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# Novel hybrid Sr-doped TiO<sub>2</sub>/magnetic Ni<sub>0.6</sub>Zn<sub>0.4</sub>Fe<sub>2</sub>O<sub>4</sub> for enhanced separation and photodegradation of organics under visible light

Fuming Liu,<sup>a</sup> Yu Xie,<sup>\*a</sup> Changlin Yu,<sup>c</sup> Xiaoming Liu,<sup>a</sup> Yuhua Dai,<sup>a</sup> Lianjun Liu<sup>\*b</sup> and Yun Ling<sup>a</sup>

Titanium dioxide (TiO<sub>2</sub>) has been intensively used as a photocatalyst for the degradation of organic pollutants in water, but is typically obstacle by a low efficiency, costly separation, limited visible light response, and poor recyclability. Herein, we provided a reliable method to simultaneously tackle these four obstacles by developing an integrated and multifunctional hybrid photocatalyst/magnetic material, *i.e.*, Sr–TiO<sub>2</sub>/Ni<sub>0.6</sub>Zn<sub>0.4</sub>Fe<sub>2</sub>O<sub>4</sub>. This novel hybrid not only demonstrated a high efficiency (90–100%) and a good cycling performance (90% maintenance) for photodegradation of bisphenol A (BPA) under both UV and visible light irradiation, but it can also efficiently work at a wide pH range (4–10) and can be easily separated from water for reuse only by introducing an external magnetic field. The materials structure-to-activity correlation has also been investigated. It was found that doping Sr<sup>2+</sup> and a coupling magnetic material with TiO<sub>2</sub> could extend the visible light response and create active defects in TiO<sub>2</sub>, which were responsible for the nearly three times higher activity than that of commercial TiO<sub>2</sub>(P25) under visible light. On the other hand, doping excessive Sr<sup>2+</sup> lowered the surface area, enlarged the crystalline size and caused particle aggregation; thus, leading to a decrease in photocatalytic activity of the hybrid. These further modifications in the hybrid materials can provide a competitive alternative to control the organic pollutants in waste water.

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## 1. Introduction

Photodegradation of organic pollutants using photocatalysts (*e.g.*, ZnO, TiO<sub>2</sub>, WO<sub>3</sub>, CdS) holds a great promise to purify water and has been investigated intensively over the last decade.<sup>1–3</sup> Among the photocatalysts, TiO<sub>2</sub> has received great interest because of its chemical stability, high photocorrosion resistance, non-toxicity, and low-cost.<sup>3–8</sup> However, bare TiO<sub>2</sub> has a very low quantum efficiency primarily because of fast recombination rates of electron and hole pair (e<sup>−</sup>–h<sup>+</sup>) and limited visible light responses (due to its wide band gap in the range of 3.0–3.2 eV).<sup>1,8</sup> The low efficiency of TiO<sub>2</sub> is a major barrier for commercializing this photocatalytic technology. Complicated separation of photocatalyst for regeneration and reuse may also impede its practical application, but this challenge is seldom addressed in the literature.<sup>9–11</sup> Generally, a TiO<sub>2</sub>-based power was suspended in a solution for the photodegradation of

organic pollutants, and it often required a filtration or centrifugation process to separate the photocatalyst from water. This process may increase the cost and brings a potential genotoxicity due to some residual organics adsorbed on the solids.<sup>2,12</sup> Therefore, it is urgent and necessary to develop high performance and easily recycled TiO<sub>2</sub>-based photocatalysts.

To improve the photocatalytic efficiency of TiO<sub>2</sub>, great efforts have been made to modify TiO<sub>2</sub> either by incorporating noble metals (*e.g.*, Ag) or metal oxides (*e.g.*, Fe<sub>2</sub>O<sub>3</sub>) to act as electron traps and inhibit the recombination of e<sup>−</sup>–h<sup>+</sup> pairs,<sup>2,8,13–16</sup> or by doping nonmetals (*e.g.*, N) or co-doping with nonmetals and transition metal ions (*e.g.*, Cr<sup>3+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Mg<sup>2+</sup>) to extend the visible light response.<sup>9,17–23</sup> Alternatively, pure or modified perovskite strontium titanate (SrTiO<sub>3</sub>) and SrTiO<sub>3</sub>/TiO<sub>2</sub> heterojunctions have also been investigated as a candidate for the photodegradation of organic pollutants.<sup>23–27</sup> However, a few studies have been conducted on Sr<sup>2+</sup> doped TiO<sub>2</sub> for the photodegradation of organic compounds. Very recently, Li *et al.*<sup>28</sup> synthesized Sr<sup>2+</sup>-doped ZnO composites and attributed its enhanced performance over ZnO for RhB degradation under visible light to the narrowed band gap and the formation of active defects to trap electrons. Along this line, it is expected that doping Sr<sup>2+</sup> into the TiO<sub>2</sub> lattice will lead to an enhanced photocatalytic degradation of bisphenol A (BPA).

<sup>a</sup>Department of Materials Chemistry, Nanchang Hangkong University, Nanchang, Jiangxi Province, 330063, PR China. E-mail: xieyu\_121@163.com; Fax: +86 791 83953373; Tel: +86 791 83953373

<sup>b</sup>Mechanical Engineering Department, University of Wisconsin–Milwaukee, Milwaukee, WI, 53211, USA. E-mail: liul@uwm.edu; Tel: +1 216 650 9842

<sup>c</sup>School of Metallurgy and Chemical Engineering, Jiangxi University of Science and Technology, Ganzhou, Jiangxi Province, 341000, PR China



To overcome the obstacle of  $\text{TiO}_2$  powder separation from solution, several efforts have been attempted to anchor  $\text{TiO}_2$  on solid substrates (e.g., Ti mesh)<sup>4,11,29–33</sup> or incorporate  $\text{TiO}_2$  with magnetic materials (e.g., ferrite).<sup>34–40</sup> Immobilizing  $\text{TiO}_2$  on solid substrates is restricted to laboratory or small-scale applications because of the complicated preparation process, weak attachment of  $\text{TiO}_2$  on the foreign substrates, and deficient immersion and dispersion of  $\text{TiO}_2$  in the slurry solution. On the other hand, magnetic separation is a promising route to recover the used photocatalysts only by applying an external magnetic field. A number of studies have been attempted to fabricate core-shell structured magnetic material/photocatalysts for the photo-degradation of organics, including  $\text{Fe/TiO}_2/\text{Ag}$ ,  $\text{Fe/V/TiO}_2$ , nickel ferrite/ $\text{N-TiO}_2$ , and strontium ferrite/ $\text{N-TiO}_2$ .<sup>9,34,37,40</sup> Unfortunately, the nanosized core magnetic materials are easily oxidized (e.g.,  $\text{Fe}_3\text{O}_4$  oxidized to  $\text{Fe}_2\text{O}_3$ ) or rapidly transform in the crystal phase (e.g.,  $\gamma\text{-Fe}_2\text{O}_3$  ferromagnetic to  $\alpha\text{-Fe}_2\text{O}_3$  paramagnetic) when the calcination temperature is over  $400^\circ\text{C}$ .<sup>34,40</sup> Obviously, it is still a challenge to produce the  $\text{TiO}_2$ -coated magnetic nanoparticles with concurrent good stability, high visible light activity and good magnetic properties.

To simultaneously overcome the challenges in the catalytic efficiency and separation of  $\text{TiO}_2$ -based photocatalysts, in this work, we designed a novel hybrid by integrating a photocatalyst with magnetic material, i.e.,  $\text{Sr-TiO}_2/\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ . We hypothesize that (1) doping  $\text{TiO}_2$  with  $\text{Sr}^{2+}$  could create some active defects and promote visible light absorption, and thus enhancing the charge separation and extending visible light response, (2) introducing Zn into  $\text{NiFe}_2\text{O}_4$  could prevent the phase transition and assure good magnetic properties,<sup>41,42</sup> and using  $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$  as magnetic core not only harvests visible light but also facilitates photocatalyst separation, and (3) an interface may be formed between  $\text{Sr}^{2+}$ -doped  $\text{TiO}_2$  and magnetic  $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ , and thus inducing a synergistic effect to remove organics with an exceptional performance. To the best of our knowledge, for the first time this multifunctional material for water treatment has been developed. All the materials used (Ti, Sr, Ni, Zn, and Fe) to build the nanostructure are inexpensive and earth-abundant. The sol-gel method employed to prepare the hybrid is also simple and easy to scale-up. Another feature in this work is to evaluate the cycling performance of the hybrid photocatalyst/magnetic material under both UV and visible light irradiation, and attempt to establish the structure-to-activity relationships.

## 2. Materials and methods

### 2.1 Synthesis of magnetic $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ nanoparticles

$\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$  nanoparticles were prepared by a self-propagating combustion method. In brief, 0.1 mol nickel nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), 0.067 mol zinc nitrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and 0.333 mol iron nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) were dispersed into 100 ml deionized water with vigorous stirring. Citric acid (0.5 mol) was then added into the solution, using ammonium hydroxide to adjust the pH around 10.0. Next, the solution was heated in a water bath at  $70^\circ\text{C}$  by microwave irradiation until

the sol was formed. The as-received sol was finally dried in an oven at  $100^\circ\text{C}$  for 24 h.

### 2.2 Synthesis of hybrid $\text{Sr-TiO}_2$ /magnetic material

The hybrid  $\text{Sr-TiO}_2$ /magnetic materials were prepared by a sol-gel method. Typically, in a beaker A, 10 ml of tetrabutyl titanate ( $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$ ), 1 g of  $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$  nanoparticles, and 40 ml of absolute ethyl alcohol were uniformly mixed. In a beaker B, a certain amount of strontium nitrate ( $\text{Sr}(\text{NO}_3)_2$ ) and starch (the mass ratio of  $\text{Sr}(\text{NO}_3)_2$  to starch is 0.02 : 0.5, 0.05 : 1, 0.1 : 1.5, 0.2 : 2.5), 5 ml de-ionized water, and 15 ml acetic acid were mixed. The mixture was heated for 5 min by microwave irradiation to get a homogeneous solution. Next, the solution in the beaker B was added dropwise to beaker A with mechanical stirring for 2 h. The mixed solution was aged at  $70^\circ\text{C}$  for 24 h. The obtained gel was then dried and calcined at  $550^\circ\text{C}$  in air for 4 h. The final hybrid materials were denoted as  $\text{Sr}_x\text{Ti/M}$  ( $\text{M} = \text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ ), where  $x$  is the nominal weight percentage of  $\text{Sr}^{2+}$  (i.e., 0.1 wt%, 0.25 wt%, 0.5 wt%, and 1 wt%). For comparison,  $\text{Ti/M}$  and  $\text{Sr}_{0.25}\text{Ti}$  were also prepared using a same procedure as  $\text{SrTi/M}$ .

### 2.3 Characterization

The crystal structure of  $\text{Sr-TiO}_2/\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$  materials were characterized by X-ray diffraction (XRD) using a Bruker D8 Advance X-ray diffractometer with monochromated high-intensity  $\text{CuK}\alpha$  radiation ( $\lambda = 0.15418 \text{ \AA}$ ) in the  $2\theta$  range of  $10\text{--}80^\circ$ . The morphology and particle size of the materials were identified by field emission scanning electron microscopy (FESEM). Transmission electron microscopy (TEM) (JEOL TEM-3010) was used to approach the lattice fringes operating at an accelerating voltage of 300 keV. The surface area and porosity of the as-synthesized materials were examined by  $\text{N}_2$  adsorption/desorption at 77 K using the Brunauer–Emmett–Teller (BET) method (Micromeritics, ASAP 2020). The UV-vis diffuse reflectance spectra were recorded using a UV-vis-NIR spectrometer (Cary 5000, Varian). The valence states of Ti and O were identified by X-ray photoelectron spectroscopy (XPS), using a PHI 5000 versaprobe system using monochromatic Al KR radiation (1486.6 eV). All binding energies were referenced to the C 1s peak at 284.6 eV. The magnetic properties of the photocatalyst were evaluated at room temperature using a vibrating sample magnetometer (VSM, 9600-1 LDJ, USA) at a maximum applied field of 10 kOe.

### 2.4 Photocatalytic activity measurement

The photocatalytic degradation of BPA was carried out in a hollow cylindrical photoreactor. The light source is a low-pressure mercury lamp (Beijing Ceaulight Co., Model CEL-LUV254, 10 W) that emits principally near 254 nm, or a long-arc xenon lamp (Beijing Ceaulight Co., Model CEL-LAX500, 500 W) to simulate visible light ( $\sim 400 \text{ nm}$ ). The photoreactor was cooled by circulating water through a quartz channel inside, and the temperature was maintained at  $25 \pm 2^\circ\text{C}$ . Prior to illumination, a 300 ml suspension with a certain amount of photocatalyst ( $0.5 \text{ g l}^{-1}$ ) was stirred for 30 min to



ensure the homogenous dispersion and full contact of BPA (10 ppm) with catalysts. The pH of the BPA solution was controlled using a NaOH solution (5 M, 1 M, 0.1 M) and an HNO<sub>3</sub> solution (2 M, 0.1 M) to prepare basic and acidic solutions, respectively. After that, the lamp was turned on to irradiate the solution. A sample of 0.5 ml of solution was withdrawn at every 30 min. Moreover, the pH of the BPA solution was recorded at different reaction times using a pH meter (Mettler Toledo). The BPA concentration in each batch was measured by high-performance liquid chromatography (HPLC) equipped with a C-18 column (LUNA 5u 100A, 4.6 mm × 250 mm, Phenomenex) and a diode array detector (SPD-M20A, Shimadzu). The isocratic methanol–water mixture (70 : 30, v/v) as an eluent was employed at a flow rate of 1 ml min<sup>−1</sup>. The residual BPA content in the aqueous solution was determined with a standard curve ( $R^2 = 0.9999$ ) using a standard BPA solution for the calibration (i.e., 0, 0.2, 0.5, 1, 2, 5, 10 and 15 ppm). The degradation efficiency (DE) of BPA was calculated by the following equation:  $DE = C_0/C_t$ , where  $C_0$  and  $C_t$  are the initial and residual BPA concentration (ppm) at different reaction times, respectively.

### 3. Results and discussion

#### 3.1 Crystal structure, morphology and texture

The crystal structure of the hybrid was identified by XRD. As shown in Fig. 1, all the samples displayed the same

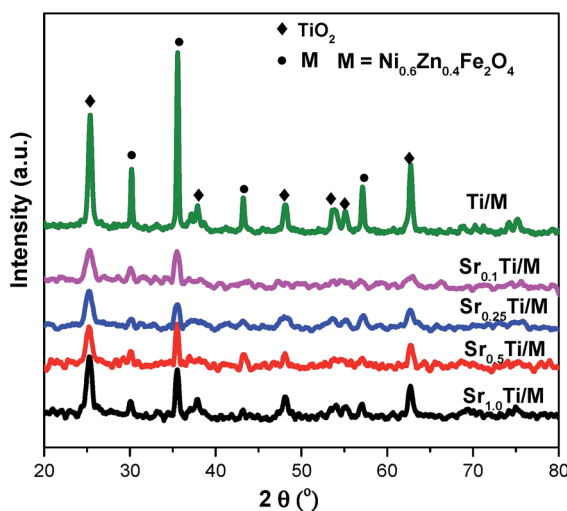


Fig. 1 XRD patterns for Sr<sup>2+</sup>-doped TiO<sub>2</sub>/Ni<sub>0.6</sub>Zn<sub>0.4</sub>Fe<sub>2</sub>O<sub>4</sub> nano-composites with a series of concentrations of Sr<sup>2+</sup>.

diffraction peaks, which are indexed to a mixture of the anatase phase of TiO<sub>2</sub> (JCPDS no. 21-1272) and the spinel phase of Ni<sub>0.6</sub>Zn<sub>0.4</sub>Fe<sub>2</sub>O<sub>4</sub>.<sup>43,44</sup> No additional peaks for perovskite SrTiO<sub>3</sub> or SrO crystallites appeared because of the low calcination temperature and low dopant concentration of Sr<sup>2+</sup>.<sup>23,27</sup> Noticeably, Ti/M without Sr<sup>2+</sup> dopant exhibited sharp diffraction peaks. By contrast, Sr<sub>x</sub>Ti/M showed broadened and weakened diffraction peaks for both the TiO<sub>2</sub> (101) plane and magnetic Ni<sub>0.6</sub>Zn<sub>0.4</sub>Fe<sub>2</sub>O<sub>4</sub>. This comparison indicated that doping Sr<sup>2+</sup> ions into the TiO<sub>2</sub> lattice could stabilize the crystal phase of TiO<sub>2</sub> anatase and inhibit the aggregation and growth of the particles, thus inducing a decrease in TiO<sub>2</sub> crystalline size. Among the samples, Sr<sub>0.1</sub>Ti/M showed the smallest crystalline size (see Table 1). Increasing the concentration of Sr<sup>2+</sup> ions resulted in an increase in the TiO<sub>2</sub> crystalline size from 15.7 nm to 18.8 nm, probably because the excessive Sr<sup>2+</sup> ions cannot be completely doped into the TiO<sub>2</sub> lattice and caused particle agglomeration. Moreover, the uniformly dispersed Sr–TiO<sub>2</sub> particles may fully attach on the surface of Ni<sub>0.6</sub>Zn<sub>0.4</sub>Fe<sub>2</sub>O<sub>4</sub> and result in a decrease in its peak intensity.

The morphology and particle size of the Sr<sub>x</sub>Ti/M samples were characterized by SEM (Fig. 2) and TEM (Fig. 3). As shown in Fig. 2, Sr<sub>0.1</sub>Ti/M and Sr<sub>0.25</sub>Ti/M have uniformly dispersed particles with an average size of 20 nm. By contrast, Sr<sub>1.0</sub>Ti/M has randomly mixed small particles and big grains (over 100 nm). The TEM image at a low magnification in Fig. 3a further confirmed that Sr<sub>0.1</sub>Ti/M was composed of relatively uniform spherical or rectangle particles with a diameter of ~20 nm. The TEM image at a high magnification in Fig. 3b clearly shows well-faceted TiO<sub>2</sub> nanocrystals with an interplanar spacing of 0.352 nm that matches the (101) plane of anatase phase.<sup>5,45,46</sup> Ni<sub>0.6</sub>Zn<sub>0.4</sub>Fe<sub>2</sub>O<sub>4</sub> nanoparticles (~15 nm), located beyond TiO<sub>2</sub> particles, was also observed with a lattice spacing of 0.187 nm.<sup>47</sup> Again, SEM and TEM images directly supported the XRD observations that a small amount of Sr<sup>2+</sup> (below 0.25 wt%) doped TiO<sub>2</sub> particles were well-patched onto the magnetic Ni<sub>0.6</sub>Zn<sub>0.4</sub>Fe<sub>2</sub>O<sub>4</sub>, while excessive Sr<sup>2+</sup> dopant easily induced particles aggregation into large grains.

Table 1 also compared the measured BET surface area, pore size, pore volume of the Sr<sub>x</sub>Ti/M samples to explore the effect of Sr<sup>2+</sup>-dopant content on the textural property. The presence of mesopores in Sr<sub>x</sub>Ti/M could result from the space between particles, as evidenced by the SEM images in Fig. 2. At low loadings of Sr<sup>2+</sup>, Sr<sub>0.1</sub>Ti/M and Sr<sub>0.25</sub>Ti/M displayed similar surface areas, pore sizes, and pore volumes, which were

Table 1 The BET surface area, pore volume, pore size, and crystallite size of TiO<sub>2</sub> for Sr<sup>2+</sup>-doped TiO<sub>2</sub>/M (M = Ni<sub>0.6</sub>Zn<sub>0.4</sub>Fe<sub>2</sub>O<sub>4</sub>)

Sample name	BET surface area (m <sup>2</sup> g <sup>−1</sup> )	Pore volume (cm <sup>3</sup> g <sup>−1</sup> )	Pore size (nm)	Crystallite size of TiO <sub>2</sub> (nm)
Sr <sub>0.1</sub> Ti/M	64	0.205	12.7	15.7
Sr <sub>0.25</sub> Ti/M	66	0.198	12.0	15.9
Sr <sub>0.5</sub> Ti/M	44	0.063	5.6	17.5
Sr <sub>1.0</sub> Ti/M	46	0.071	6.1	18.8





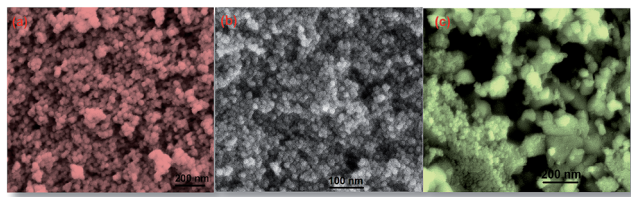


Fig. 2 SEM images for (a)  $\text{Sr}_{0.1}\text{Ti/M}$ , (b)  $\text{Sr}_{0.25}\text{Ti/M}$ , and (c)  $\text{Sr}_{1.0}\text{Ti/M}$  composites ( $\text{M} = \text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ ).

considerably higher than those of  $\text{Sr}_{0.5}\text{Ti/M}$  and  $\text{Sr}_{1.0}\text{Ti/M}$  at high loadings of  $\text{Sr}^{2+}$ . The data in Table 1 agrees well with XRD and SEM observations that high contents of  $\text{Sr}^{2+}$  results in the aggregation of the particles and the growth in crystalline size, which could block the micro/meso-pores within  $\text{TiO}_2$  particles and decrease the BET surface area, pore size, and pore volume.

### 3.2 Optical property and chemical state

UV-vis spectra, displayed in absorbance units, have been recorded to investigate the light response of the  $\text{Sr}_x\text{Ti/M}$  samples. As shown in Fig. 4, the absorption edge of bare  $\text{TiO}_2(\text{P25})$  is located around 400 nm, corresponding to a band gap of about 3.10 eV. By contrast, incorporating the magnetic  $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$  with  $\text{TiO}_2$  induced the appearance of a tail extending to a longer wavelength of 600 nm. All the  $\text{Sr}_x\text{Ti/M}$  samples display similar broad bands extending to nearly 800 nm, which is consistent with the dark gray physical appearance of the samples. Furthermore, the band edge of  $\text{Sr}_{0.1}\text{Ti/M}$  red shifted to about 520 nm, corresponding to a small band gap of 2.4 eV. The UV-vis results confirmed our original hypothesis that doping  $\text{Sr}^{2+}$  into  $\text{TiO}_2$  and coupling it with magnetic  $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$  could narrow the band gap of  $\text{TiO}_2$  and harvest visible light.

XPS has been conducted to approach the chemical states of  $\text{TiO}_2$  with and without doping Sr. As shown in Fig. 5a,  $\text{Ti/M}$  displayed  $\text{Ti } 2p_{3/2}$  and the  $\text{Ti } 2p_{1/2}$  binding energies at 458.6 and 464.2 eV, respectively, corresponding to a typical characteristic of the  $\text{Ti}^{4+}$  oxidation state.<sup>16,40</sup> Interestingly, the  $\text{Ti } 2p$  binding energies of  $\text{Sr}_{0.1}\text{Ti/M}$  slightly shifted to a lower level (by 0.4 eV). Similarly, doping  $\text{Sr}^{2+}$  into  $\text{TiO}_2$  also led to a chemical shift in the  $\text{O } 1s$  binding energy at 529.9 eV that is

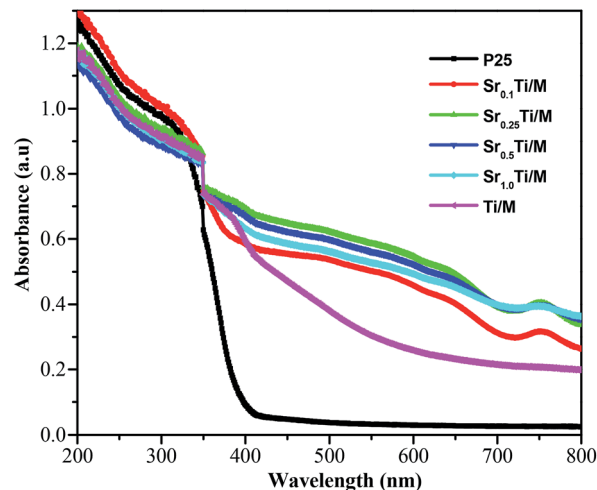


Fig. 4 UV-vis spectra for  $\text{Sr}^{2+}$ -doped  $\text{TiO}_2/\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$  nano-composites with different  $\text{Sr}^{2+}$  concentrations.

associated with lattice oxygen ( $\text{O}_l$ ) bonded to metal ions, while the  $\text{O } 1s$  related to surface oxygenated species ( $\text{O}_a$ ) (e.g., OH groups, adsorbed  $\text{H}_2\text{O}$ ) remained at a same position at 531.5 eV.<sup>45</sup> Moreover, the relative amount of  $\text{O}_l$  (by calculating the peak area ratio of  $\text{O}_l/(\text{O}_l + \text{O}_a)$  in Fig. 5b) in  $\text{Sr}_{0.01}\text{Ti/M}$  (78.6%) was slightly higher than that in  $\text{Ti/M}$  (74.8%). Generally, the chemical shifts in XPS spectra resulted from either the formation of a new oxidation state or the changes in the local chemical and physical environment. Because no shoulder peak for the new state of  $\text{Ti}^{3+}$  was observed in  $\text{Sr}_{0.1}\text{Ti/M}$ , the slight chemical shift is primarily related to a change in the local chemical environment of  $\text{TiO}_2$ . In other words,  $\text{Sr}^{2+}$  has been successfully doped into  $\text{TiO}_2$  lattice. Because some  $\text{Ti}^{4+}$  sites have been substituted by  $\text{Sr}^{2+}$  ions, some defects (e.g., oxygen vacancy,  $\text{V}_\text{O}$ ) were formed for charge compensation.<sup>16,29</sup> This is also supported by the XPS quantitative analysis that  $\text{Ti/M}$  has a higher ratio of  $\text{O}/(\text{Ti} + \text{Zn} + \text{Ni} + \text{Fe})$  (2.61) than does  $\text{Sr}_{0.1}\text{Ti/M}$  (2.02). Hence, the change in the chemical environment of  $\text{TiO}_2$  was possibly caused by the partial replacement of  $\text{Ti}^{4+}$  by  $\text{Sr}^{2+}$  dopants and the formation of  $\text{V}_\text{O}$  in  $\text{TiO}_2$ .

### 3.3 Photocatalytic performance measurement

Photocatalytic degradation of BPA over the hybrid  $\text{Sr}_x\text{Ti/M}$  was first conducted under UV (254 nm) irradiation. Fig. 6 compares the photodegradation efficiency of various  $\text{Sr}_x\text{Ti/M}$ . Right before the photodegradation, a background experiment was carried out without UV irradiation in the presence of  $\text{Sr}_{0.1}\text{Ti/M}$ . The result showed that in the dark process, the concentration of BPA almost remained same as the initial one within 4 h, indicating that no photocatalytic reaction took place without photo-illumination. At low contents of  $\text{Sr}^{2+}$ ,  $\text{Sr}_{0.1}\text{Ti/M}$  and  $\text{Sr}_{0.25}\text{Ti/M}$  exhibited similar photodegradation activity. Furthermore, increasing the concentration of  $\text{Sr}^{2+}$  resulted in a decrease in the activity over  $\text{Sr}_{0.5}\text{Ti/M}$  and  $\text{Sr}_{1.0}\text{Ti/M}$ . By correlating the structure and property of the materials (see the results in Table 1, Fig. 1 and 2), the inferior activity at a high content of  $\text{Sr}^{2+}$  is probably

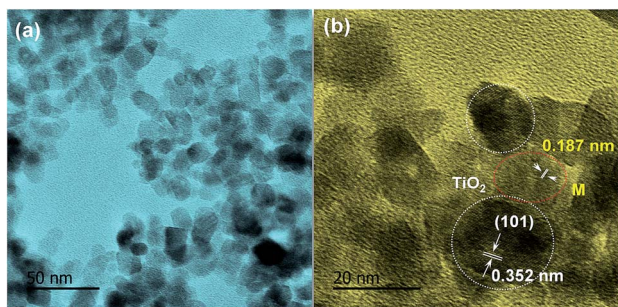


Fig. 3 (a) TEM and (b) HRTEM images for  $\text{Sr}_{0.1}\text{Ti/M}$  ( $\text{M} = \text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ ).



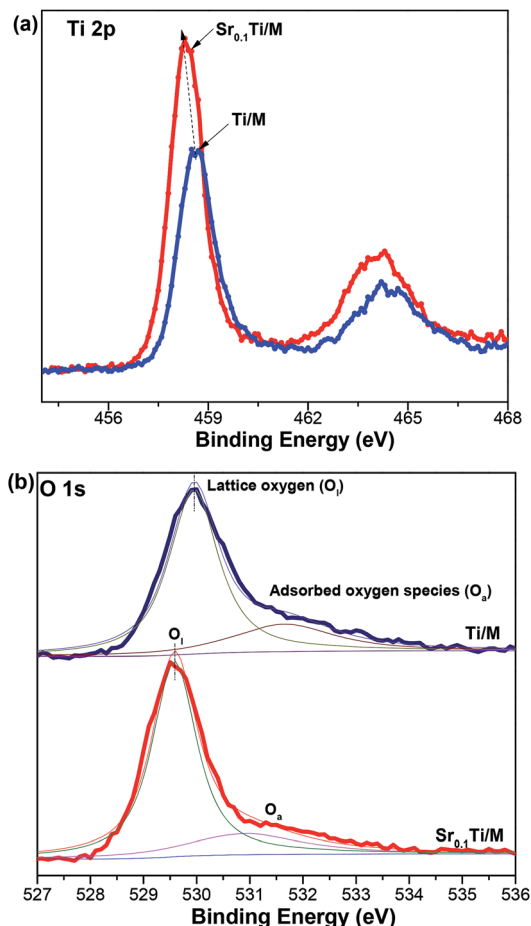


Fig. 5 XPS spectra for undoped  $\text{TiO}_2/\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$  and  $\text{Sr}_{0.1}\text{Ti}/\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$  composites: (a) Ti 2p, and (b) O 1s.

because  $\text{Sr}_{0.5}\text{Ti}/\text{M}$  and  $\text{Sr}_{1.0}\text{Ti}/\text{M}$  have larger crystalline sizes, smaller specific surface areas and pore volumes, and less uniform particle dispersions. These drawbacks on  $\text{Sr}_{0.5}\text{Ti}/\text{M}$  and  $\text{Sr}_{1.0}\text{Ti}/\text{M}$  could hinder the adsorption and activation of BPA on the surface. Excessive  $\text{Sr}^{2+}$  may also induce the formation of a new  $e^-$ - $h^+$  recombination center that shortened the lifetime of photogenerated charge carriers.<sup>28</sup> Another important result in Fig. 6 is that  $\text{Sr}_{0.1}\text{Ti}/\text{M}$  and  $\text{Sr}_{0.25}\text{Ti}/\text{M}$  displayed a considerably higher efficiency compared to  $\text{Ti}/\text{M}$ ,  $\text{Sr}_{0.25}\text{Ti}$ , commercial  $\text{TiO}_2(\text{P25})$ , and bare M.  $\text{Sr}_{0.1}\text{Ti}/\text{M}$  is able to eliminate nearly 100% BPA at 4 h, while  $\text{TiO}_2(\text{P25})$  and bare M can only reach 40% and 25%, respectively. In addition,  $\text{Sr}_{0.25}\text{Ti}$  and  $\text{Ti}/\text{M}$  was even more active than bare  $\text{TiO}_2(\text{P25})$  and M. In this regard, it is believed that there is a synergy between  $\text{Sr}^{2+}$  dopant and magnetic M that remarkably prevents the charge recombination in  $\text{TiO}_2$ , as a consequence of leading to a superior activity of  $\text{Sr}_{0.1}\text{Ti}/\text{M}$ .

We also performed photocatalytic degradation of BPA at different pH conditions using a  $\text{Sr}_{0.25}\text{Ti}/\text{M}$  composite under UV irradiation because the waste water may be acidic or basic. The initial pH of the reactant solution was controlled by adding a desired amount of NaOH or  $\text{HNO}_3$ . Fig. 7a compares the photocatalytic performance of  $\text{Sr}_{0.25}\text{Ti}/\text{M}$  in a pH range of 4–10. It

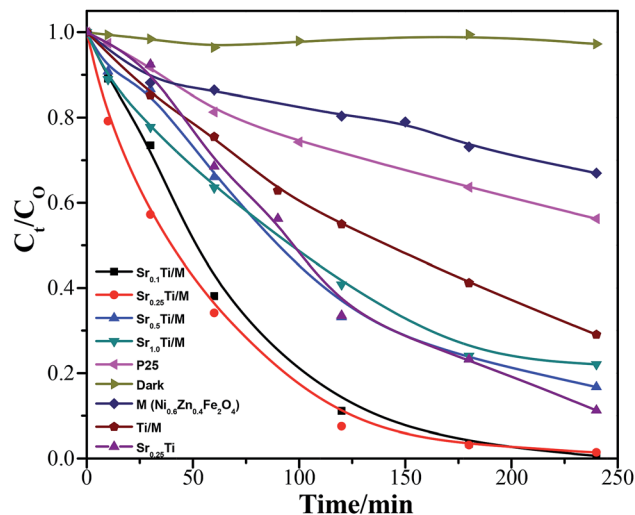


Fig. 6 Photodegradation of BPA by various  $\text{Sr}^{2+}$ -doped  $\text{TiO}_2/\text{M}$  ( $\text{M} = \text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ ) catalysts under UV-254 nm irradiation as a function of time (catalyst dosage =  $0.5 \text{ mg mL}^{-1}$ , initial BPA concentration = 10 ppm, near neutral pH).

was found that either at basic (pH = 10) or acidic conditions (pH = 4),  $\text{Sr}_{0.25}\text{Ti}/\text{M}$  displayed a higher efficiency than at near neutral conditions (pH = 6–8) within the beginning 2 h, while the efficiency eventually remained almost the same at the later stage and reached as high as nearly 99% at 3.5 h in the entire pH range (4–10). This result strongly suggested that our novel hybrid  $\text{Sr}_x\text{Ti}/\text{M}$  is able to efficiently work at a wide pH range. Moreover, the pH evolution during the photocatalytic reaction was also monitored, as shown in Fig. 7b. At a basic condition, the pH gradually decreased and reached a steady state to near neutral, while at an acidic condition, the initial pH gradually increased. If starting with a near neutral solution, the pH only slowly decreased. The evolution of solution pH revealed that both proton ( $\text{H}^+$ ) and  $\text{OH}^\cdot$  radicals play a critical role in the photodegradation of BPA. A possible mechanism has been proposed to explain the pH impacts, as shown in Fig. 8. The starting solution with a high pH contains more  $\text{OH}^-$  anions, which could act as hole ( $h^+$ ) scavengers and react with photo-generated  $h^+$  to form active  $\text{OH}^\cdot$  radicals (Fig. 8a).<sup>16,27</sup> Hence, the consumption of  $\text{OH}^-$  led to the decrease in pH over the reaction time. The  $\text{OH}^\cdot$  radicals have a strong oxidation ability to degrade BPA to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , which could explain why the activity is higher at pH = 10. On the other hand, the starting solution with a low pH contains more  $\text{H}^+$  ions, which serves as electron scavengers and inhibits the recombination of  $e^-$ - $h^+$  pairs (Fig. 8b). Moreover, the  $\text{H}^\cdot$  radicals, generated from  $\text{H}^+ + e^- \rightarrow \text{H}^\cdot$ , could react with  $\text{O}_2$  to form hydrogen peroxide that decomposes into oxidative  $\text{OH}^\cdot$  under UV irradiation.<sup>48</sup> Thus, the suppressed recombination and the formation of  $\text{OH}^\cdot$  leads to an increase in pH over time and a higher efficiency than at neutral pH values.

The photocatalytic performance of the  $\text{Sr}_x\text{Ti}/\text{M}$  samples was also evaluated under visible light (400–1000 nm) irradiation, as shown in Fig. 9. The order of activity of the hybrids was  $\text{Sr}_{0.1}\text{Ti}/\text{M}$



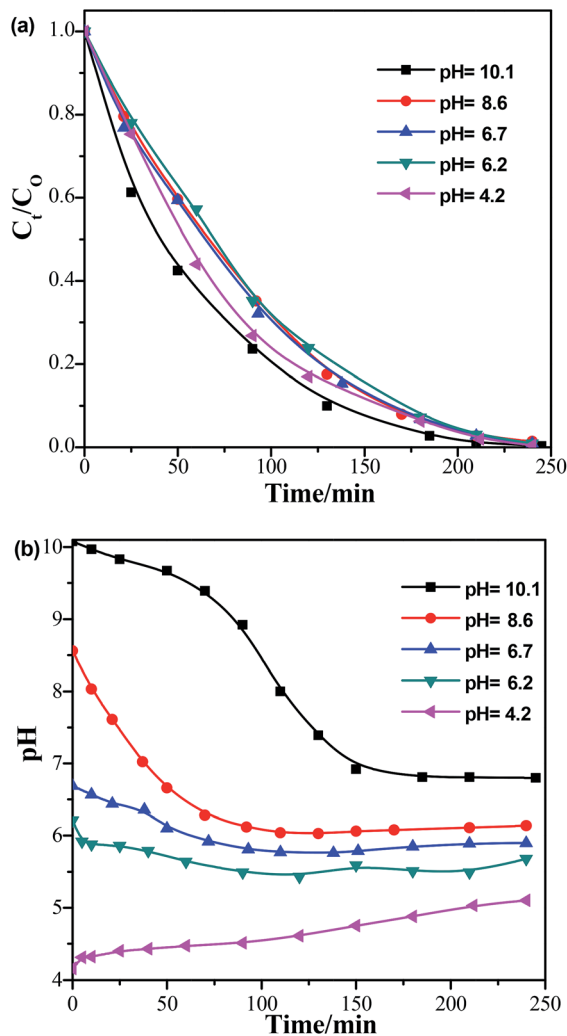


Fig. 7 Photodegradation of BPA by  $\text{Sr}_{0.25}\text{Ti}/\text{M}$  ( $\text{M} = \text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ ) under UV-254 nm irradiation (a) at different pH environments and (b) the evolution of pH as a function of time (catalyst dosage =  $0.5 \text{ mg ml}^{-1}$ , initial BPA concentration =  $10 \text{ ppm}$ ).

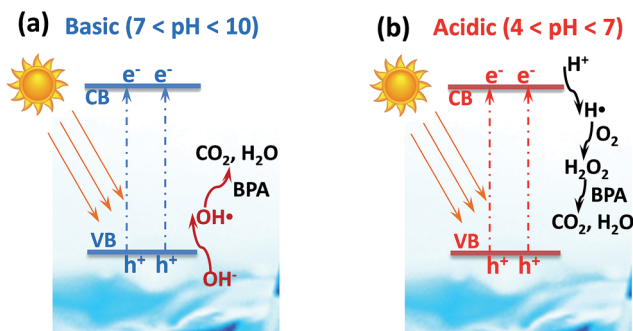


Fig. 8 The possible mechanism for BPA photodegradation under (a) basic and (b) acidic conditions.

$\text{M} > \text{Sr}_{0.25}\text{Ti}/\text{M} \approx \text{Sr}_{0.5}\text{Ti}/\text{M} \approx \text{Sr}_{1.0}\text{Ti}/\text{M} > \text{Sr}_{0.25}\text{Ti} > \text{Ti}/\text{M} > \text{P25} > \text{M}$ , which is very similar to the trend under UV irradiation (see Fig. 6). Even under visible light irradiation, the photodegradation efficiency of  $\text{Sr}_{0.1}\text{Ti}/\text{M}$  could reach as high as 90%

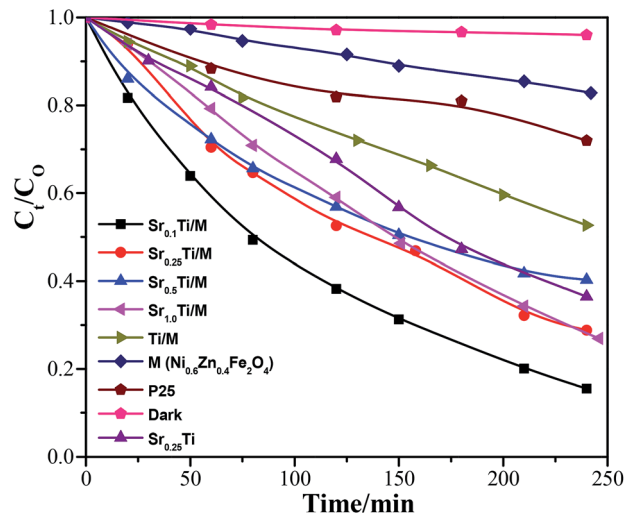


Fig. 9 Photodegradation of BPA by various  $\text{Sr}^{2+}$ -doped  $\text{TiO}_2/\text{M}$  ( $\text{M} = \text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ ) catalysts under visible light irradiation (400–1000 nm) as a function of time (catalyst dosage =  $0.5 \text{ mg ml}^{-1}$ , initial BPA concentration =  $10 \text{ ppm}$ , near neutral pH).

at 4 h, nearly 4 times higher than bare  $\text{TiO}_2(\text{P25})$  and  $\text{M}$  (only 15–20%). In addition to the larger surface area, smaller crystalline size, and more uniform particle dispersion, the superior performance of  $\text{Sr}_{0.1}\text{Ti}/\text{M}$  under visible light is probably also due to another two reasons. First, incorporating an appropriate amount of  $\text{Sr}^{2+}$  dopant and magnetic  $\text{M}$  with  $\text{TiO}_2$  narrowed its band gap (see UV-vis spectra in Fig. 4); thus, enhancing the harvest and utilization of visible light. Second, as evidenced by XPS results, doping  $\text{Sr}^{2+}$  into  $\text{TiO}_2$  also created some active defect sites (oxygen vacancies), which may induce the formation of the new energy state located below the conduction band minimum of  $\text{TiO}_2$ . The active defect sites could facilitate charge separation and trap electrons even under visible light.<sup>16,28,49</sup> The electrons accumulated at defect sites could easily attach on  $\text{O}_2$  molecules to produce powerful superoxide radicals ( $\text{O}_2^{\bullet-}$ ) that promote the activation and oxidation of BPA molecules.

### 3.4 Material separation and cycling performance

The above photocatalytic activity results indicated that among all the tested samples,  $\text{Sr}_{0.1}\text{Ti}/\text{M}$  has an outstanding performance under both UV and visible light irradiation. To further understand its superiority, we measured the cycling performance of  $\text{Sr}_{0.1}\text{Ti}/\text{M}$  during three runs of photodegradation alternations. In between each cycle, the spent  $\text{Sr}_{0.1}\text{Ti}/\text{M}$  was separated only by adding an external magnetic field around the solution and washed with water without any high temperature treatment or centrifugation. Above all, we measured the magnetic property of  $\text{Sr}_{0.1}\text{Ti}/\text{M}$  at room temperature using vibrating magnetometer. Fig. 10 shows the magnetization ( $M$ )–magnetic field ( $H$ ) loop of  $\text{Sr}_{0.1}\text{Ti}/\text{M}$ . It was found that  $\text{Sr}_{0.1}\text{Ti}/\text{M}$  exhibited a typical soft ferrite behavior with a saturated magnetization ( $M_s$ ) of  $19.04 \text{ emu g}^{-1}$ , the number of which was lower than the literature reported for pure  $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ .<sup>42,43</sup> This is because our  $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$  was





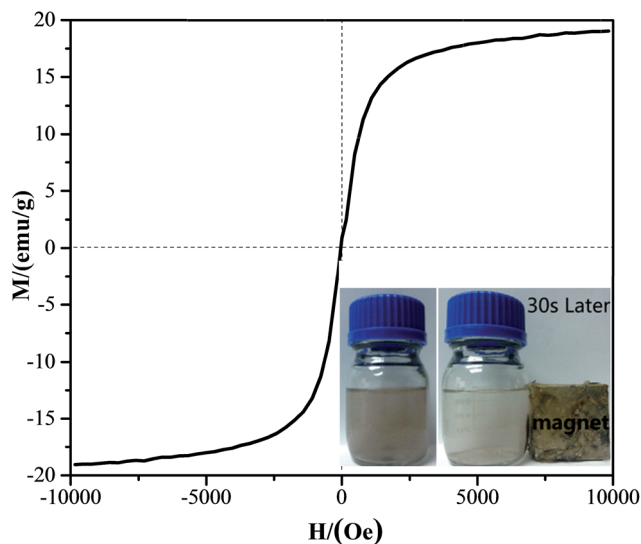


Fig. 10 Room temperature hysteresis behaviour of  $\text{Sr}_{0.1}\text{Ti/M}$  ( $\text{M} = \text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ ). Inset photograph shows a separation process of  $\text{Sr}_{0.1}\text{Ti/M}$  from aqueous solution using a magnet.

encapsulated with nonmagnetic  $\text{Sr}_{0.1}\text{TiO}_2$  nanoparticles. Although  $\text{Sr}_{0.1}\text{Ti/M}$  has a relatively low  $M_s$ , it still can be easily magnetically separated for reuse. As evidenced by the inset photograph in Fig. 10, the suspended solution quickly became clear once placing a magnet near the bottle wall for 30 s, and the powder was accumulated and attached on the wall.

Fig. 11 compares the photodegradation efficiency of  $\text{Sr}_{0.1}\text{Ti/M}$  in each cycle under both UV and visible light irradiation after 4 h. After three cycles, the efficiency in the 3<sup>rd</sup> run only slightly dropped at both conditions, but still maintained as high as 89% and 78% under UV and visible light irradiation, respectively. Obviously,  $\text{Sr}_{0.1}\text{Ti/M}$  demonstrated a good stability and recyclability, where M could provide a magnetic field for

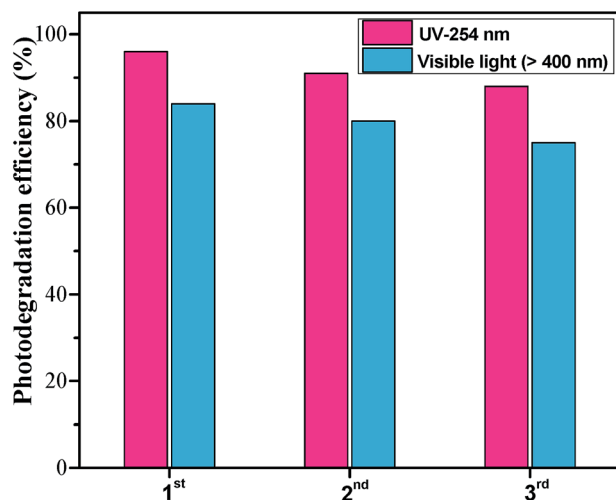


Fig. 11 The cycling performance of  $\text{Sr}_{0.1}\text{Ti/M}$  ( $\text{M} = \text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ ) for photodegradation of BPA under UV-254 nm and visible light (>400 nm) irradiation (in each cycle, BPA concentration = 10 ppm, near neutral pH).

separation and harvest visible light concurrently. This good cycling performance also confirms our original hypothesis that integrating metal ion doped photocatalysts (e.g.,  $\text{Sr-TiO}_2$ ) and magnetic materials (e.g.,  $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ ) is a reliable and convenient method to simultaneously enhance material separation and visible light activity for water purification.

## 4. Conclusions

In this work, we designed a novel hybrid photocatalyst/magnetic material, i.e.,  $\text{Sr}^{2+}$  doped  $\text{TiO}_2/\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ , in order to enhance the efficiency of photo-degrading organic pollutants under visible light and to easily separate and reuse the material. The hybrid was synthesized by a simple sol-gel method. We found that doping a low concentration of  $\text{Sr}^{2+}$  (below 0.25 wt%) induced a smaller crystalline size, larger surface area and pore volume, and more uniform particle dispersion than did loading a high concentration of  $\text{Sr}^{2+}$ . Moreover, doping  $\text{Sr}^{2+}$  ions and coupling a magnetic material with  $\text{TiO}_2$  narrowed the band gap and induced the generation of defect sites in  $\text{TiO}_2$ . As a result, the integrated hybrid with a low loading of  $\text{Sr}^{2+}$  not only demonstrated a high efficiency (over 90%) and a good recycling performance (90% maintenance) under both UV and visible light irradiation, but also can efficiently work at a wide pH range (4–10) and be easily separated only by adding an external magnetic field. Furthermore, the hybrid  $\text{Sr-TiO}_2/\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$  showed an over two-times higher activity than those of  $\text{TiO}_2/\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ , commercial  $\text{TiO}_2(\text{P}25)$  and bare  $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ , as well as 50% higher activity than that of  $\text{Sr}$ -doped  $\text{TiO}_2$ , indicating that there is a synergy between the doped photocatalyst and magnetic material. The findings in this work suggest a new direction to engineer a smart photocatalyst/magnetic material heterojunction and control the interface between them, and it sheds light on the material's application in other aqueous-solid phase photocatalytic reactions.

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