Transition-Metal Ion-Doped Flower-Like Titania Nanospheres as Nonlight-Driven Catalysts for Organic Dye Degradation with Enhanced Performances

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ABSTRACT: Titania has recently been identified as a new and effective nonlight-driven catalyst for degradation of organic pollutant with the use of H2O2, as an oxidant; however, either relatively low surface area or lack of diversity in chemical composition largely limits its catalytic performance. In this work, a series of transition-metal ion (Mn2+, Co2+, Ni2+, and Cu2+)-doped titania nanomaterials with regular flower-like morphology, good crystallinity (anatase), and large specific surface areas (71.4–124.4 m² g⁻¹) were facilely synthesized and utilized as catalysts for methylene blue (MB) degradation in the presence of H2O2 without light irradiation. It was revealed that the doping of transition-metal ions (especially Mn2+) into titania could significantly improve the catalytic efficiency. At 30 °C, 10 mL of MB with a concentration of 50 mg L⁻¹ could be completely degraded within 60–100 min for these doped samples, whereas the removal rate was only 35.1% within 100 min with the use of pure flower-like titania. Temperature-dependent kinetic studies indicated that the presence of transition-metal ion dopants could markedly lower the activation energy and thus resulted in enhanced catalytic performances. Test of reusability exhibited that these doped catalysts could well keep their original catalytic activities after reuse for several cycles, indicating their excellent catalytic durability.

1. INTRODUCTION

Titania (TiO2) has attracted widespread interest during past few decades owing to its high structural stability, nontoxicity, biocompatibility, and unique physicochemical characteristics.1–3 Significant successes in the application of titania have already been achieved, for instance, as a catalyst for photocatalytic degradation,4,5 as a solar-energy material for use in battery,6,7 and as a tool for sensing detection.8,9 Recently, considerable efforts have been also dedicated to determining the new application possibility of titania in other research fields.

It has long been known that exposure of TiO2 particles to hydrogen peroxide (H2O2) solution will enable the formation of a yellowish substance on the surface of TiO2, which has been identified as a surface titanium peroxide complex.10,11 Interestingly, this complex is proven to be readily transformed into reactive oxygen species, such as hydroxyl radical (·OH) and hydroperoxyl radical (·OOH), under ambient conditions. Accordingly, the TiO2–H2O2 oxidative systems have been widely studied in the context of nanoparticle toxicity because of their possible damage to physiological tissues.12,13 However, up until now, only a few studies have been carried out to investigate their potential applications in environmental remediation.14,15 Ogino et al.16 reported for the first time that the TiO2 particles after incubation in H2O2 solution could degrade methylene blue (MB) in the dark because of the strong oxidation ability of the surface titanium peroxide complex. Recently, Romanias et al.17 and Wiedmer et al.18 suggested a simplified protocol, that is, simultaneous addition of TiO2 and H2O2 to the MB solution without incubation treatment and found that the MB molecules could be also degraded effectively. Noticeably, these pioneering works not only confirmed the feasibility of using TiO2–H2O2 to degrade organic pollutants (e.g., MB) under nonlight-irradiation conditions but also opened new opportunities for expanding the application scope of TiO2. Unfortunately, almost all of these early used TiO2 samples possessed relatively small surface areas (i.e., 4.2–53.6 m² g⁻¹) with low porosities and therefore exhibited relatively weak catalytic abilities, which somewhat limited their applications.

Three-dimensional (3D) hierarchical structures have aroused significant research interests in recent years because of their novel properties and fundamental importance in various application fields.19–22 In particular, a number of unique 3D hierarchical structures (e.g., urchin-like and flower-like structures) well organized by low-dimensional nano-building units are found to be highly attractive catalysts.23,24 Compared to the nonporous or low-porosity structures, the 3D hierarchical structures usually possess larger surface areas and thus are expected to exhibit higher catalytic abilities. Moreover, they can provide much more exposed surface region, which will be fairly advantageous for facilitating easy access of...
reactants. Very recently, Liu et al.25 reported the fabrication of an urchin-like titania microstructure assembled by nanowires and its application as a nonlight-driven catalyst toward MB degradation in the presence of H2O2. Because of the large specific surface area (158.8 m² g⁻¹) and highly open structure, this titania indeed showed a significantly higher catalytic activity than the conventional TiO² samples (e.g., P25). Moreover, this catalyst was highly reusable for the H₂O₂-mediated MB degradation, that is, no significant activity loss after several cycles. Nevertheless, despite achieving high catalytic activities at relatively high temperatures (e.g., 60 °C), the catalyst was significantly less efficient when the reaction temperature was below 50 °C. Therefore, further efforts are still necessary to develop highly active hierarchical titania nanostructures, which can achieve high efficiencies especially at relatively low temperatures.

In fact, in many cases, tuning the chemical composition of a solid catalyst is also an efficient pathway to improve its catalytic activity.26 It is now well documented that many nontitania oxide catalysts, once doped with transition-metal ions, can exhibit markedly enhanced catalytic performances toward H₂O₂-mediated oxidative degradation. For example, Costa et al.27 introduced transition-metal ion (Co²⁺, Mn²⁺, and Cu²⁺) into the magnetite (Fe₃O₄) structure and found that the presence of these ion dopants could obviously increase the catalytic activity of the catalyst for the organic pollutant oxidation. Divya et al.28 fabricated a series of transition-metal ions (Cu²⁺, Fe³⁺, Zr⁴⁺, Dy³⁺, and La³⁺) incorporated ceria (CeO₂) materials and demonstrated that the resulting materials had largely enhanced activities in MB degradation as compared to pure ceria. Recently, our group synthesized several Mn²⁺-doped magnetite samples with different doping amounts and confirmed that the presence of Mn²⁺ dopant led to a more than twenty-fold increase in catalytic efficiency.29 Inspired by these impressive findings, we envisioned that the doping of some typical transition-metal ions into titania substrates, especially those with 3D hierarchical structures, might be able to address the current limitations of titania-based nonlight-driven catalysis.

Herein, we reported the synthesis of transition-metal ion (Mn²⁺, Co²⁺, Ni²⁺, and Cu²⁺)-doped 3D hierarchical titania nanospheres with flower-like morphologies by a simple “hydrothermal treatment—calcination” approach and their nonlight-driven catalytic performances toward H₂O₂-mediated MB degradation were systematically evaluated. The selection of Mn²⁺, Cu²⁺, Co²⁺, and Ni²⁺ as dopants was mainly because they have versatile redox chemistry which might be able to significantly improve the catalytic activity of titania.30−32 For comparison purpose, the flower-like titania nanospheres without metal ion doping were also fabricated. It was confirmed that the presence of transition-metal ion dopants (especially Mn²⁺) was indeed highly useful to improve the catalytic activity of titania. For instance, the Mn²⁺-doped titania nanoflowers could decompose 100% of MB within 60 min in the presence of H₂O₂ at 30 °C, whereas only 21.6% of MB was removed under identical conditions using the undoped sample as a catalyst. In addition, the degradation kinetics of undoped and doped samples at varied temperatures were investigated in depth and the results indicated that the presence of transition-metal ion dopants could markedly lower the activated energy and thus resulted in enhanced catalytic performances. Through test of reusability, it was revealed that all of these doped samples had excellent durability, showing relative constant activities after reuse for several cycles.

2. RESULTS AND DISCUSSION

2.1. Characterization of Materials. The transition-metal ion (i.e., Mn²⁺, Co²⁺, Ni²⁺, and Cu²⁺)-doped 3D hierarchical titania nanospheres were synthesized via a “hydrothermal treatment—calcination” process using amorphous TiO₂ spheres
as a precursor, as illustrated by Scheme 1. Corresponding to the types of dopants (Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$, and Cu$^{2+}$), the as-synthesized doped samples were designated as Mn-FTiO$_2$, Co-FTiO$_2$, Ni-FTiO$_2$, and Cu-FTiO$_2$, respectively. For comparison, the undoped TiO$_2$ (designated as FTiO$_2$) was also synthesized. Scanning electron microscopy (SEM) images for the as-synthesized samples are shown in Figure 1. Clearly, the TiO$_2$ precursor (pTiO$_2$) is composed of monodisperse and uniform spherical particles with diameters of 300−500 nm (Figure 1a). Upon hydrothermal treatment in ethylenediamine (EDA)−ethylene glycol (EG) solution at 150 °C for 24 h regardless of the absence or presence of transition-metal salt, these amorphous TiO$_2$ nanospheres would be etched by EDA because of their amorphous nature and converted to amine titanate.33 In all cases, the resulting amine titanate particles exhibited a unique flower-like architecture that is well organized by nanosheets (not shown). Moreover, these nanoflowers also display a high monodispersity, and their size is almost unchanged as compared to the pTiO$_2$ precursor. After calcination at 500 °C for 2 h, all of the samples (FTiO$_2$, Mn-FTiO$_2$, Co-FTiO$_2$, Ni-FTiO$_2$, and Cu-FTiO$_2$) still exhibit a 3D hierarchical flower-like morphology without significant aggregation (Figure 1b−f). However, there is some difference in the substructure between the calcined products. The nanosheets of Mn-FTiO$_2$, Co-FTiO$_2$, and Ni-FTiO$_2$ exhibit a decrease in regularity and a slight increase in thickness related to the FTiO$_2$ sample. Particularly, the flower-like architecture of Cu-FTiO$_2$ seems to be assembled by many nanograins rather than nanosheets.

Phase structures of FTiO$_2$, Mn-FTiO$_2$, Co-FTiO$_2$, Ni-FTiO$_2$, and Cu-FTiO$_2$ were investigated using an X-ray diffraction (XRD) technology, and the results are presented in Figure 2. The peaks in the XRD pattern of FTiO$_2$ should be assigned to the diffractions of (101), (103), (105), (004), (200), (204), (112), (116), (211), and (220) crystalline facets of anatase (JCPDS card; no. 21-1272), reflecting that FTiO$_2$ is composed of pure anatase.34 From Figure 2b−e, one can see that the doped samples (Cu-FTiO$_2$, Co-FTiO$_2$, Ni-FTiO$_2$, and Mn-FTiO$_2$) are still characteristic of anatase and only exhibit a slight decrease in the intensity as compared to FTiO$_2$. Moreover, no other diffraction peaks appear, indicating that the metal ions have been doped successfully into the TiO$_2$ lattice. Further investigations were conducted to confirm the existence of doped metal ions and to identify their oxidation states through UV-diffuse reflectance spectroscopy (DRS) and X-ray photoelectron spectroscopy (XPS) analyses. As shown in Figure 3, FTiO$_2$ shows a strong absorption edge at 383 nm, corresponding to the energy gap of 3.2 eV, which should be explained by the electronic transition from the valence band of TiO$_2$ to its conduction band.35 Upon incorporation of metal ions, the absorption edge displays an obvious shift to the red light zone, leading to various degree of change for energy gap values (2.6 eV for Mn-FTiO$_2$, 2.9 eV for Co-FTiO$_2$, 3.1 eV for Ni-FTiO$_2$, and 3.1 eV for Cu-FTiO$_2$). Moreover, the doping of transition-metal ions also makes the color significantly deepen in comparison with the initial white of FTiO$_2$ (insets of Figure 3). These observations in combination with the XRD results further support the successful introduction of transition-metal ions into the TiO$_2$ lattice. Figure 4 gives the XPS survey spectra in which the carbon peak should result from surface contamination because of exposure to air. In addition, the evident 2p peaks appear in the spectrum of each doped sample; however, no corresponding peaks exist in the XPS spectrum of FTiO$_2$. The high-resolution XPS spectrum of the Ti 2p region indicates that Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ have the binding energies of 459.5 and 465.2 eV, respectively. The separation value (5.7 eV) between the two peaks should be assigned to the Ti$^{4+}$ ions in FTiO$_2$.36 The 2p$_{3/2}$ peaks are found at 855.4, 779.4, 933.3, and 641.7 eV, whereas the 2p$_{1/2}$ peaks are located at binding energies of 873.1, 795.2, 953.0, and 653.7 eV for Ni-FTiO$_2$, Co-FTiO$_2$, Cu-FTiO$_2$, and Mn-FTiO$_2$, respectively, revealing that the oxidation states for all of these investigated transition-metal ions are +2, well consistent with the previously reported XPS data.37−40 Moreover, the separation value (17.7 eV) between Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ peaks also reflects that Ni is presented in the form of Ni$^{2+}$ in the Ni-FTiO$_2$ sample. The XPS analysis also indicates an oxidation state of +2 for Co in Co-FTiO$_2$ because the separation value (15.8 eV) is very close to the reported result (16 eV). In addition, there are strong shake-up satellites in the spectra of both Ni-FTiO$_2$ and Co-FTiO$_2$, which provide a further evidence of the oxidation state of +2.

Porous characteristics of the as-synthesized materials were investigated by analyzing the nitrogen adsorption/desorption isotherms. As illustrated by Figure 5, all of these isotherms exhibit typical type IV curves, which reflect the characteristics of mesoporous materials.35 Pore size distribution obtained by the Barrett−Joyner−Halenda (BJH) method shows a relatively narrow mesopore distribution (Figure 5b−e). The texture parameters were further calculated, and the results are summarized in Table 1. Evidently, the 3D hierarchical flower-like structures of FTiO$_2$, Mn-FTiO$_2$, Co-FTiO$_2$, Ni-
FTiO₂ and Cu-FTiO₂ endow them with large surface areas (71.4−124.4 m² g⁻¹) and relatively high porosities (0.16−0.50 cm³ g⁻¹). Such textual characteristics should be considerably beneficial for achieving high catalytic performances.

2.2. Catalytic Performances. Availability of Mn-FTiO₂, Co-FTiO₂, Ni-FTiO₂, and Cu-FTiO₂ as non-light-driven catalysts for organic pollutant degradation was studied in neutral aqueous solutions with the use of H₂O₂ as an oxidant. MB, a well-known organic dye, was chosen as a model pollutant to test catalytic efficiency of these samples. For comparison purpose, the catalytic performance of FTiO₂ toward MB was also studied. From Figure 6, it can be seen that FTiO₂ exhibits a considerably limited catalytic ability for the degradation of MB at 30 °C and only about 35.1% of MB molecules is degraded within 100 min. Instead, the doped samples show high catalytic efficiencies (Figure 6b−e). Under identical conditions, the MB can be degraded completely within 60−100 min using the doped samples as catalysts (i.e., 60 min for Mn-FTiO₂ and Co-FTiO₂; 100 min for Ni-FTiO₂ and Cu-FTiO₂). Obviously, the transition-metal ion doping indeed significantly enhances the catalytic performance. Moreover, a number of previous studies have showed that the times required to achieve a nearly complete removal of MB (≤50 mg L⁻¹) for some heterogeneous catalysts are in the range of 120−1200 min, for example, 120 min for Prussian-blue-modified γ-Fe₂O₃ (MB = 20 mg L⁻¹), 240 min for Fe₃O₄/FeMnO₆ (MB = 25 mg L⁻¹), 240 min for manganese-functionalized silicate (MB = 50 mg L⁻¹), 300 min for α-Fe₂O₃/MCM-41 (MB = 10 mg L⁻¹), 360 min for GT-Fe NPs (MB = 50 mg L⁻¹), and 1200 min for Bi₂CuO₄ (MB = 20 mg L⁻¹). The time values (60−100 min) reported in this study are lower than the bottom value of the range, suggesting

| samples      | FTiO₂ | Mn-FTiO₂ | Co-FTiO₂ | Ni-FTiO₂ | Cu-FTiO₂ |
|--------------|-------|----------|----------|----------|----------|
| surface area (m² g⁻¹) | 85.7  | 124.4    | 131.5    | 81.9     | 71.4     |
| pore size (nm)    | 3.5   | 8.0      | 21.0     | 5.7      | 16.8     |
| pore volume (cm³ g⁻¹) | 0.28  | 0.36     | 0.50     | 0.16     | 0.31     |

FTiO₂ and Cu-FTiO₂ endow them with large surface areas (71.4−124.4 m² g⁻¹) and relatively high porosities (0.16−0.50 cm³ g⁻¹). Such textual characteristics should be considerably beneficial for achieving high catalytic performances.

**Table 1. Detailed Textural Parameters of the Undoped and Doped Samples**
the high catalytic activities of these transition-metal ion-doped FTiO$_2$.

In order to further ascertain contribution of FTiO$_2$, Mn-FTiO$_2$, Co-FTiO$_2$, Ni-FTiO$_2$, and Cu-FTiO$_2$ to the MB degradation, several control experiments were carried out and the obtained results are presented in Figure 6f. Not surprisingly, the MB exhibits an almost unchanged concentration over the whole investigated process without additions of any catalyst and H$_2$O$_2$ because MB itself is chemically stable in aqueous solution. Moreover, it is observed that the use of H$_2$O$_2$ alone only induces a negligible MB degradation within 100 min. When undoped or doped titania is added without the use of H$_2$O$_2$ only a small part (<5%) of MB molecules is removed, indicating that there is a weak interaction between MB molecules and the surfaces of these materials investigated. In combination of results shown in Figure 6a−e, it can be concluded that the MB degradation is mediated by H$_2$O$_2$, which can be effectively promoted by the TiO$_2$-based catalysts, especially these doped samples.

Subsequent experiments were conducted with temperatures ranging from 30 to 50 °C so as to detect the influence of reaction temperature on the catalytic degradation of MB; the results are shown in Figure 7. By observing the plots of ln($C_0/C_t$) versus time, it can be found that the degradation reactions of MB generally obey the pseudo-first-order kinetic model in all cases. Accordingly, the rate constant $k$ values (min$^{-1}$ m$^{-2}$) were calculated, and the data are summarized in Table 2. The reaction rate constants increase with increasing reaction temperature, which well agrees with the previously reported results.$^{29}$ Moreover, the rate constants of transition-metal ion-doped samples are always much higher than that of undoped FTiO$_2$ under the identical conditions, further implying that the doping of transition-metal ions is very effective in promoting the catalytic efficiency. Here, it should be noted that although the doped samples have identical doping contents of transition-metal ions (M$^{2+}$/Ti$^{4+}$ = 1:20; M$^{3+}$: Mn$^{2+}$, Co$^{2+}$, Cu$^{2+}$, or Ni$^{2+}$), their specific surface areas differ from each other (Table 1). Thus, further analysis is necessary to obtain reliable quantitative structure−activity relationships. According to the previously reported method,$^{48,49}$ the pseudo-first-order kinetic constants can be normalized to the surface areas of

![Table 2. Reaction Rate Constants of Different Systems under Varied Temperatures](image)

![Figure 6. UV−vis spectra of degradation of MB (50 mg L$^{-1}$) with different catalysts (a−e), degradation kinetic curves of different systems (f).](image)

![Figure 7. Fitting curves of kinetic data under different reaction temperatures and the corresponding plots of ln $k$ vs 1/T.](image)
catalysts, thereby offering the practical descriptors of contaminant degradation kinetics. In our catalytic systems, each catalyst dosage was set at 0.005 g; thus, the absolute surface areas of FTiO₂, Mn-FTiO₂, Co-FTiO₂, Ni-FTiO₂, and Cu-FTiO₂ were estimated to be 0.4285, 0.6220, 0.6575, 0.4095, and 0.3570 m², respectively. Accordingly, the surface-area-normalized kinetic constants (k_<script>SA</script>, min⁻¹ m⁻²) were calculated out, and the data are also listed in Table 2. Results show that the catalytic activities of these undoped and doped samples should be ranked as follows: Mn-FTiO₂ > Cu-FTiO₂ > Ni-FTiO₂ ≅ Co-FTiO₂ > FTiO₂.

Then, the activation energy (E_a) can be calculated according to the Arrhenius formula: k = A exp(⁻E_a/RT), in which k represents the kinetic constant; A represents the pre-exponential factor; R represents the gas constant with a value of 8.314 J K⁻¹ mol⁻¹; and T represents the reaction temperature in kelvin. As the results presented, the E_a for MB degradation of FTiO₂ reaches 52.23 kJ mol⁻¹, which is much higher than those with the use of the doped samples as catalysts (27.34 for Co-FTiO₂, 29.95 for Mn-FTiO₂, 30.59 for Ni-FTiO₂, and 31.64 kJ mol⁻¹ for Cu-FTiO₂). These results indicate that the introduction of transition-metal dopants can obviously lower the activation energy. Consequently, it can be understandable that the doped samples show enhanced catalytic performances for degradation of MB as compared to the pure titania sample (i.e., FTiO₂). Meanwhile, it is also found that the catalytic activity order of the four doped samples is inconsistent with the magnitude of the dopants can obviously lower the activation energy, which may due to the diverse Arrhenius pre-exponential factors.

The stability and recyclability of heterogeneous catalysts are crucial for their use in long-term processes. For this reason, we tested the reusability of Mn-FTiO₂, Co-FTiO₂, Ni-FTiO₂, and Cu-FTiO₂ by repeatedly using them as catalysts for H₂O₂-mediated degradation of MB. After each cycle, the catalysts were collected via centrifugation and then washed with water for the subsequent catalysis cycle. Five consecutive cycles were studied, and the results are presented in Figure 8. Evidently, the removal efficiencies of MB catalyzed by all of the doped samples remain almost unchanged after five cycles. Compared with some recently reported heterogeneous catalysts such as Fe⁹⁻Fe₃O₄⁻RGO (removal efficiency decreased by 25.6% after 5 cycles), Fe₈O₆@SiO₂ (removal efficiency decreased by 57.5% after 5 cycles), Fe₉S₇B₁₃ (removal efficiency decreased by 29.6% after 4 cycles), Fe@C-BN (removal efficiency decreased by 37.2% after 5 cycles), and Cu/MnO₂, (removal efficiency decreased by 33.3% after 5 cycles), our catalysts show significantly more satisfactory reusability.

3. CONCLUSIONS

In summary, a series of transition-metal ion-doped TiO₂-based catalysts (Mn-FTiO₂, Co-FTiO₂, Ni-FTiO₂, and Cu-FTiO₂) were successfully synthesized with 3D hierarchical flower-like morphology, anatase crystal phase, and large surface areas (71.4–124.4 m² g⁻¹). Owing to the remarkable textural features and the presence of transition-metal ion dopants, the doped catalysts, especially Mn-FTiO₂, were proven to be highly efficient for MB degradation at relatively low temperature (i.e., 30 °C). Compared to FTiO₂, the doped catalysts can significantly lower the activation energies for oxidative degradation of MB and thus display notably faster catalytic kinetics. In addition, the as-fabricated catalysts remained high activities even after being recycled several times, demonstrating their excellent durability. Further investigation on the activated mechanism of H₂O₂ by these doped catalysts is in progress. We believe that the transition-metal ion-doped TiO₂ nanomaterials developed in this work will be very promising for decontamination of wastewater-containing organic pollutants.

4. EXPERIMENTAL SECTION

4.1. Chemicals and Reagents. EDA, acetonitrile, EG, concentrated ammonium hydroxide (NH₄H₂O, 28 wt %), ethanol, hydrogen peroxide (H₂O₂, 30 wt %), manganese chloride tetrahydrate (MnCl₂·4H₂O), cobalt chloride hexa-hydrate (CoCl₂·6H₂O), nickel chloride hexahydrate (NiCl₂·6H₂O), copper chloride dehydrate (CuCl₂·2H₂O), and MB were all purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Titanium isopropoxide (98%) was obtained from by J&K Scientific Ltd. (Beijing).

4.2. Material Synthesis. First, an amorphous TiO₂ precursor (designated as pTiO₂) with the monodisperse spherical morphology was prepared according to the previously reported procedure. Afterward, transition-metal ion-doped TiO₂ catalysts were synthesized via a hydrothermal treatment followed by a calcination process. Briefly, 0.4 g of TiO₂ powders (5 mmol) was dispersed in a mixed solution containing 32 mL of EG and 8 mL of H₂O₂ in which 0.25 mmol of transition-metal chloride (i.e., MnCl₂·4H₂O, CoCl₂·6H₂O, NiCl₂·6H₂O, or CuCl₂·2H₂O) was predissolved. Then, 96 mL of EDA was added rapidly under stirring. The mixture was sealed in a 200 mL Teflon-lined autoclave. The hydrothermal reaction was carried out at 150 °C for 24 h, and then the reaction solution was allowed to be cooled to room temperature. The solid powders were collected via centrifugation, followed by repeatedly washing with water and ethanol. The final products (Mn-FTiO₂, Co-FTiO₂, Ni-FTiO₂, and Cu-FTiO₂) were formed by calcination at 500 °C for 2 h with a heating rate of 1 °C min⁻¹. For comparison, the undoped FTiO₂ was also synthesized according to the same process without addition of transition-metal salt.

4.3. Material Characterization. Morphologies and sizes of the as-synthesized samples were determined on a field-emission scanning electron microscope (SEM, SU8010, Hitachi, Japan). XRD analyses were performed on an X-ray diffractometer (D8-FOCUS, Bruker, Germany). Nitrogen adsorption/desorption measurements were carried out on a Micromeritics ASAP2020 surface area analyzer at a temperature of 77 K. Absorbance spectra were recorded by a UV–vis
diffuse reflectance spectrometer (UV-DRS, UV-2550PC, Shimadzu Co., Japan). XPS analyses were investigated using a VG Scientific ESCALAB Mark II spectrometer that was equipped with two ultrahigh vacuum chambers.

4.4. Catalytic Activity Testing. Catalytic activities of the as-synthesized catalysts were examined by MB degradation in the presence of H$_2$O$_2$. Typically, 20 mL of MB solution (50 mg L$^{-1}$) containing 4.5 wt % H$_2$O$_2$ was added into a glass bottle that contained 10 mg of solid catalyst (0.5 g L$^{-1}$), and the resulting mixture was shaken (200 rpm) in the dark at 30 °C. At different time points, the catalyst powders were separated from the reaction solution by filtration. MB concentrations in the course of degradation were determined using the UV-vis spectrophotometer to monitor the absorption intensity at a wavelength of 665 nm.

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Notes

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REFERENCES

1. Lai, Y.; Huang, J.; Cui, Z.; Ge, M.; Zhang, K.-Q.; Chen, Z.; Chi, L. Recent advances in TiO$_2$-based nanosized surfaces with controllable wettability and adhesion. Small 2016, 12, 2201–2224.
2. Chen, X.; Mao, S. S. Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications. Chem. Rev. 2007, 107, 2891–2959.
3. Linsebigler, A. L.; Lu, G.; Yates, J. T. Photocatalysis on TiO$_2$ surfaces: Principles, mechanisms, and selected results. Chem. Rev. 1995, 95, 753–758.
4. Pitchaimuthu, S.; Honda, K.; Suzuki, S.; Naito, A.; Suzuki, N.; Katsumata, K.-i.; Nakata, K.; Ishida, N.; Kitamura, N.; Idenoto, Y.; Kondo, T.; Yusa, M.; Takai, O.; Ueno, T.; Saito, N.; Fujishima, A.; Terasima, C. Solution Plasma Process-Derived Defect-Induced Heterophase Anatase/Brookite TiO$_2$ Nanocrystals for Enhanced Gaseous Photocatalytic Performance. ACS Omega 2018, 3, 898–905.
5. Konstantinou, I. K.; Albannis, T. A. TiO$_2$-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations a review. Appl. Catal B: Environ. 2004, 49, 1–14.
6. Longoni, G.; Pena Cabrera, R. L.; Polizzi, S.; D’Arienzo, M.; Mari, C. M.; Cui, Y.; Ruffo, R. Shape-controlled TiO$_2$ nanocrystals for Na-ion battery electrodes: The role of different exposed crystal facets on the electrochemical properties. Nano Lett. 2017, 17, 992–1000.
7. Liu, H.; Li, W.; Shen, D.; Zhao, D.; Wang, G. Graphitic carbon conformal coating of mesoporous TiO$_2$ hollow spheres for high-performance lithium ion battery anodes. J. Am. Chem. Soc. 2015, 137, 13161–13166.
8. Zhu, Z.; Chang, J.-L.; Wu, R.-J. Fast ozone detection by using a core–shell Au@TiO$_2$ sensor at room temperature. Sens. Actuators B 2015, 214, 56–62.
9. Nikfarjam, A.; Salehifar, N. Improvement in gas-sensing properties of TiO$_2$ nanofiber sensor by UV irradiation. Sens. Actuators B 2015, 211, 146–156.
10. Ohno, T.; Masaki, Y.; Hirayama, S.; Matsumura, M. TiO$_2$-photocatalyzed epoxidation of 1-decene by H$_2$O$_2$ under visible light. J. Catal. 2001, 204, 163–168.
11. Matsubara, C.; Kawamoto, N.; Takamura, K. Oxo[5, 10, 15, 20-tetra(4-pyridyl)porphyrinato]titanium(IV): an ultra-high sensitivity spectrophotometric reagent for hydrogen peroxide. Analyst 1992, 117, 1781–1784.
12. Fubini, B.; Ghiazzia, M.; Fenoglio, I. Physico-chemical features of engineered nanomaterials relevant to their toxicity. Nanotoxicology 2010, 4, 347–363.
13. Fenoglio, I.; Greco, G.; Livraghi, S.; Fubini, B. Non-UV-Induced radical reactions at the surface of TiO$_2$ nanoparticles that may trigger toxic responses. Chem. – Eur. J. 2009, 15, 4614–4621.
14. Garcia, J.; Oliveira, J.; Silva, A.; Oliveira, C.; Nozaki, J.; Desouza, N. Comparative study of the degradation of real textile effluents by photocatalytic reactions involving UV/TiO$_2$/H$_2$O$_2$ and UV/Fe$^{2+}$/H$_2$O$_2$ systems. J. Hazard. Mater. 2007, 147, 105–110.
15. Harir, M.; Gaspar, A.; Kanawati, B.; Fekete, A.; Fromberger, M.; Martens, D.; Kettrup, A.; El Azzouzi, M.; Schmitt-Kopplin, P. Photocatalytic reactions of imazamox at TiO$_2$, H$_2$O$_2$ and TiO$_2$/H$_2$O$_2$ in water interfaces: Kinetic and photoproducts study. Appl. Catal B: Environ. 2008, 84, 524–532.
16. Ogino, C.; Dadjour, M. F.; Iida, Y.; Shimizu, N. Decolorization of methylene blue in aqueous suspensions of titanium peroxide. J. Hazard. Mater. 2008, 153, 551–556.
17. Romanias, M. N.; El Zein, A.; Bedjanian, Y. Heterogeneous interaction of H$_2$O$_2$ with TiO$_2$ surface under dark and UV light irradiation conditions. J. Phys. Chem. A 2012, 116, 8191–8200.
18. Wiedmer, D.; Sagstuen, E.; Welch, K.; Haugen, H. J.; Tiainen, H. Oxidative power of aqueous non-irradiated TiO$_2$–H$_2$O$_2$ suspensions: Methylene blue degradation and the role of reactive oxygen species. Appl. Catal B: Environ. 2016, 198, 9–15.
19. Adhikari, S.; Charanpahari, A. V. K.; Madras, G. Solar-Light-Driven Improved Photocatalytic Performance of Hierarchical ZnIn$_2$S$_4$ Architectures. ACS Omega 2017, 2, 6926–6938.
20. Chen, R.; Zhao, T.; Lu, J.; Wu, F.; Li, L.; Chen, J.; Tan, G.; Ye, Y.; Amine, K. Graphene-based three-dimensional hierarchical sandwich-type architecture for high-performance Li/S batteries. Nano Lett. 2013, 13, 4642–4649.
21. Liu, Z.; Nie, H.; Yang, Z.; Zhang, J.; Jin, Z.; Lu, Y.; Xiao, Z.; Huang, S. Sulfur-nitrogen co-doped three-dimensional carbon foams with hierarchical pore structures as efficient metal-free electrocatalysts for oxygen reduction reactions. Nanoscale 2013, 5, 3283–3288.
22. Ding, Y.-S.; Shen, X.-F.; Gomez, S.; Luo, H.; Aindow, M.; Suib, S. L. Hydrothermal growth of manganese dioxide into three-dimensional hierarchical nanoarchitectures. Adv. Funct. Mater. 2006, 16, 549–555.
23. Mendoza-Garcia, A.; Su, D.; Sun, S. Sea urchin-like cobalt–iron phosphide as an active catalyst for oxygen evolution reaction. Nanoscale 2016, 8, 3244–3247.
24. Moretti, E.; Storaro, L.; Talon, A.; Lenarda, M.; Riello, P.; Frattini, R.; de Yuso, M. d. V. M.; Jiménez-López, A.; Rodríguez-Castellón, E.; Ternero, F.; Caballero, A.; Holgado, J. P. Effect of thermal treatments on the catalytic behaviour in the CO preferential oxidation of a CuO–CeO$_2$–ZrO$_2$ catalyst with a flower-like morphology. Appl. Catal B: Environ. 2011, 102, 627–637.
25. Liu, Z.; Wang, T.; Yu, X.; Gong, Z.; Sang, Y.; Liu, H. In situ alternative switching between Ti$^{4+}$ and Ti$^{3+}$ driven by H$_2$O$_2$ in TiO$_2$ nanostructures: Mechanism of pseudo-Fenton reaction. Mater. Chem. Front. 2017, 1, 1989–1994.
26. Zhou, Z.; Ye, J.; Sayama, K.; Arakawa, H. Direct splitting of water under visible light irradiation with an oxide semiconductor photocatalyst. Nature 2001, 414, 625–627.
(27) Costa, R.; Leis, M.; Oliveira, L.; Fabris, J.; Ardisson, J.; Rios, R.; Silva, C.; Lago, R. Novel active heterogeneous Fenton system based on Fe3+−Mn4+O2− (Fe, Co, Mn, Ni): the role of M4+ species on the reactivity towards H2O2 reactions. J. Hazard. Mater. 2006, 129, 171−178.

(28) Divya, T.; Renuka, N. K. Modulated heterogeneous Fenton-like activity of M-doped nanocrystallites: Radio-frequency thermal plasma nanoparticles as a Fenton-type catalyst for water purification by Cotman, M.; Pintar, A.; Kaucigel process. Nanoscale Res. Lett. 2013, 25, 808−817.

(29) Li, M.; Gao, Q.; Wang, T.; Gong, Y.-S.; Han, B.; Xia, K.-S.; Zhou, C.-G. Solvothermal synthesis of MnFe2O4 nanoparticles with interesting physicochemical characteristics and good catalytic degradation activity. Mater. Des. 2016, 97, 341−348.

(30) Surpățeanu, M.; Zaharia, C. Advanced oxidation processes for decolorization of aqueous solution containing Acid Red G azo dye. Open Chem. 2004, 2, 573−588.

(31) Rashad, M. M.; Elsayed, E. M.; Al-Kotb, M. S.; Shalan, A. E. The structural, optical, magnetic and photocatalytic properties of transition metal ions doped TiO2 nanoparticles. J. Alloys Compd. 2013, 581, 71−78.

(32) Shalan, A. E.; Rashy, M.; Rashad, M. M. Organic acid precursor synthesis and environmental photocatalysis applications of mesoporous anatase TiO2 nanorods with different transition metal ions. J. Mater. Sci. 2014, 25, 3141−3146.

(33) Jitpuppi, J.; Rattanavoravipa, T.; Chuangchote, S.; Pavasupree, S.; Suzuki, Y.; Yoshikawa, S. Low temperature hydrothermal synthesis of monodisperssed flower-like titania nanosheets. Catal. Commun. 2009, 10, 379−382.

(34) Nag, M.; G combustion, and morphology of titania nanoparticles with peroxotitaniaan complex: Experimental and theoretical insights. J. Phys. Chem. Lett. 2010, 1, 2881−2885.

(35) Chen, X.; Burda, C. The electronic origin of the visible-light absorption properties of C-, N- and S-doped TiO2 nanomaterials. J. Am. Chem. Soc. 2008, 130, 5018−5019.

(36) Ren, Z.-H.; Li, H.-T.; Gao, Q.; Wang, H.; Han, B.; Xia, K.-S.; Zhou, C.-G. An nanoparticle embedded on urilichine-like TiO2 nanosphere: An efficient catalyst for dyes degradation and 4−nitrophenol reduction. Mater. Des. 2017, 121, 167−175.

(37) Tian, J.; Gao, H.; Kong, H.; Yang, P.; Zhang, W.; Chu, J. Influence of transition metal doping on the structural, optical, and magnetic properties of TiO2 films deposited on Si substrates by a sol−gel process. Nanoscale Res. Lett. 2013, 8, 533−543.

(38) Li, J.-G.; Büchel, R.; Isobe, M.; Mori, T.; Ishigaki, T. Cobalt-doped TiO2 nanocrystallites: Radio-frequency thermal plasma preparation, phase structure, and magnetic properties. J. Phys. Chem. C 2009, 113, 8009−8015.

(39) Khalid, N. R.; Ahmad, E.; Hong, Z.; Ahmad, M.; Zhang, Y.; Khalid, S. Cu-doped TiO2 nanoparticles/graphene composites for efficient visible-light photocatalysis. Ceram. Int. 2013, 39, 7107−7113.

(40) Zheng, W.; Zhou, Z.; Wright, J. H.; Kim, Y. N.; Liu, D.; Xiao, X. Mn-doped TiO2 nanosheet-based anodes as anode materials for lithium-ion batteries with high performance at elevated temperatures. ACS Appl. Mater. Interfaces 2014, 6, 7292−7300.

(41) Gao, Q.; Xu, W.; Xu, Y.; Wu, D.; Sun, Y.; Deng, F.; Shen, W. Amino acid adsorption on mesoporous materials: Influence of types of amino acids, modification of mesoporous materials, and solution conditions. J. Phys. Chem. B 2008, 112, 2261−2267.

(42) Wang, H.; Huang, Y. Prussian-blue-modified iron oxide magnetic nanoparticles as effective peroxidase-like catalysts to degrade methylene blue with H2O2. J. Hazard. Mater. 2011, 181, 163−169.

(43) Chen, F.; Gao, Q.; Wang, H.; Yang, P.; Zhang, W.; Wu, Y. Characterization and reactivity of Fe3O4/FcMnO4 core/shell nanoparticles for methylene blue discoloration with H2O2. Appl. Catal. B: Environ. 2011, 107, 386−392.

(44) Tušar, N. N.; Maučec, D.; Rangus, M.; Arčon, I.; Mazaj, M.; Cotman, M.; Pintar, A.; Kaucigel, V. Manganese functionalized silicate nanoparticles as a Fenton-type catalyst for water purification by advanced oxidation processes (AOP). Adv. Funct. Mater. 2012, 22, 820−826.

(45) Ursachi, I.; Stancu, A.; Vasilie, A. Magnetic α-Fe2O3/MCM-41 nanocomposites: Preparation, characterization, and catalytic activity for methylene blue degradation. J. Colloid Interface Sci. 2012, 377, 184−190.

(46) Shahwan, T.; Abu Sirriah, S.; Nairat, M.; Boyaci, E.; Eroğlu, A. E.; Scott, T. B.; Hallam, K. R. Green synthesis of iron nanoparticles and their application as a Fenton-like catalyst for the degradation of aqueous cationic and anionic dyes. Chem. Eng. J. 2011, 172, 258−266.

(47) Chen, X.; Ma, C.; Li, X.; Chen, P.; Fang, J. Hierarchical Bi2CuO5 microspheres: Hydrothermal synthesis and catalytic performance in wet oxidation of methylene blue. Catal. Commun. 2009, 10, 1020−1024.

(48) Johnson, T. L.; Scherer, M. M.; Tratnyek, P. G. Kinetics of halogenated organic compound degradation by iron metal. Environ. Sci. Technol. 1996, 30, 2634−2640.

(49) Zhang, W.; Wang, C.; Lien, H.-L. Treatment of chlorinated organic contaminants with nanoscale bimetallic particles. Catal. Today 1998, 40, 387−395.

(50) Davidson, E. A.; Janssens, I. A. Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. Nature 2006, 440, 165−173.

(51) Binner, J. G. P.; Hassine, N. A.; Cross, T. E. The possible role of the pre-exponential factor in explaining the increased reaction rates observed during the microwave synthesis of titanium carbide. J. Mater. Sci. 1995, 30, 5389−5393.

(52) Yang, B.; Tian, Z.; Zhang, L.; Guo, Y.; Yan, S. Enhanced heterogeneous Fenton degradation of methylene blue by nanoscale zero valent iron (nZVI) assembled on magnetic Fe3O4/reduced graphene oxide. J. Water Process. Eng. 2015, 5, 101−111.

(53) Yang, S.-T.; Zhang, W.; Xie, J.; Liao, R.; Zhang, X.; Yu, B.; Wu, R.; Liu, X.; Li, H.; Guo, Z. Fe3O4@SiO2 nanoparticles as a high-performance Fenton-like catalyst in a neutral environment. RSC Adv. 2015, 5, 5485−5463.

(54) Jia, Z.; Kang, J.; Zhang, W. C.; Wang, W. M.; Yang, C.; Sun, H.; Habibi, D.; Zhang, L. C. Surface aging behaviour of Fe-based amorphous alloys as catalysts during heterogeneous photo Fenton-like process for water treatment. Appl. Catal. B: Environ. 2017, 204, 537−547.

(55) Yao, Y.; Chen, H.; Qin, J.; Wu, G.; Lian, C.; Zhang, J.; Wang, S. Iron encapsulated in boron and nitrogen codoped carbon nanotubes as synergistic catalysts for Fenton-like reaction. Water Res. 2016, 101, 281−291.

(56) Zhang, Y.; Liu, C.; Xu, B.; Qi, F.; Chu, W. Degradation of benzotriazole by a novel Fenton-like reaction with mesoporous Cu/MnO2: Combination of adsorption and catalysis oxidation. Appl. Catal. B: Environ. 2016, 199, 447−457.

(57) Pan, J. H.; Wang, X. Z.; Huang, Q.; Shen, C.; Koh, Z. Y.; Wang, Q.; Engel, A.; Bahnemann, D. W. Large-scale synthesis of urilichine-like mesoporous TiO2 hollow spheres by targetted etching and their photoelectrochemical properties. Adv. Funct. Mater. 2014, 24, 95−104.