

**Research** Letter

# Preparation of Mn-doped ZrO<sub>2</sub>/TiO<sub>2</sub> photocatalysts for efficient degradation of Rhodamine B

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#### Abstract

The Mn-doped  $ZrO_2/TiO_2$  nanostructured photocatalysts had been prepared by the simple hydrothermal method. The morphologies and structures of the as-prepared photo-catalyst were characterized by transmission electron microscopy, x-ray diffraction, x-ray photoelectron spectroscopy, and electron paramagnetic resonance. The resultant nanostructured photocatalysts exhibited high photocatalytic activity under ultraviolet (UV) light irradiation, attributing to the improvement of the photo-absorption property and the separation efficiency of photogenerated electrons and holes. The hydroxyl radicals (•OH), superoxide radical (•O<sub>2</sub><sup>-</sup>), and holes (h<sup>+</sup>) are the main active species in aqueous solution under UV light irradiation.

#### Introduction

Owing to industrialization and urbanization, organic pollutants in water become a serious environmental killer along with the advancement of technology and industry.<sup>[1-4]</sup> Thus, it is important to develop simple and effective methods to address these issues. A promising method for destroying a wide spectrum of organic compounds is photo-degradation route, which has been studied extensively for destructive oxidation of various organic pollutants. This has proved to be very effective, since many organic compounds can be degraded successfully to safer end-products such as CO2, H2O, and mineral acids.<sup>[5-7]</sup> In particular, titanium dioxide (TiO<sub>2</sub>) has been the focus in this field due to its unique physical and chemical properties, including high efficiency, good stability, nontoxicity, etc.<sup>[8–10]</sup> However, the easy recombination of the electronhole pairs and the absorption of light only at ultraviolet (UV) wavelengths have hindered its further applications.<sup>[11]</sup> Therefore, it is still a challenge to find a highly reactive photocatalyst to meet the present demands for environmental and fuel application.

In order to improve its photocatalytic activity, researchers have made many efforts to modify TiO<sub>2</sub> with different methods, including doping with noble metal deposition,<sup>[12]</sup> nonmetals deposition,<sup>[13]</sup> and establishing junctions between TiO<sub>2</sub> and other semiconductors.<sup>[14–18]</sup> Zirconium dioxide (ZrO<sub>2</sub>) is an

inexpensive, stable, non-toxic, wide bandgap oxide semiconductor ( $E_g \approx 5.0 \text{ eV}$ ), and has appropriate flat-band potentials for photocatalytic purposes.<sup>[19–22]</sup> In previous studies, TiO<sub>2</sub> coupled with zirconia has been investigated extensively in degradation of organic compounds.<sup>[23]</sup> However, due to the large band gap of ZrO<sub>2</sub>, there is almost no charge transfer between TiO<sub>2</sub> and ZrO<sub>2</sub>. It impedes the efficient separation of charge carriers and inhibits the corresponding photocatalytic performance.<sup>[24]</sup> Other metal ions such as iron, nickel, vanadium, chromium, platinum, ruthenium, copper, manganese, cerium, and tin have been investigated as potential dopant of TiO2 to promote the photocatalytic activity of TiO<sub>2</sub>. Metal ion doping is able to enhance interfacial charge-transfer reactions.<sup>[25]</sup> It has also been proven that the transition metal dopants also inhibit the photogenerated charge recombination as the Meta sites are considered to act as trapping site by accepting the photogenerated electrons from the  $TiO_2$  valence band (VB).<sup>[26]</sup>

In this paper, the Mn-doped  $ZrO_2/TiO_2$  nanostructured composites were synthesized via a simple hydrothermal method. The photocatalytic activities of the samples were determined by degradation of Rhodamine B (RhB). Compared with the pure TiO<sub>2</sub> nanoparticles and non-doped sample, the 0.5% Mn-doped  $ZrO_2/TiO_2$  composite has showed better photocatalytic activity due to the narrowed band gap and shifted up the conduction band (CB) edge.



#### **Experimental** Propagation of mater

Preparation of materials

The Mn-doped ZrO<sub>2</sub>/TiO<sub>2</sub> catalysts were synthesized by the hydrothermal reaction. 3 mL of zirconium n-propoxide (70 wt%) and 3 mL of tetrabutyl titanate (98 wt%) were added into deionized water under magnetic stirring. Next, the appropriate amounts of Mn(NO<sub>3</sub>)<sub>2</sub> were added. Then, the resultant solution was transferred into a Teflon-lined stainless steel autoclave, followed by a hydrothermal reaction at 160 °C for 24 h. After cooling to room temperature, the precipitates were filtered and washed with deionized water and ethanol six times. The products were dried in a vacuum oven at 60 °C for 12 h to get the fine photocatalysts. The Mn concentrations in the samples were 0%, 0.5%, 1%, and 1.5%, respectively.

#### Characterization

The structures and crystal phase of the as-prepared samples were analyzed with a SIEMENS Diffraktometer D5000 x-ray diffractometer with Cu  $K_{\alpha}$  radiation source at 35 kV, with a scan rate of 4°/s in the  $2\theta$  range of 10°-80°. x-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al  $K_{\alpha}$  radiation. JSM-2100 transmission electron microscopy (TEM) was used to characterize the morphology of the as-prepared samples. The Brunauer-Emmet-Teller (BET) specific surface area was measured using a specific surface and pore size analysis instrument (3H-2000PS1/2 static volume method, China). Electron paramagnetic resonance (EPR) spectra recorded at room temperature was run on an X-band CW-EPR Bruker EMX spectrometer equipped with a cylindrical cavity operating at 100 kHz field modulation frequency. TEM map (Tecnai G2 F30 S-Twin), UV-visible (JASCO V-570, Japan).

#### Measurement of photocatalytic activity

The photocatalytic activities of the samples were evaluated by the photo-degradation of RhB in aqueous solution under UV light irradiation with a 300 W lamp to provide UV light ( $\lambda \le$  400 nm). Before irradiation, 20 mg amount of the as-prepared catalysts were added into 50 mL of RhB solution under magnetic stirring for 1 h to ensure the adsorption-desorption equilibrium. Then the solution was stirred and exposed to the UV light irradiation. An amount of aliquots were taken away and separated as-prepared catalysts with centrifugation at the designated time. The upper layer was appropriately diluted and the RhB concentration (C) was measured by JASCO V-570 UV-vis-NIR spectrophotometer (Japan).

The degradation rate could be expressed as the following formula.

Decolonization rate of RhB:  $R = (C_0 - C_t)/C_0 * 100\%$ 

#### **Results and discussion**

TEM is employed to determine the morphology of the products. Typical morphology of the 0.5% Mn-doped ZrO<sub>2</sub>/TiO<sub>2</sub> nanocomposite is shown in Fig. 1(a). The size of the products is less than 10 nm and can be founded for the 0.5% Mn-doped ZrO<sub>2</sub>/TiO<sub>2</sub> nanocomposite sample. The ZrO<sub>2</sub>/TiO<sub>2</sub> nanocomposite without Mn doping shows the similar morphology and size (see Fig. S1 in support information). The selected area electron diffraction (SAED) image of 0.5% Mn-doped ZrO<sub>2</sub>/ TiO<sub>2</sub> nanocomposite exhibits the combination of bright ring and single crystalline spot, as shown in Fig. 1(b). It indicates the poly-crystalline nature of the as-prepared product. The crystalline nature of the 0.5% Mn-doped ZrO<sub>2</sub>/TiO<sub>2</sub> nanocomposite is further investigated by high resolution TEM (HR-TEM). The HRTEM image presented in Fig. 1(c) shows the lattice spacing at 0.341 nm which is close to the (101) (0.35 nm) plane of the anatase phase of TiO<sub>2</sub>. The lattice spacings at 0.323 and 0.295 nm are contributed to the (111) (0.3164 nm) monoclinic and [111] (0.2964 nm) tetragonal crystalline structures of ZrO<sub>2</sub>, as shown in Figs. 1(d) and 1(e). The crystalline phases of the as-prepared powders are further identified by x-ray diffraction (XRD) analysis. Figure 1(f) shows the XRD patterns of the products with different Mn doping content. It can be found that all as-prepared samples exhibit a peak located around 26° which indicates the presence of anatase crystal structure of TiO<sub>2</sub>. The distinctive peak at  $\sim 28^{\circ}$  and  $30^{\circ}$  is the typical signal of tetragonal and tetragonal ziirconia structure.<sup>[27,28]</sup>



Figure 1. TEM image (a), SAED pattern (b), HR-TEM images of 0.5% Mn-doped  $ZrO_2/TiO_2$  (c-e), and XRD patterns of the doped  $ZrO_2/TiO_2$  samples with different doping ration of Mn (f).

No detectable Mn dopant-related peaks can be observed in the samples except a little asymmetry of the peaks due to the low content and high dispersity of dopants.

Nitrogen adsorption-desorption isotherms and the corresponding pore size distribution curves are conducted to investigate the porous structure of the as-prepared samples. The as-prepared samples exhibit the Type IV isotherms characteristic of mesoporosity (see Fig. S2 in the support information). The BET specific surface areas, mean pore diameters, and total pore volumes of the as-prepared samples are summarized in Table S1. The 0.5% Mn-doped ZrO<sub>2</sub>/TiO<sub>2</sub> exhibits the highest specific surface area (160.51  $m^2/g$ ) and the lowest mean pore diameter (6.60 nm). The absorption edge and band-gap energies of the as-prepared samples are determined by UV-vis diffuse reflectance spectra analysis (see Fig. S2 in the support information). It can be founded that the 0.5% Mn-doped ZrO<sub>2</sub>/TiO<sub>2</sub> nanocomposite exhibits the strongest absorption under the UV light region. The band gap energy of the 0.5% Mn-doped ZrO<sub>2</sub>/TiO<sub>2</sub> nanocomposite is estimated to be 3.31 eV by fitting to a plot of Kubelka-Munk function versus energy (hv) which is much lower than that of other samples. The stronger absorption and the smaller band gap are contributed to the enhancement of photocatalytic activity of the as-prepared samples.<sup>[29, 30]</sup>

Fig. 2(a) shows a bright field TEM image taken under scanning TEM (STEM) mode. The morphology is corresponding with the TEM. The energy dispersive x-ray spectroscopy (EDS) analysis (shown in Fig. 2(b)) suggests the presence of Mn, O, Ti, and Zr elements in the product. It can be known

that the Mn is well doped in 0.5% Mn-doped  $ZrO_2/TiO_2$  nanocomposites. Mn, O, Ti, and Zr K edge mapping are shown in Figs. 2(c)–2(f), respectively. It can be seen that the green color (assigned to Mn), red color (assigned to O), yellow color (assigned to Ti), and blue color (assign to Zr) are uniformly distributed in the sample of  $ZrO_2/TiO_2$  which indicates the formation of uniform nanocomposite.

The chemical composition of the obtained composites is confirmed by XPS measurement. The XPS spectrum of the 0.5% Mn-doped ZrO<sub>2</sub>/TiO<sub>2</sub> nanocomposite exhibits prominent peaks of Ti, Zr, O, and relatively feeble peaks of Mn, as shown in Fig. 3(a). The high-resolution XPS spectrum of Zr 3d on the composite photocatalyst is shown in Fig. 3(b), which can be fitted as two peaks with binding energies at 184.5 and 182.7 eV. It implies two different chemical environments of Zr existed in the products that are assigned to the Ti-Zr, and Zr-O, respectively. The high-resolution XPS spectrum of Ti 2p can be fitted as two peaks with binding energies at 464.8 and 458.5 eV which are assigned to Ti-Zr and Ti-O, respectively (Fig. 3(c)). The O 1s peak localized at 531.38 eV can be ascribed to Ti-O, while the peak at 529.8 eV is assigned to Ti-O and Zr-O (Fig. 3(d)). And the presence of Mn dopant is confirmed by Mn 2p core level, as shown in Fig. 3(e). As for Mn 2p peak with the binding energy at 642.4 eV originates from the Mn<sup>4+</sup>.<sup>[26]</sup> The VB of ZrO<sub>2</sub>/TiO<sub>2</sub> nanocomposite and 0.5% Mn-doped ZrO<sub>2</sub>/TiO<sub>2</sub> nanocomposite that measured by XPS valence spectra (Fig. 3 (f)) are 2.84 and 2.58 eV, respectively. The composition of the 0.5% Mn-doped ZrO<sub>2</sub>/TiO<sub>2</sub> nanocomposite from XPS analvsis is showed in Table S2. The amount of Mn element is 0.41%



Figure 2. STEM mode image (a), EDS (b), and Elemental mapping (c-f) of 0.5% Mn-doped ZrO<sub>2</sub>/TiO<sub>2</sub> nanocomposite.



Figure 3. XPS spectrum of 0.5% Mn-doped ZrO<sub>2</sub>/TiO<sub>2</sub> nanocomposite (a), the high-resolution XPS spectra of Zr 3d (b), Ti 2p (c), 0 1s (d) Mn 2p (e), and VB of samples (f).

in the resultant sample which closes to the composition of feed ratio. However, the high-resolution XPS spectra of Zr 3d, Ti 2p, and O 1s of non-doped  $ZrO_2/TiO_2$  product exhibits the similar chemical environments compared with the Mn doped  $ZrO_2/TiO_2$  product which indicates the doped Mn has no change in the structure of  $ZrO_2/TiO_2$  composite (see Fig. S3 in the support information). The composition of the non-doped  $ZrO_2/TiO_2$  nanocomposite from XPS analysis is showed in Table S3.

The photocatalytic activity of the as-prepared products is evaluated by degradation of RhB under the UV light irradiation. As shown in Fig. 4(a), the adsorption-desorption equilibrium for photocatalysts can be reached after stirring for 1 h in the dark. The 0.5% Mn-doped  $ZrO_2/TiO_2$  photocatalyst exhibits the highest activity, and more than 95% of RhB could be degraded within 50 min. However, only about 77.6% of RhB has been degraded over non-doped  $ZrO_2/TiO_2$  composite with the same irradiation time and about 58.2% RhB are removed by ZrO2 under same conditions. No higher activities have been observed for the photocatalysts with Mn doping at higher concentration (1% and 1.5%). It implies that the introduction of Mn doping play an important role for the improvement of the photocatalytic activities and excess of the Mn doping is of no help to improve their activities. The relatively higher photocatalytic activity of Mn-doped ZrO<sub>2</sub>/TiO<sub>2</sub> nanocomposite photocatalysts may result from the doped of foreign species. Owing to its relatively smaller ionic radius, Mn<sup>4+</sup> ions may enter into the lattice of ZrO<sub>2</sub>/TiO<sub>2</sub> composities. It is beneficial to improve of photo-adsorption property, forming interband-gap localized levels to reduce band gap and enlarge specific surface area and the pore volume.<sup>[31,32]</sup> In order to test the re-use performances of composite photocatalyst, the 0.5% Mn-doped ZrO<sub>2</sub>/TiO<sub>2</sub> photocatalyst is used to take the recycle photocatalytic decoloration



**Figure 4.** Photocatalytic degradation of RhB over different photocatalytic materials (a) and cycling runs for the photodegradation of RhB over 0.5% Mn-doped ZrO<sub>2</sub>/TiO<sub>2</sub> nanocomposite (b).

of RhB solution, as shown in Fig. 4(b). The products still maintained their higher photocatalytic activates after 5 time cycles which indicates the good durability of the nanocomposite photocatalysts.

For investigation of a plausible reaction mechanism for the excellent photocatalytic activity of 0.5% Mn-doped ZrO<sub>2</sub>/TiO<sub>2</sub> nanocomposite and detecting the active species during photocatalytic reactivity, hydroxyl radicals (•OH), superoxide radical  $(\bullet O_2^-)$ , and holes  $(h^+)$  are investigated by adding 1.0 mM isopropyl alcohol (IPA) (a quencher of •OH), p-benzoquinone (BQ) (a quencher of  $\bullet O_2^-$ ), and triethanolamine (TEOA) (a quencher of h<sup>+</sup>), respectively.<sup>[27]</sup> The method is similar to the former photocatalytic activity test. Figure 5(a) displays the trapping experiment of active species during the photocatalytic reaction. It can be seen that the photocatalytic degradation of RhB obviously decreased with the addition of TEOA, BQ, and IPA. Therefore, it can be concluded that the  $h^+$ ,  $\bullet O_2^-$ , and  $\bullet OH$  are the main active species of the obtained products in aqueous solution under UV light irradiation. Many types of point defects present in solids, in particular, oxides are paramagnetic. EPR spectroscopy is one of the most suitable techniques to investigate defective materials. It can be seen in the Fig. 5(b), the intensity of 0.5% Mn-doped  $ZrO_2/TiO_2$  nanocomposite is stronger than that of non-doped product. Under UV light irradiation, the intensity of EPR signal of doped product increased obviously which indicates the production of more active radicals assisted by the UV irradiation. More active radicals can improve the photocatalysis performances.<sup>[33,34]</sup>

A possible photocatalytic mechanism of the Mn-doped  $ZrO_2/TiO_2$  photocatalysts is depicted in Scheme 1. Under the UV light irradiation, the photogenerated h<sup>+</sup>,  $\bullet O_2^-$ , and  $\bullet OH$  are in their VB and CB, respectively. The Mn doping not only narrows the band gap but also shifts up the CB edge. The doping with Mn introduced a VB of impurities which can narrow the band gap of  $ZrO_2/TiO_2$ .<sup>[35]</sup> The doping of Mn ions improved the quantity of the photogenerated electron-hole under visible light irradiation which formed new states closed to the CB and VB. The doping of Mn ions also inhibited the recombination of the photogenerated electron-hole pairs. The Mn ions with suitable concentration could trap the photogenerated electron-ated electrons. As can be observed, 0.5% Mn-doped  $ZrO_2/TiO_2$  exhibited the maximum photocatalytic activity for RhB



Figure 5. Trapping experiment of active species during the photocatalytic reaction (a) and EPR spectra of the ZrO<sub>2</sub>/TiO<sub>2</sub> doped with different mass ratio of Mn (b).



**Scheme 1.** Schematic illustration of the  $ZrO_2/TiO_2$  photocatalytic mechanism of RhB degradation over Mn-doped  $ZrO_2/TiO_2$  photocatalyst.

degradation.<sup>[26]</sup> In fact, although RhB is active to light, the lowest unoccupied molecular orbital (LUMO) potential of RhB  $(-0.75 \text{ eV})^{[36]}$  is more positive than the CB minimum (CBM) of ZrO<sub>2</sub> (-1 eV). The CBM of RhB is more negative than TiO<sub>2</sub> (-0.4 eV), the excited electrons of RhB can have a further react with O<sub>2</sub> on the surface of TiO<sub>2</sub>. The photogenerated h<sup>+</sup> in CB also has a strong oxidation potential and serve as active sites responsible for RhB photodegradation.

# Conclusion

In summary, the Mn-doped  $ZrO_2/TiO_2$  nanocomposites with UV light photocatalytic properties have been prepared by hydrothermal reaction. The doping with Mn can narrow the band gap of  $ZrO_2/TiO_2$ , which is beneficial to improve photoadsorption property. At the same time, it also proves that the h<sup>+</sup>, •OH, and  $•O_2^-$  are the main active species of Mn-doped  $ZrO_2/TiO_2$  photocatalysts in aqueous solution. The photocatalytic activity of the as-prepared products was evaluated by degradation of RhB under the UV light irradiation. The optimal concentration of dopant that improves the photocatalytic activity of the nanoplates was determined. These observations provide a new possibility in the investigation of photocatalytic performance of nanocomposites and are expected to promote its practical applications in the field of environmental science.

# **Supplementary materials**

For supplementary material for this article, please visit http:// dx.doi.org/10.1557/mrc.2015.59

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