO<sub>2</sub> shows higher visible light photocatalytic activity than pure TiO<sub>2</sub> owing to its red-shift and lower recombination rate. However, there are also studies have shown that the photocatalytic activity of TiO<sub>2</sub> is reduced after metal ion doping.<sup>23,27</sup> For instance, Kundu *et al.*<sup>27</sup> synthesized Fe-doped and pure TiO<sub>2</sub> nanoparticles and it is found that pure TiO<sub>2</sub> shows the highest degradation rate of MB under sunlight. Cu-doped TiO<sub>2</sub> films were prepared by sol-gel dip-coating method, and their photo-degradation rates are lower than that of pure TiO<sub>2</sub> film, which has been reported by Bensouici *et al.*<sup>23</sup>

Compared with single element modification, multi-elements may produce a synergistic effect and further improve the photocatalytic activity of TiO<sub>2</sub>.<sup>1,4,7,22,28</sup> Zhang *et al.*<sup>28</sup> synthesized Ln<sup>3+</sup>/Ag<sup>0</sup>-TiO<sub>2</sub>, Ln<sup>3+</sup>-TiO<sub>2</sub>, Ag<sup>0</sup>-TiO<sub>2</sub> and pure TiO<sub>2</sub>, and photocatalytic tests show that Ln<sup>3+</sup>/Ag<sup>0</sup>-TiO<sub>2</sub> exhibits the best photocatalytic activity. Ln<sup>3+</sup>/Ag<sup>0</sup>-TiO<sub>2</sub> presents the lowest PL intensity because the synergistic effect of Ln<sup>3+</sup> doping and Ag<sup>0</sup> deposition provides more trap centers, which promotes the transfer of photoinduced electrons, suppressing the charge recombination effectively. Meanwhile, some studies have shown that single element displays better modification effect than multi-elements.<sup>24,29</sup> Khan *et al.*'s research<sup>29</sup> indicates that

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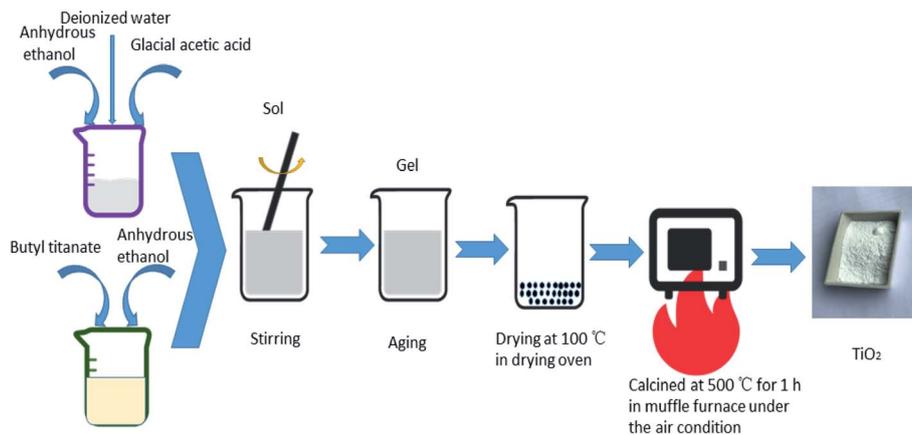


Fig. 1 The preparation process of TiO<sub>2</sub>.

Ga-doped TiO<sub>2</sub> exhibits better photocatalytic performance than N/Ga co-doped TiO<sub>2</sub>. Malengreaux *et al.*<sup>24</sup> reported that Eu/Fe co-doped TiO<sub>2</sub> shows lower photocatalytic efficiency than Fe-doped TiO<sub>2</sub> and pure TiO<sub>2</sub>.

Therefore, to explore the effects of single element modification and two elements co-modification on the photocatalytic performance of TiO<sub>2</sub>, the pure, Ag-modified, Fe-doped and Ag/Fe-modified TiO<sub>2</sub> were prepared and their photocatalytic activities were investigated. The effects of Ag and Fe addition on the

structure, morphology, optical and photocatalytic properties of TiO<sub>2</sub> were analyzed systematically.

## Experimental

### Preparation of materials

All the TiO<sub>2</sub> photocatalysts were prepared by sol-gel method. The specific process of preparation pure TiO<sub>2</sub> was as follows: solution A was prepared by adding butyl titanate in a volume

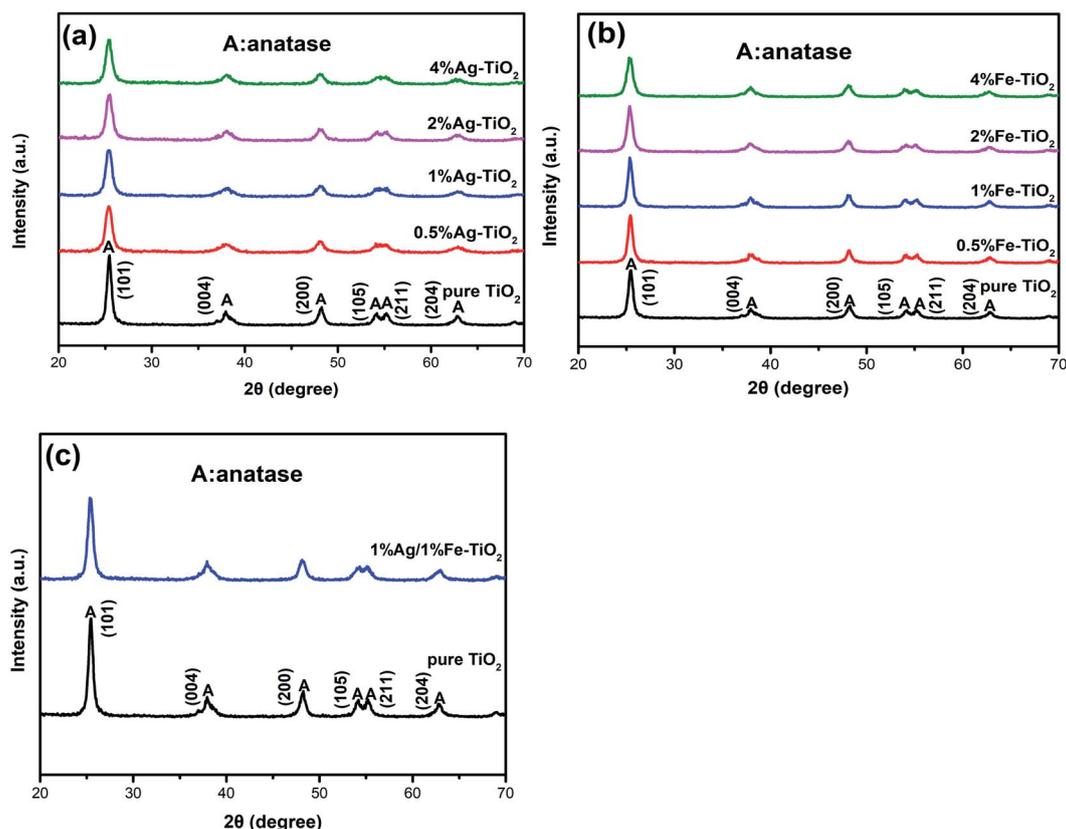


Fig. 2 XRD patterns of (a) Ag-TiO<sub>2</sub>, (b) Fe-TiO<sub>2</sub> and (c) 1% Ag/1% Fe-TiO<sub>2</sub>.



Table 1 The crystallite sizes of samples

Samples	Crystallite size (nm)	Samples	Crystallite size (nm)
Pure TiO <sub>2</sub>	16.0	0.5% Fe-TiO <sub>2</sub>	15.1
0.5% Ag-TiO <sub>2</sub>	11.2	1% Fe-TiO <sub>2</sub>	15.9
1% Ag-TiO <sub>2</sub>	11.6	2% Fe-TiO <sub>2</sub>	13.7
2% Ag-TiO <sub>2</sub>	11.9	4% Fe-TiO <sub>2</sub>	12.3
4% Ag-TiO <sub>2</sub>	12.0	1% Ag/1% Fe-TiO <sub>2</sub>	13.3

ratio of 1 : 2 to anhydrous ethanol in a beaker. Solution B was prepared by adding anhydrous ethanol, glacial acetic acid and deionized water in a volume ratio of 4 : 5 : 5. Solution B was added to solution A dropwise. The resulting mixture was stirred until a sol formed. A gel formed after aging. The obtained gel was dried at 100 °C and then heat treated at 500 °C for 1 h to obtain pure TiO<sub>2</sub>. For the preparation of Ag-modified TiO<sub>2</sub> and Fe-doped TiO<sub>2</sub>, certain amounts of AgNO<sub>3</sub> or Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were added into solution B. The atomic percentages of Ag/Ti or Fe/Ti were 0.5%, 1%, 2% and 4%, respectively. Keep other steps

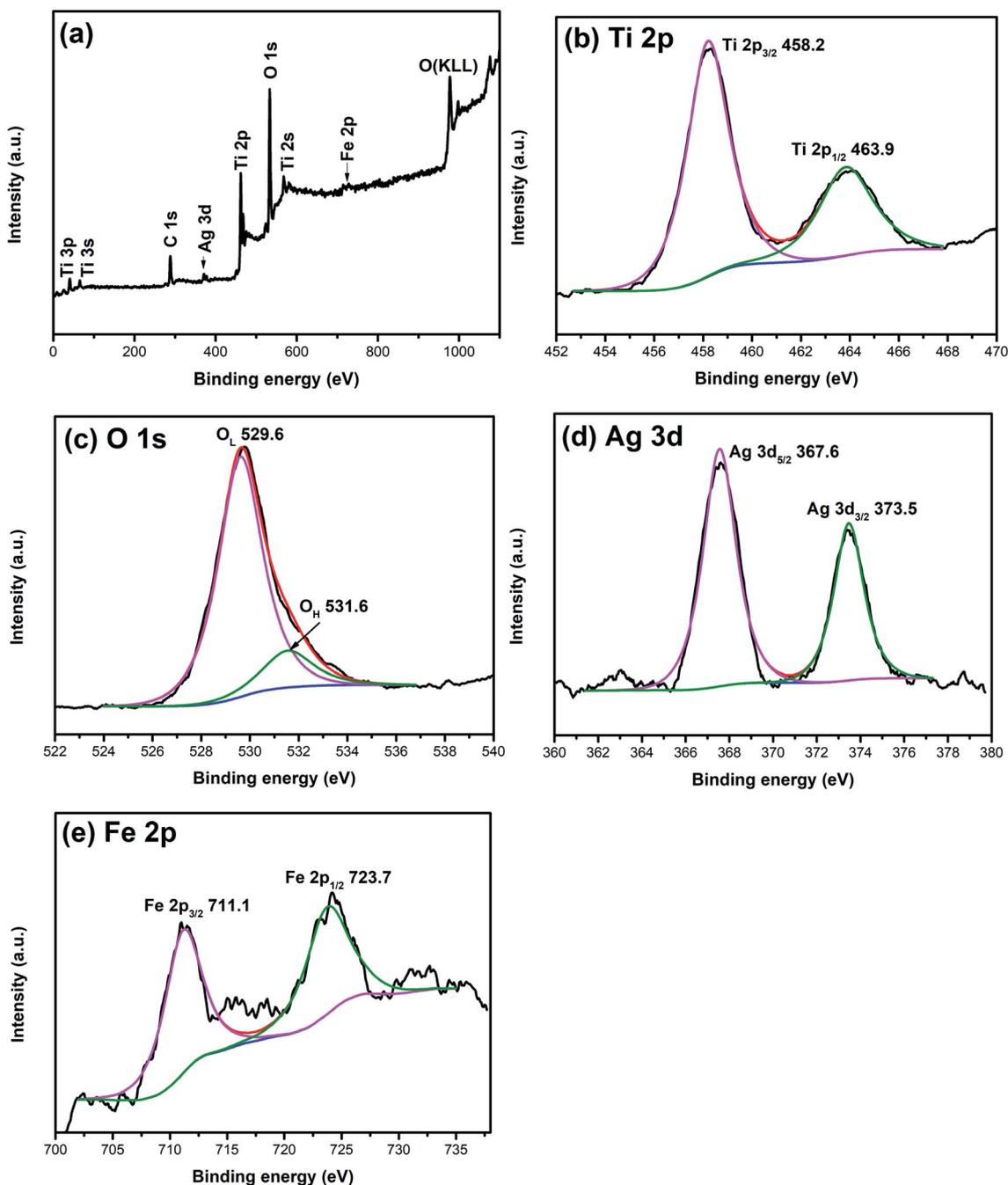


Fig. 3 XPS spectra of 1% Ag/1% Fe-TiO<sub>2</sub>: (a) total spectrum, (b) Ti 2p, (c) O 1s, (d) Ag 3d and (e) Fe 2p.



unchanged to obtain different concentrations of Ag modified TiO<sub>2</sub> and Fe doped TiO<sub>2</sub> which are recorded as 0.5% Ag–TiO<sub>2</sub>, 1% Ag–TiO<sub>2</sub>, 2% Ag–TiO<sub>2</sub>, 4% Ag–TiO<sub>2</sub>, 0.5% Fe–TiO<sub>2</sub>, 1% Fe–TiO<sub>2</sub>, 2% Fe–TiO<sub>2</sub> and 4% Fe–TiO<sub>2</sub>. AgNO<sub>3</sub> and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were simultaneously added into solution B to prepare Ag/Fe co-modified TiO<sub>2</sub>. Both the molar ratios of Ag/Ti and Fe/Ti are 1%, and the Ag/Fe co-modified TiO<sub>2</sub> is labeled as 1% Ag/1% Fe–TiO<sub>2</sub>. The preparation process is shown in Fig. 1.

### Characterization

The phase structure of photocatalysts was determined using an X-ray diffractometer (XRD). Element composition and valence state were analyzed by an X-ray photoelectron spectroscopy (XPS). Surface morphologies were observed by a field emission scanning electron microscopy (FESEM) and a transmission electron microscopy (TEM). Photoluminescence (PL) spectra were recorded through a luminescence spectrometer. UV-vis diffuse reflectance spectra (DRS) were recorded using a spectrophotometer. Specific surface areas were determined by the Brunauer Emmett Teller (BET) method.

### Photocatalytic test

Add 100 mL rhodamine B (RhB) solution (10 mg L<sup>-1</sup>) and 0.1 g of TiO<sub>2</sub> photocatalyst to the beaker. The mixture was ultrasonically dispersed for 10 minutes, and then stirred to establish the adsorption–desorption equilibrium in dark for 30 min. A 250 W

xenon lamp was employed as a light source and a small amount of suspension was taken every 30 minutes. After centrifugation, the supernatant was extracted and the absorbance of RhB was measured with a spectrophotometer at the wavelength of 553 nm. The decolorization rate  $D$  (%) was calculated as follows:

$$D = (1 - A_t/A_0) \times 100$$

In the formula,  $A_0$  is the initial absorbance, and  $A_t$  is the absorbance at time  $t$ .

## Results and discussion

### XRD analysis

Fig. 2 shows the XRD patterns of pure TiO<sub>2</sub>, Ag–TiO<sub>2</sub>, Fe–TiO<sub>2</sub> and 1% Ag/1% Fe–TiO<sub>2</sub>. In Fig. 2(a), the peaks of pure TiO<sub>2</sub> at 25.3°, 37.9°, 48.1°, 53.9°, 55.1° and 62.8° correspond to (101), (004), (200), (105), (211) and (204) crystal planes of anatase structure, respectively. It is observed that Ag–TiO<sub>2</sub>, Fe–TiO<sub>2</sub> and 1% Ag/1% Fe–TiO<sub>2</sub> also form anatase structure, suggesting that the crystal structure of TiO<sub>2</sub> is not significantly affected by Ag or Fe adding. However, the widths of diffraction peaks in Ag–TiO<sub>2</sub>, Fe–TiO<sub>2</sub> and 1% Ag/1% Fe–TiO<sub>2</sub> are wider and the intensities are lower than pure TiO<sub>2</sub>, indicating that the crystallinity of TiO<sub>2</sub> is reduced and the crystal grain is refined.<sup>26,30</sup> The grain sizes of TiO<sub>2</sub> are calculated by Scherrer formula<sup>21</sup> and the results are

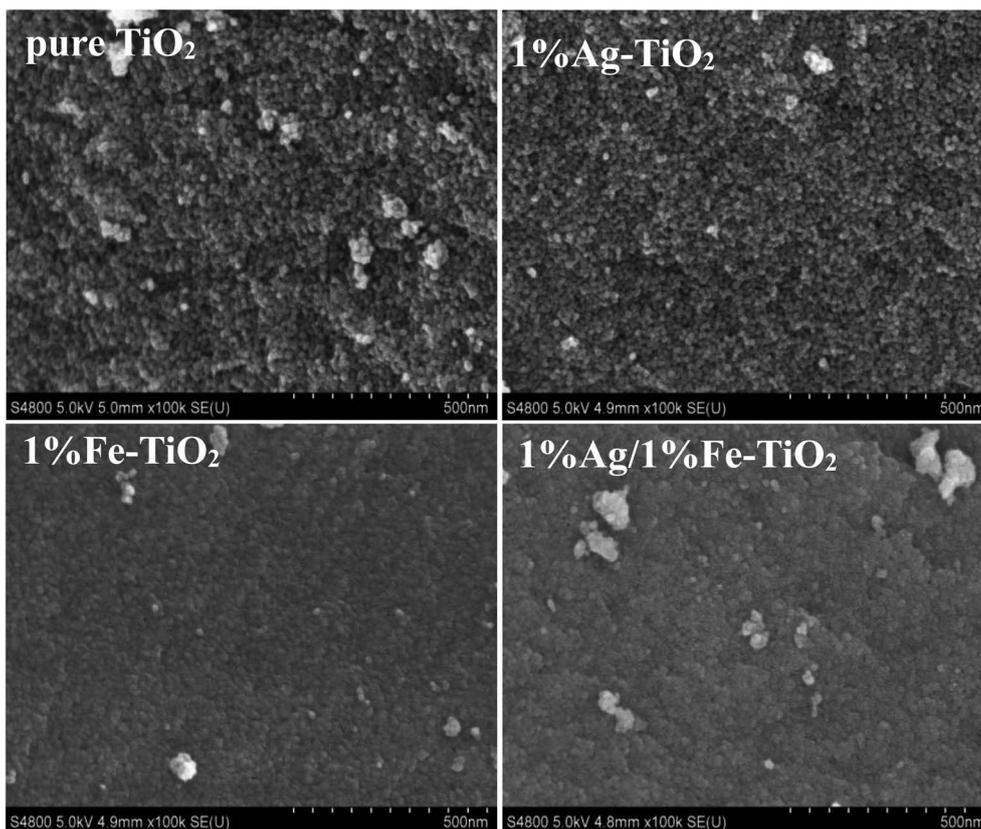


Fig. 4 SEM images of pure TiO<sub>2</sub>, 1% Ag–TiO<sub>2</sub>, 1% Fe–TiO<sub>2</sub> and 1% Ag/1% Fe–TiO<sub>2</sub>.



shown in Table 1. Yu *et al.*<sup>31</sup> believe that the addition of dopants hinders the contact between TiO<sub>2</sub> particles and inhibits the growth of grains during the heat treatment process, resulting in the decrease of grain size. The absence of diffraction peaks associated with Fe may be attributed to the fact that Fe<sup>3+</sup> ions can replace Ti<sup>4+</sup> ions into TiO<sub>2</sub> lattices due to their close ionic radius.<sup>26,32,33</sup> On the other hand, since the radius of Ag atom is much larger than that of Ti<sup>4+</sup>, it is difficult to enter TiO<sub>2</sub> lattices. Ag particles probably disperse on TiO<sub>2</sub> surface in the form of metallic Ag.<sup>34,35</sup>

### XPS analysis

XPS is widely used to investigate the chemical valence of elements. To verify the valence states of Ag and Fe elements, XPS analysis of 1% Ag/1% Fe-TiO<sub>2</sub> has been carried out and the results are shown in Fig. 3. The C, Ti, O, Ag and Fe signal peaks appear in the full spectrum (Fig. 3(a)), meaning that there are C, Ti, O, Ag and Fe elements in the sample. The appearance of C 1s peak may be derived from C remaining in the organic calcination process. In Fig. 3(b), two peaks at 458.2 eV and 463.9 eV corresponding to Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub> and the splitting energy between Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub> (5.7 eV) indicate that the state of Ti ions is Ti<sup>4+</sup>.<sup>36–38</sup> Fig. 3(c) presents two peaks at 529.6 eV and 531.6 eV, ascribing to Ti–O bonds in TiO<sub>2</sub> lattices (O<sub>T</sub>) and

surface hydroxyl groups (O<sub>H</sub>), respectively.<sup>39,40</sup> In Fig. 3(d), the peaks at 367.6 eV and 373.5 eV can be assigned to Ag 3d<sub>5/2</sub> and Ag 3d<sub>3/2</sub>, respectively, which suggests that the Ag element exists as Ag<sup>0</sup> in the sample.<sup>34,41,42</sup> Two peaks at 711.1 eV and 723.7 eV in Fig. 3(e) attribute to Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub>, which indicates Fe element exists as Fe<sup>3+</sup>.<sup>27,32,43,44</sup>

### SEM and TEM images

Fig. 4 presents the SEM images of pure TiO<sub>2</sub>, 1% Ag-TiO<sub>2</sub>, 1% Fe-TiO<sub>2</sub>, and 1% Ag/1% Fe-TiO<sub>2</sub>. It is observed that the particles are nearly spherical. Among them, pure TiO<sub>2</sub> and 1% Ag-TiO<sub>2</sub> particles are fine and disperse relatively uniform, however, the particles in 1% Fe-TiO<sub>2</sub> and 1% Ag/1% Fe-TiO<sub>2</sub> present obvious agglomeration.

Fig. 5(a) and (b) are TEM images of pure TiO<sub>2</sub> and 1% Ag/1% Fe-TiO<sub>2</sub>, from which we can see that the particle size in pure TiO<sub>2</sub> is about 15–20 nm, while it is arranged from 10 to 15 nm in 1% Ag/1% Fe-TiO<sub>2</sub>. Moreover, pure TiO<sub>2</sub> shows better particle dispersion than 1% Ag/1% Fe-TiO<sub>2</sub>, which is consistent with SEM images. The HRTEM images of pure TiO<sub>2</sub> and 1% Ag/1% Fe-TiO<sub>2</sub> are presented in Fig. 5(c) and (d), respectively. Both the labeled interplanar spacing values in pure TiO<sub>2</sub> (0.352 nm) and 1% Ag/1% Fe-TiO<sub>2</sub> (0.364 nm) correspond to the anatase (101) crystal plane.<sup>45</sup> Since the radius of Fe<sup>3+</sup> ions is larger than of Ti<sup>4+</sup>

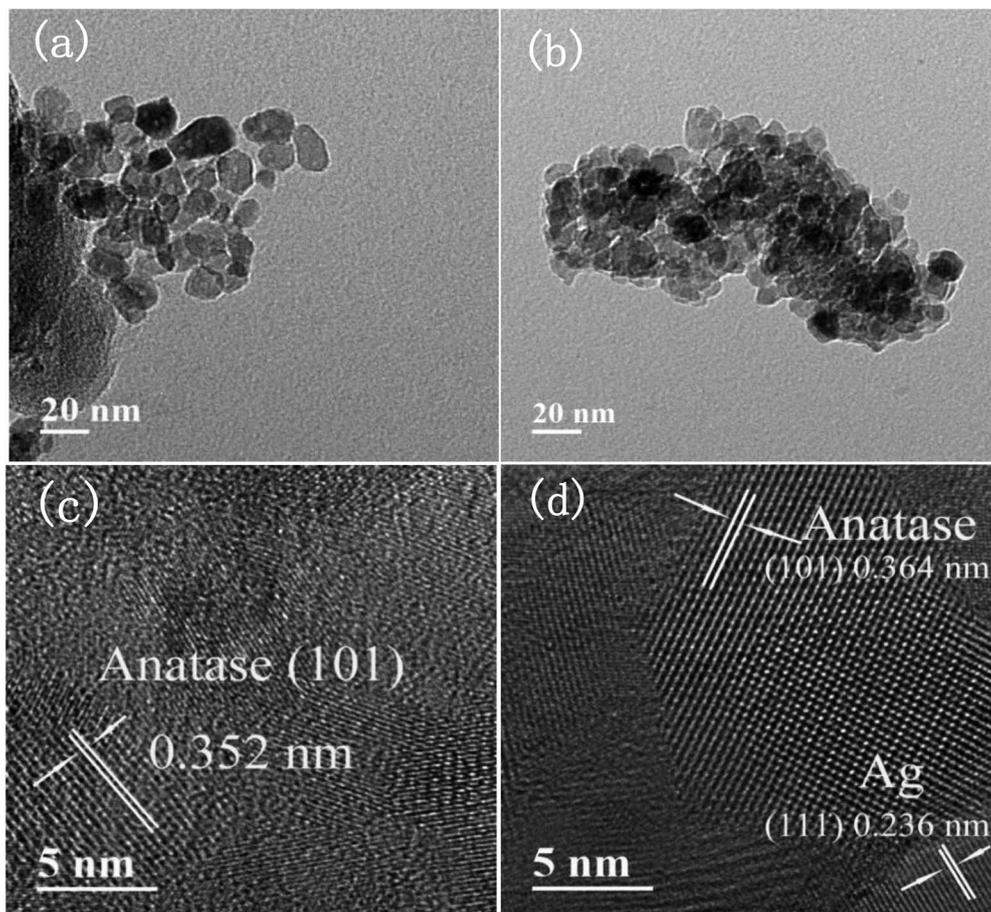


Fig. 5 TEM images of (a) pure TiO<sub>2</sub>, (b) 1% Ag/1% Fe-TiO<sub>2</sub>, HRTEM images of (c) pure TiO<sub>2</sub>, and (d) 1% Ag/1% Fe-TiO<sub>2</sub>.



ions, the substitution of  $\text{Fe}^{3+}$  for  $\text{Ti}^{4+}$  into crystal lattices causes lattice expansion, consequently, the anatase (101) plane spacing of 1% Ag/1% Fe-TiO<sub>2</sub> is slightly larger than that of pure TiO<sub>2</sub>.<sup>25</sup> In Fig. 5(d), the marked interplanar spacing (0.236 nm) can be attributed to the (111) crystal plane of metallic Ag<sup>0</sup>,<sup>34,39</sup> which is in accord with XPS results.

### Photocatalytic performance

**Photodegradation results.** The photocatalytic activity of photocatalysts was evaluated *via* the decolorization rate of RhB and the results are presented in Fig. 6. The RhB decolorization rate of pure TiO<sub>2</sub> is 85.7% after 90 min of reaction. Ag-TiO<sub>2</sub> samples show higher photocatalytic activity than pure TiO<sub>2</sub>. The decolorization rates of 0.5% Ag-TiO<sub>2</sub>, 1% Ag-TiO<sub>2</sub>, 2% Ag-TiO<sub>2</sub> and 4% Ag-TiO<sub>2</sub> are 88.8%, 95.4%, 92.8% and 92.5%, respectively. 1% Ag-TiO<sub>2</sub> exhibits the best photocatalytic activity and the decolorization rate of RhB decreases when Ag content exceeds 1%. Unexpectedly, the photocatalytic activity of TiO<sub>2</sub> decreases after Fe doping. The decolorization rates of 0.5% Fe-TiO<sub>2</sub>, 1% Fe-TiO<sub>2</sub>, 2% Fe-TiO<sub>2</sub> and 4% Fe-TiO<sub>2</sub> are 33.3%, 51.3%, 39.9% and 30.6%, respectively. It is clear that the addition of Ag improves the photocatalytic performance, while Fe is the opposite. The decolorization rate of 1% Ag/1% Fe-TiO<sub>2</sub> is 64.3%, suggesting that its photocatalytic activity is higher than Fe-TiO<sub>2</sub> but lower than pure TiO<sub>2</sub>. The decolorization of RhB by

TiO<sub>2</sub> can be considered as a first-order reaction,<sup>17,19,46</sup> and the calculation formula of the reaction rate constant  $k$  is as follows:

$$\ln(C_t/C_0) = -kt$$

where  $t$  is the reaction time,  $C_0$  and  $C_t$  are the initial concentration and the concentration at time  $t$ . The first-order reaction kinetics fit curves are shown in Fig. 7. It is calculated that the reaction rate constant of pure TiO<sub>2</sub> is 0.020 min<sup>-1</sup>. Ag-TiO<sub>2</sub> samples show higher reaction rates than pure TiO<sub>2</sub>, and the reaction rate constants of 0.5% Ag-TiO<sub>2</sub>, 1% Ag-TiO<sub>2</sub>, 2% Ag-TiO<sub>2</sub> and 4% Ag-TiO<sub>2</sub> are 0.024 min<sup>-1</sup>, 0.034 min<sup>-1</sup>, 0.030 min<sup>-1</sup> and 0.029 min<sup>-1</sup>, respectively. The reaction rate constants of 0.5% Fe-TiO<sub>2</sub>, 1% Fe-TiO<sub>2</sub>, 2% Fe-TiO<sub>2</sub> and 4% Fe-TiO<sub>2</sub> are 0.0036 min<sup>-1</sup>, 0.0075 min<sup>-1</sup>, 0.0041 min<sup>-1</sup> and 0.0034 min<sup>-1</sup>, respectively, implying that the reaction rates of Fe-TiO<sub>2</sub> are much lower than pure TiO<sub>2</sub>. The reaction rate constant of 1% Ag/1% Fe-TiO<sub>2</sub> is 0.0099 min<sup>-1</sup>, which is higher than Fe-TiO<sub>2</sub> but lower than pure TiO<sub>2</sub>.

### PL spectra

In order to analyze the influence of addition with Ag and Fe on the photogenerated electron-hole recombination of TiO<sub>2</sub>, the PL tests have been implemented and the results are shown in Fig. 8. The PL peaks originate from the recombination of photoinduced electrons and holes. Therefore, a lower PL peak

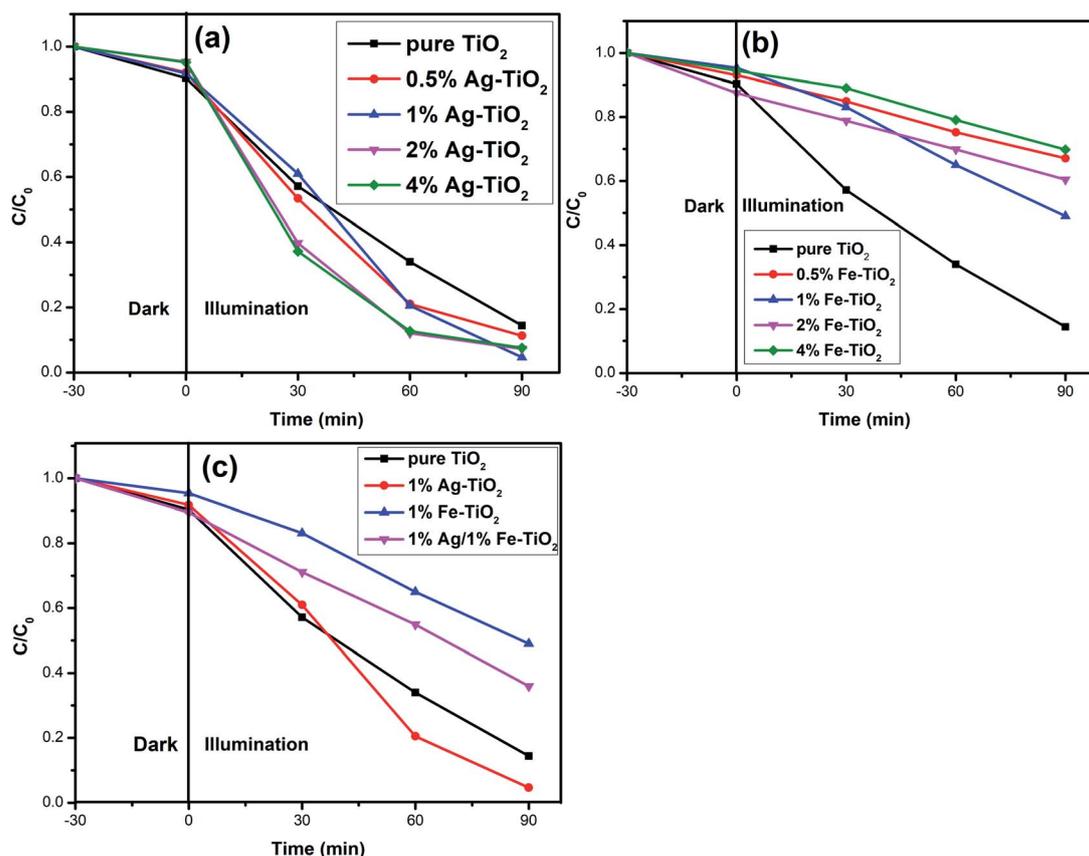


Fig. 6 Decolorization rate curves of RhB for (a) Ag-TiO<sub>2</sub>, (b) Fe-TiO<sub>2</sub>, and (c) 1% Ag/1% Fe-TiO<sub>2</sub>.



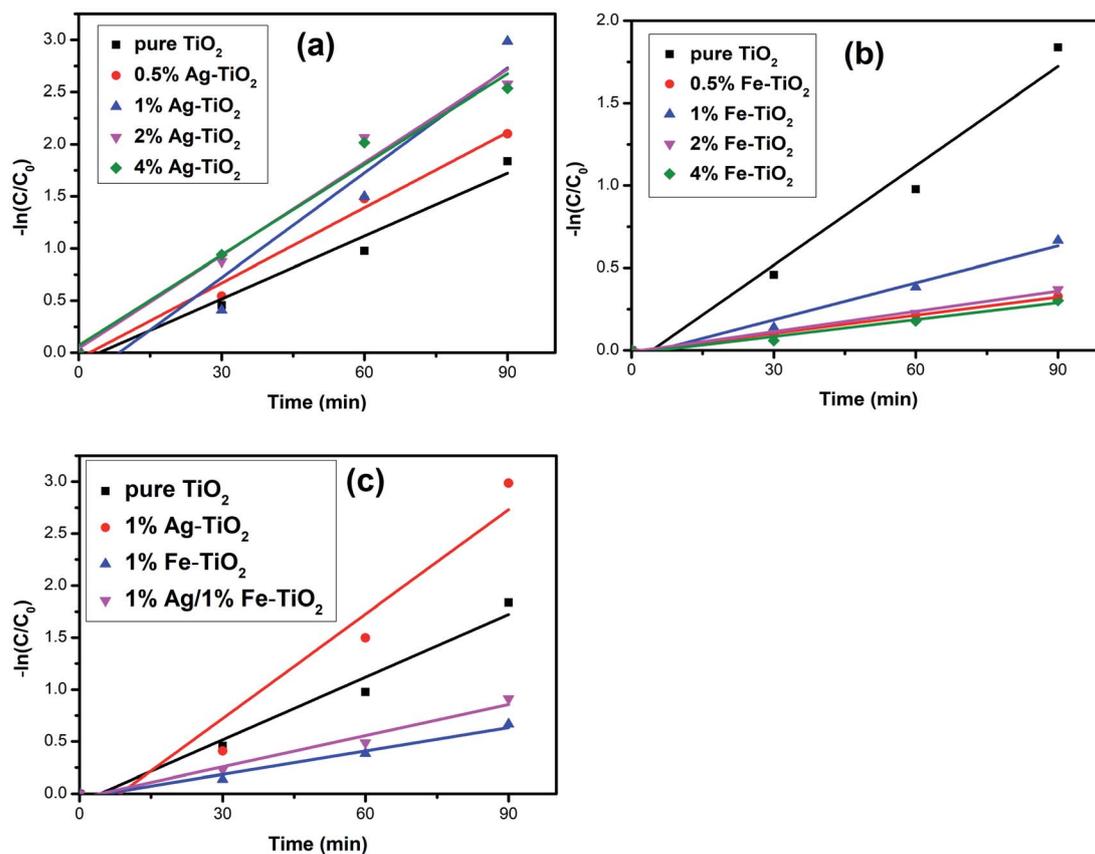


Fig. 7 Kinetics linear simulation curves of (a) Ag-TiO<sub>2</sub>, (b) Fe-TiO<sub>2</sub>, and (c) 1% Ag/1% Fe-TiO<sub>2</sub>.

intensity represents a lower recombination rate.<sup>27,38</sup> The PL peak intensity of Ag-TiO<sub>2</sub> is lower than that of pure TiO<sub>2</sub>, which suggests that the recombination of photoinduced pairs is inhibited by Ag modification. When exposed to light source, electrons in the valence band are excited to the conduction band, forming photogenerated electrons, leaving photo-generated holes on valence band. Photoinduced electrons can be transferred to Ag<sup>0</sup> particles which are deposited on TiO<sub>2</sub> surface, reducing the recombination.<sup>6,18,19,34</sup> Several researches have reported that there is an optimum concentration of Ag, above which new recombination centers will be formed thus increases recombination rate.<sup>18,34</sup> However, PL peak intensity decreases with the increasing Ag concentration in the present work, indicating that new recombination centers have not been formed when the Ag concentration reaches 4%. The PL peak intensity decreases with the increase of the amount of noble metal element, which also has been reported in previous work.<sup>47</sup> Photocatalytic experiments show that high Ag concentration is not conducive to photocatalytic activity and 1% Ag-TiO<sub>2</sub> exhibits the highest decolorization rate. The decrease in photocatalytic performance of 2% Ag-TiO<sub>2</sub> and 4% Ag-TiO<sub>2</sub> should be attributed to the fact that Ag<sup>0</sup> particles are deposited on the surface of TiO<sub>2</sub> particles, and as the Ag concentration increases, excessive Ag particles will cover TiO<sub>2</sub> surface, reducing the utilization of light and reactive sites.<sup>13,34</sup>

The photocatalytic activities of Fe-TiO<sub>2</sub> and 1% Ag/1% Fe-TiO<sub>2</sub> are lower than pure TiO<sub>2</sub>. Similar results have also been reported that the addition of metal ions reduces the photocatalytic performance of TiO<sub>2</sub>.<sup>23</sup> There is a viewpoint that doping metal ions leads to a decrease in crystallinity and an increase in lattice defects. The formed lattice defects act as recombination centers, promoting the recombination of photoinduced pairs and suppressing the photocatalytic activity.<sup>23,48,49</sup> In contrast, from Fig. 8(b), it is clear that the PL intensities of 1% Fe-TiO<sub>2</sub> and 1% Ag/1% Fe-TiO<sub>2</sub> are lower than that of pure TiO<sub>2</sub>, proving that the addition of Fe is beneficial to decreasing the recombination. Fe<sup>3+</sup> ions entering the crystal lattices to replace Ti<sup>4+</sup> ions will cause lattice distortion and defects, capturing photo-generated electrons and reducing the recombination of photo-generated charges.<sup>7,33</sup> Moreover, 1% Ag/1% Fe-TiO<sub>2</sub> shows the lowest PL intensity, suggesting that there is a synergistic effect in suppressing photoinduced pairs recombination owing to adding Ag and Fe simultaneously. Therefore, we can conclude that the decrease in photocatalytic performance of Fe-TiO<sub>2</sub> and 1% Ag/1% Fe-TiO<sub>2</sub> should not be attributed to the promotion of recombination with Fe adding.

#### DRS analysis

The energy gap ( $E_g$ ) of photocatalyst affects the absorption of light source, which is an important factor for photocatalytic performance. The influence of doping on the  $E_g$  of TiO<sub>2</sub> is



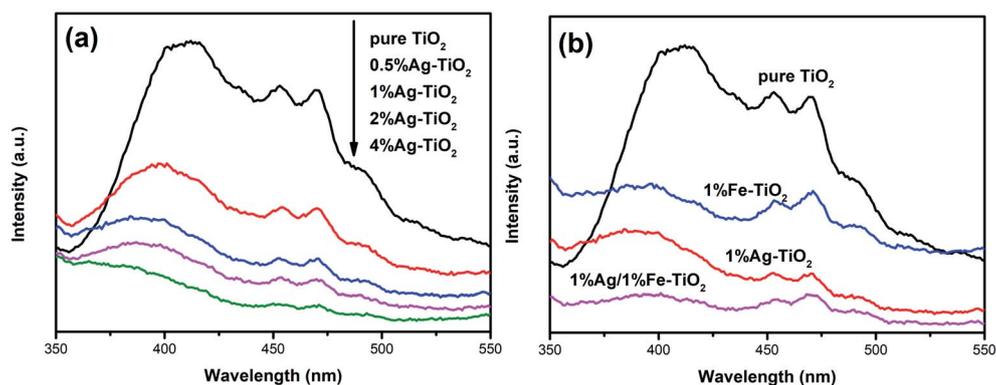


Fig. 8 PL spectra of (a) Ag-TiO<sub>2</sub>, (b) pure TiO<sub>2</sub>, 1% Ag-TiO<sub>2</sub>, 1% Fe-TiO<sub>2</sub> and 1% Ag/1% Fe-TiO<sub>2</sub>.

controversial, and both redshift<sup>6,7,9,26,27,34</sup> and blueshift<sup>24</sup> have been reported. Fig. 9 depicts the UV-visible absorption spectra of pure TiO<sub>2</sub> and 1% Ag-TiO<sub>2</sub>, 1% Fe-TiO<sub>2</sub> and 1% Ag/1% Fe-TiO<sub>2</sub>. It is observed that the addition of Ag and Fe causes a redshift in the absorption edge of TiO<sub>2</sub>. The  $E_g$  was calculated based on the Kubelka-Munk equation and Tauc's plots.<sup>3,32,35,50</sup> The  $E_g$  of pure TiO<sub>2</sub>, 1% Ag-TiO<sub>2</sub>, 1% Fe-TiO<sub>2</sub> and 1% Ag/1% Fe-TiO<sub>2</sub> are estimated to be 3.20 eV, 3.09 eV, 2.69 eV and 2.87 eV, respectively. The results show that the addition of Ag and Fe is beneficial to increasing the absorption of visible light. It can be concluded from XPS and TEM results that Ag element exists in the form of Ag<sup>0</sup>. Due to the surface plasmon resonance (SPR) effect of Ag particles deposited on TiO<sub>2</sub> surface, the absorption of visible light can be enhanced, reducing the  $E_g$ .<sup>15,16,34,36,37</sup> On the other hand, the substitutions of Ti<sup>4+</sup> ions with Fe<sup>3+</sup> ions form impurity energy levels between the conduction band and valence band in the forbidden band, thereby decreasing the  $E_g$ .<sup>5,7,10,21,33,43,51</sup> Therefore, the change of  $E_g$  is not the main reason for the decreased photocatalytic performance of Fe-TiO<sub>2</sub> and 1% Ag/1% Fe-TiO<sub>2</sub>.

### BET analysis

As is well known, photocatalyst with a larger specific surface area will provide more active reaction sites and increase light

absorption, which is advantageous for photocatalytic performance.<sup>19,22,27,33</sup> It is observed from SEM images that the 1% Fe-TiO<sub>2</sub> particles have a larger agglomeration than pure TiO<sub>2</sub>, which may lead to the decrease of specific surface area. To verify this assumption, we have performed BET specific surface area tests and the results are shown in Table 2. The specific surface area of 1% Fe-TiO<sub>2</sub> is 16.1 m<sup>2</sup> g<sup>-1</sup>, which is much lower than that of pure TiO<sub>2</sub> (63.8 m<sup>2</sup> g<sup>-1</sup>). Some researchers believe that reduction in grain size will lead to an increase in specific surface area.<sup>48,51</sup> In our work, the grain size of TiO<sub>2</sub> is reduced by Ag or Fe modification, which is proved by XRD results, however, 1% Fe-TiO<sub>2</sub> and 1% Ag/1% Fe-TiO<sub>2</sub> possess smaller specific surface areas than pure TiO<sub>2</sub>. Wang *et al.*<sup>52</sup> and Adyani *et al.*<sup>22</sup> are convinced that the specific surface area of TiO<sub>2</sub> is largely related to agglomeration degree. SEM and TEM images confirm an increase in particle agglomeration after Fe addition, which is the major reason for the decrease in specific surface area. It is the significant reduce in specific surface areas of Fe-TiO<sub>2</sub> and 1% Ag/1% Fe-TiO<sub>2</sub> that causes the decrease in their photocatalytic performance.

From another perspective, as the surface areas of samples are quite different, the intrinsic photocatalytic activity (normalized by BET surface area) can be used as a reference. The intrinsic photocatalytic activity ( $I_{PA}$ ) is calculated as follows:<sup>53</sup>

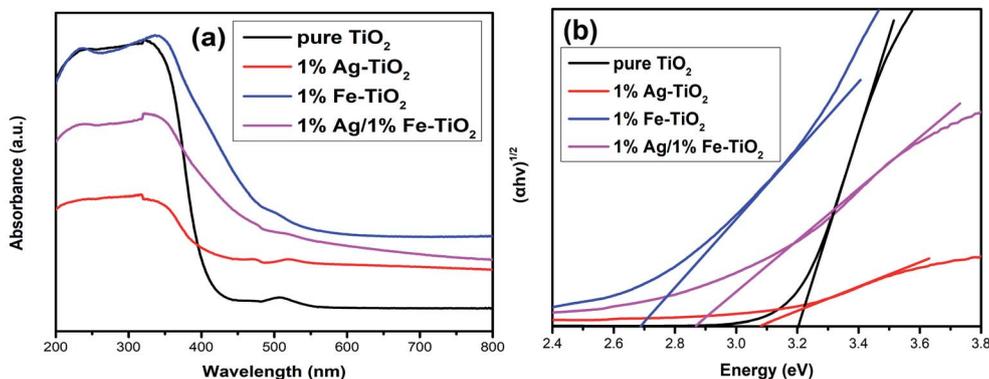


Fig. 9 (a) UV-visible absorption spectra and (b) plots of  $(\alpha h\nu)^{1/2}$  versus energy ( $h\nu$ ) of pure TiO<sub>2</sub>, 1% Ag-TiO<sub>2</sub>, 1% Fe-TiO<sub>2</sub> and 1% Ag/1% Fe-TiO<sub>2</sub>.



**Table 2** Specific surface areas ( $S_{\text{BET}}$ ) of pure  $\text{TiO}_2$ , 1%  $\text{Ag-TiO}_2$ , 1%  $\text{Fe-TiO}_2$  and 1%  $\text{Ag/1\% Fe-TiO}_2$ 

Samples	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )
Pure $\text{TiO}_2$	63.8
1% $\text{Ag-TiO}_2$	59.4
1% $\text{Fe-TiO}_2$	16.1
1% $\text{Ag/1\% Fe-TiO}_2$	49.8

$$I_{\text{PA}} (\text{mg min}^{-1} \text{m}^{-2}) = m_{\text{RhB}}/tS_{\text{BET}}m_s$$

where  $m_{\text{RhB}}$  is the weight of RhB which has been degraded,  $t$  is the reaction time (90 min),  $S_{\text{BET}}$  is the surface area, and  $m_s$  is the weight of sample used in each test (0.1 g).

The  $I_{\text{PA}}$  of pure  $\text{TiO}_2$ , 1%  $\text{Ag-TiO}_2$ , 1%  $\text{Fe-TiO}_2$  and 1%  $\text{Ag/1\% Fe-TiO}_2$  are  $0.00149 \text{ mg min}^{-1} \text{m}^{-2}$ ,  $0.00178 \text{ mg min}^{-1} \text{m}^{-2}$ ,  $0.00354 \text{ mg min}^{-1} \text{m}^{-2}$  and  $0.00143 \text{ mg min}^{-1} \text{m}^{-2}$ . The results show that 1%  $\text{Fe-TiO}_2$  has relatively high intrinsic photocatalytic activity.

## Conclusions

In summary, pure  $\text{TiO}_2$ ,  $\text{Ag-TiO}_2$ ,  $\text{Fe-TiO}_2$  and 1%  $\text{Ag/1\% Fe-TiO}_2$  were prepared by sol-gel method. The results of the decolorization rate of RhB indicate that the photocatalytic activities of  $\text{Ag-TiO}_2$  are higher than pure  $\text{TiO}_2$ , while the photocatalytic activities of  $\text{Fe-TiO}_2$  and 1%  $\text{Ag/1\% Fe-TiO}_2$  are lower than pure  $\text{TiO}_2$ . The increased photocatalytic activity of  $\text{Ag-TiO}_2$  can be attributed to the reduction of photoinduced pairs recombination rate and energy gap. The specific surface areas of  $\text{Fe-TiO}_2$  and 1%  $\text{Ag/1\% Fe-TiO}_2$  are much lower than pure  $\text{TiO}_2$ , leading to the decreases in their photocatalytic properties.

## Conflicts of interest

There are no conflicts to declare.

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