In-situ generation of gold nanoparticles on MnO₂ nanosheets for the enhanced oxidative degradation of basic dye (Methylene Blue)

Xueqin Bao, Zhen Qin, Tianshu Zhou, Jingjing Deng*

School of Ecological and Environmental Sciences, East China Normal University, Shanghai 200241, China

ARTICLE INFO

Article history:
Received 21 October 2016
Accepted 3 March 2017
Available online 11 March 2017

Keywords:
MnO₂/Au-NPs nanocomposite
In-situ generation
Dye degradation
Synergistic effect and interfacial effect
Enhanced oxidative degradation

ABSTRACT

In this work, the gold nanoparticles (Au-NPs) were in-situ generated on the surface of MnO₂ nanosheets to form MnO₂/Au-NPs nanocomposite in a simple and cost-effective way. Multiple experiments were carried out to optimize the oxidation of basic dye (Methylene Blue (MB)), including the molar ratio of MnO₂ to chloroauric acid (HAuCl₄), the pH of the solution and the effect of initial material. Under the optimal condition, the highest degradation efficiency for MB achieved to 98.9% within 60 min, which was obviously better than commercial MnO₂ powders (4.3%) and MnO₂ nanosheets (74.2%). The enhanced oxidative degradation might attribute to the in-situ generation of ultra-small and highly-dispersed Au-NPs which enlarged the synergistic effect and/or interfacial effect between MnO₂ nanosheets and Au-NPs and facilitated the uptake of electrons by MnO₂ from MB during the oxidation, thus validating the application of MnO₂/Au-NPs nanocomposite for direct removal of organic dyes from wastewater in a simple and convenient fashion.

© 2017 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

Introduction

With the fast development of social economy and the rapid pace of industrialization, more and more attention has been paid to water quality preservation (Wang et al., 2014; Sun et al., 2015). Up-to-date, growing public concern has invigorated interest in effective treatment of dyes in wastewater, since the direct release of colored wastewaters into the aquatic ecosystems is both environmentally unsafe and esthetically unacceptable, particularly in this industrial century with the lack of water resources (Bibi et al., 2009; Saygıli et al., 2014). For example, the discharge of dyes in wastewater from industry increases the toxicity and the chemical oxygen demand of water, decreases the penetration of light, threatens human health and ecological equilibrium (Bulut and Aydin, 2006). Therefore, the development of a clean and efficient water purification technology to remove dyes from aqueous solution is of great importance.

Towards this end, several elegant methods have been proposed, among which chemical oxidation has emerged as one of the most efficient and economic methods. For instance, the advanced oxidation processes (AOPs) have been applied successfully to degrading organic pollutants into harmless chemicals such as CO₂ and H₂O (Bizani et al., 2006; Low et al., 2011). However, the chemical methods are often strongly relied on the highly efficient oxidative catalysts or extra addition of oxidative agents such as H₂O₂ (Bhuyan et al., 2015; Ma et al., 2013; Soutsas et al., 2010; Zhang et al., 2006), which render difficulty for rapid and direct practical applications for effective recovery of the water quality with simplicity both in principle and in operation.

In recent years, manganese dioxide (MnO₂) has been demonstrated as one of the outstanding candidates for the
practical application in removal of dye from wastewater in different surroundings (Fathy et al., 2013; Kuan and Chan, 2012; Ramesh et al., 2016; Yang et al., 2014). This is likely due to its physical adsorption ability and universal oxidation ability, and which make it an active metal oxide to offer efficient and innovative solutions. As far as we know, the oxidative degradation often depends on the surface area of dye approximate to MnO2, however, the MnO2 particles produced by traditional methods or improved methods exhibited low specific surface area, which render difficulty in efficient dye degradation (Martha et al., 2013; Yang et al., 2014; Yu et al., 2014). Thus, single-layer MnO2 nanosheets with high surface area is highly desired and expected to show superior property in dye degradation. Moreover, according to the literature, the dispersion of fine gold nanoparticles (Au-NPs) on certain metal oxide support exhibited surprisingly high catalytic activity towards various chemical oxidation (Jiang et al., 2013; Wang et al., 2011). It has been studied that the combination of MnO2 nanostructures and Au-NPs could lead to a significant enhancement in the oxidation electrocatalytic activity of MnO2 (Hoflund et al., 1995). Herein, in order to realize the advanced oxidation process in a simple and rapid fashion, we established an in-situ generation strategy of Au-NPs on MnO2 nanosheets for the enhanced oxidative degradation of basic dye Methylene Blue (MB) as a model.

MnO2 nanosheets was prepared by simple method as reported before (Zhai et al., 2014), then Au-NPs were in-situ generation on the surface of the MnO2 through spontaneous chemical reduction of chloroauric acid (HAuCl4) by sodium borohydride (NaBH4) with polyvinyl pyrrolidone (PVP) as a protecting agent in aqueous media (Scheme 1). The main physical and chemical properties of the prepared MnO2/Au-NPs nanocomposite were fully characterized and the obtained nanocomposite was employed for the oxidative degradation of MB. It was found that the high degradation ability of MnO2/Au-NPs nanocomposite was strongly dependent on the particle size and density of Au-NPs in-situ generation on the surface adjusting by the molar ratio of MnO2 to HAuCl4, the pH of the solution and the effect of initial material. With the optimal condition here, the enhanced oxidation for degradation of MB could be easily achieved within 60 min and the degradation efficiency was up to 98.9% rather than commercial MnO2 powders (4.3%) and MnO2 nanosheets (74.2%). All the features make this simple and convenient procedure an effective route for the elimination of environmental pollution in wastewater treatment.

1. Experimental methods

1.1. Reagents and materials

The tetramethylammonium hydroxide pentahydrate was purchased from J&K (Beijing, China). Other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. Proprietary chemicals were analytical grade reagents at least and used without further purification. All aqueous solutions were prepared with Milli-Q water (18.2 MΩ·cm) and all experiments were carried out at room temperature unless otherwise noted.

1.2. Synthesis of single-layer MnO2 nanosheets

The single-layer MnO2 nanosheets were synthesized according to the literature before (Zhai et al., 2014). Twenty milliliters of a mixture containing tetramethylammonium (TMA, 2.175 g·1.0 mol/L in 12 mL H2O), H2O2 (30 wt.% in H2O, 2 mL), and 6 mL H2O was added into the aqueous solution of MnCl2·4H2O (0.593 g, 10 mL) within 15 sec. The as-prepared dark brown suspension was stirred vigorously overnight at room temperature in the open air. The obtained MnO2 nanosheets were used for the next synthesis step. And the concentration of the as-formed MnO2 nanosheets was calculated according to Lambert–Beer’s Law with the molar extinction efficient at 9.6 × 10³ L/(mol·cm) at 380 nm (Kai et al., 2008).

1.3. In-situ generation of Au-NPs on the surface of MnO2 nanosheets

To prepare MnO2/Au-NPs nanocomposite, 10 μL PVP (0.02 g/L) was added into 10 mL suspension solution of MnO2 nanosheets (10.9 g/L) firstly. A certain dosage of 24 mmol/L HAuCl4 was then added into the mixture and stirred for 40 min at room temperature. One milliliter NaBH4 (8 mg) aqueous solution was then added dropwise. The resulting suspension was stirred for another 60 min at room temperature. Finally, the MnO2/Au-NPs nanocomposite was collected and washed with Milli-Q water for several times until the pH of the supernatant was neutral.

1.4. Characterization

The elemental composition and chemical oxidation state were investigated by X-ray photoelectron spectroscopy (XPS, ESCALAB 250 Xi, Thermo Scientific, America) with Al Kα radiation as the excitation source (300 W). Binding energies were calibrated versus the carbon signal at 284.64 eV. The surface morphology was characterized by high resolution-transmission electron microscope (HRTEM, JEM-2010F, JEOL, Japan) equipped with energy dispersive spectroscopy analysis (EDS, INCA-PentaFET-×3, Oxford, England) to determine the...
composition of the samples, operating at 200 kV. The Fourier transform infrared (FT–IR) spectra were recorded on a FT–IR spectrophotometer (Nicolet 560, Nicolet, America).

1.5. Degradation experiments

The degradation experiment was carried out by stirring 10 mL of the mixed aqueous solution of MB (6.25 mg/L) and MnO2/Au-NPs nanocomposite (0.14 mmol/L). The solution of MB was separated from the suspension by centrifugation at 8000 r/min for 2 min. Then 1 mL of the supernatant was taken out at certain time intervals and the concentration of MB was monitored by the UV–vis (ultraviolet–visible) spectra of the supernatant of the mixture at the wavelength of 664 nm (UV-1800 spectrophotometer, Shimadzu, Japan) and photographed with a digital camera (IXUS 951S, Canon, Japan).

2. Results and discussion

2.1. Characterization for MnO2/Au-NPs nanocomposite

With the protection of PVP, the addition of NaBH4 in the presence of HAuCl4 resulted in the formation of MnO2/Au-NPs nanocomposite. The morphologies of MnO2 nanosheets and as-formed MnO2/Au-NPs nanocomposite were then analyzed by transmission electron microscopy (TEM), as shown in Fig. 1a and b. The Au-NPs were nearly equally distributed on the surface of MnO2 nanosheets with narrow size distribution in the range of 1–3.5 nm and the mean particle diameter was 2 ± 1.22 nm (Fig. 1b, inset). The in-situ generation of Au-NPs on the surface of MnO2 nanosheets seemed not largely changing the structure of the nanosheets and still kept its original morphology after the chemical reactions. The HRTEM was next used to investigate lattice fringes of Au-NPs and MnO2 nanosheets. As displayed in Fig. 1c, the interlayer spacing of 0.23 nm agreed with (111) planes of Au, indicating their nice crystallinity (Zhang et al., 2015a, 2015b). Moreover, the presence of Mn, O and Au elements in transmission electron microscope-energy dispersive spectroscopy analysis (TEM–EDS) again confirmed the successful formation of Au-NPs on the MnO2 nanosheets, as shown in Fig. 1d. Note that, during the synthesis process, the presence of such amount of reducing agent (NaBH4) would not weaken the crystal of MnO2, as shown in the X-ray diffraction patterns of MnO2 nanosheets (Appendix A Fig. S1, black curve) and MnO2/Au-NPs nanocomposite (Appendix A Fig. S1, red curve).

To verify the mechanism, we next investigated the in-situ generation of Au-NPs by FT–IR analysis (Fig. 2). For single-layer

![TEM image](image-url)
MnO₂ nanosheets, the absorption band appearing at 1661 cm⁻¹ was normally due to hydroxyl group (O–H) bending vibrations combined with Mn atoms and the peaks appearing at 665, 641, and 611 cm⁻¹ might be ascribed to Mn–O vibrations in MnO₂ octahedra (Fig. 2, black curve) (Chen et al., 2009; Hu et al., 2016; Han et al., 2011; Liu et al., 2002). With the growth of Au-NPs on the surface of MnO₂ nanosheets, the absorption bands red-shifted to 1682, 670, 645, and 620 cm⁻¹, respectively (Fig. 2, red curve). This spectral red shift was further confirmed that it was originated from the in-situ generation of Au-NPs on MnO₂ nanosheets rather than reduction caused by NaBH₄, as shown in Fig. S2. From these results, we concluded that: (1) the formation of Au–O on the surface of MnO₂ nanosheets weakened O–H bending vibrations combined with Mn atoms, and more importantly, this kind of decrease of active O–H by Au–O binding prevented further accumulation thus ensuring the equally distribution of Au-NPs on the surface (Huang and Yang, 2004); (2) the doping of Au in MnO₂ might result in the lattice expansion which decreased the bands energy of Mn–O and consequently, increased the band length. Moreover, the lattice expansion of MnO₂ also increased the ratio of surface area to volume, which was of great importance in further degradation application (Li et al., 2009).

To more clearly understand the surface composition, charge transfer tendencies and oxidation states of MnO₂/Au-NPs nanocomposite, X-ray photoelectron spectroscopy (XPS) analysis of O 1s, Mn 2p, 3s and Au 4f were conducted for MnO₂ nanosheets and MnO₂/Au-NPs nanocomposite,

Fig. 2 – Fourier transform infrared spectrums of MnO₂ nanosheets (black curve) and MnO₂/Au-NPs nanocomposite (red curve). σ: wave number.

Fig. 3 – XPS spectra of O 1s (a), Mn 2p (b) and Mn 3s (c) core levels for MnO₂ nanosheets and MnO₂/Au-NPs nanocomposite and of Au 4f (d) for MnO₂/Au-NPs nanocomposite. XPS: X-ray photoelectron spectroscopy.
respectively, as depicted in Fig. 3a-d. For O 1s, the binding energies between 529.9–529.5 eV was characterized as the lattice oxygen (denoted as O_l), and the binding energies between 532.0–531.4 eV was attributed to oxygen vacancies (denoted as O_v). The O_l and O_v XPS peak of MnO_2 are at 529.9 and 531.4 eV, respectively (Fig. 3a). There was a decrease in the O_l/O_v ratio from 3.01 to 2.90, demonstrating the enrichment of oxygen vacancies, which may be ascribed to the doping of Au in the surface of MnO_2 that reduced the oxygen vacancy energy formation (Appendix A Fig. S3) (Roldán et al., 2010), and/or charge transfer resulted from the interfacial effect (metal-support interactions) between semi-conductor MnO_2 nanosheets, the main peak at the Mn 2p3/2 region shifted slightly to 642.18 eV, which meant the existence of Mn species in a bit lower oxidation states, and thus a little amount of Mn^{4+} was reduced into Mn^{3+} (< 4) at the surface. However, it is difficult to judge the oxidation state of Mn only by the Mn 2p peak, as the splitting between Mn^{3+} and Mn^{4+} is less than 1 eV (Dicastro and Polzonetti, 1989). According to the literature (Alhumainess et al., 2014), the average Mn valence (\(\nu_{Mn}\)) shows a linear relationship with the binding energy separation between the two peaks of the Mn 3s doublet. Hence the extent of Mn 3s doublet splitting would provide more accurate information, the XPS of Mn 3s was then examined (Fig. 3c). As displayed in Table 1, the calculated \(\nu_{Mn}\) of MnO\_2/Au-NPs nanocomposite (3.27 eV) was lower than that of MnO\_2 nanosheets (3.86 eV), implying that the content of Mn^{3+} in MnO\_2/Au-NPs nanocomposite was more than that in MnO\_2 nanosheets. Mn^{3+} forms weaker Mn-O bonds due to the occupation of the antibonding \(\varepsilon_g\) orbital. Mn^{IV}-O bonds in edge sharing octahedra at the surface are more reactive because they are longer and more flexible than Mn^{IV}-O bonds (Kuo et al., 2015), which may facilitate the uptake of electrons by MnO\_2 from MB during the oxidation process and this property is envisaged to improve the oxidative degradation ability of MnO\_2 nanosheets.

In addition to the surface change of the original components, the Au 4f XPS spectra (Fig. 3d) for the MnO\_2/Au-NPs nanocomposite displayed broad peaks in the Au 4f region, suggesting the presence of different oxidation states (Casaletto et al., 2006; Chen et al., 2013). The Au 4f_{7/2} region could be de-convoluted into two peaks: one at 84.68 eV was assigned to Au\^0 species and another at 85.68 eV was concerned to Au\^+ species. Previous experimental and theoretical studies demonstrated that the most catalytically active sites in oxidation reactions might be attributed to Au\^+ surface species (Silva et al., 2015; Slater et al., 2014; Sudarsanam et al., 2014). Remarkably, for our MnO\_2/Au-NPs nanocomposite, 34.06% Au\^+ species (Table 2) that appeared at the surface of MnO\_2 nanosheets might also result in high activities towards oxidation reactions of MB. All of these results substantially demonstrated the successful in-situ generation of Au-NPs on MnO\_2 nanosheets, which might combine the inherent properties of both the Au-NPs and the MnO\_2 nanosheets, thus could be used for enhanced oxidative degradation of MB, as demonstrated below.

### 2.2. Optimization of experimental conditions

#### 2.2.1. The time for degradation equilibrium

In this work, the degradation efficiency (Q) of MB was calculated by Eq. (1):

\[
Q = \left( \frac{A_0 - A_t}{A_0} \right) \times 100\%
\]

where, \(A_0\) (mg/L) and \(A_t\) (mg/L) are the initial and at different time intervals MB concentrations, respectively. Based on this, the time for degradation equilibrium was optimized firstly, the degradation efficiency of MB at different time intervals of 3, 10, 20, 30, 60, 90, and 120 min was studied as shown in Fig. 4A. It was observed that the degradation efficiency of MB increased rapidly in the initial stage and up to 60 min. After 60 min, the performance reached equilibrium and stabilized at a maximum value, so 60 min was chosen as the degradation time in the subsequent experiments.

#### 2.2.2. Effect of the molar ratio of MnO\_2 to HAuCl\_4

It is well-known that the catalytic property of Au-NPs is strongly dependent on their content, size and dispersity. Hence, the influence of HAuCl\_4 concentration (used in the synthesizing step) on the degradation performance of MnO\_2/Au-NPs nanocomposite was then investigated. Fig. 4B showed the degradation efficiency of MnO\_2/Au-NPs nanocomposite with different MnO\_2 to HAuCl\_4 molar ratio during the synthesizing process (the molar ratio of MnO\_2 to HAuCl\_4 (a-e) was 640:1, 320:1, 160:1, 80:1, 40:1) at 60 min. It was found that the molar ratio of MnO\_2 to HAuCl\_4 was 160:1 (Fig. 4Bc), the highest degradation efficiency was achieved. This could be elucidated that when the molar ratio was lower than 160:1 (Fig. 4Ba and Bb), the degradation performance might be limited by the small content of Au-NPs, as shown in Appendix A Fig. S4a and b, while when the ratio was higher (Fig. 4Bd, Table 1 - X-ray photoelectron spectroscopy (XPS) peak analyses of Mn 3s in MnO\_2 nanosheets, MnO\_2/Au-NPs nanocomposite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn 3s (eV)</th>
<th>ΔE</th>
<th>Average valence</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO_2 nanosheets</td>
<td>84.88</td>
<td>4.60</td>
<td>3.86</td>
</tr>
<tr>
<td>MnO_2/Au-NPs nanocomposite</td>
<td>28.3</td>
<td>12.0</td>
<td>116</td>
</tr>
</tbody>
</table>

| ΔE: the multiplet splitting energies of Mn 3s; NPs: nanoparticles. |
Be)), the bigger size and the lower degree of the dispersion might also affect the degradation performance (Appendix A Figs S4d and e). Finally, 160:1 was confirmed as the optimal molar ratio of MnO₂ to HAuCl₄ for further application.

2.2.3. Effect of pH on degradation efficiency
According to the literature (Zhao et al., 2013), pH of solution demonstrated a fundamental role in efficient degradation of dyes in aqueous environment. It was found that the degradation efficiency of MB increased with decreasing pH over the range 1.0–9.0 (Fig. 4C). When the pH of the solution was lower than 3.0, the degradation efficiency for MB reached maximum (97%). This might be ascribed to the fact that, during the oxidation process, MnO₂ was reduced into Mn²⁺, which could be expressed as $\delta$-MnO₂ + 4H⁺ + 2e⁻ → Mn²⁺ + 2H₂O (Stumm et al., 1981). As known from the Nerst equation, the reducing potential is correlated well with the concentration of H⁺. A decreased pH in the solution would improve the reducing potential of MnO₂/Mn²⁺, and then increase the oxidation ability of the system. Thereby, it is plausible to infer that lower pH is beneficial to the oxidation process. Nevertheless, there was no significant change in degradation efficiency of MB when pH decreased from 3.0 to 1.0, pH 3.0 was selected as the optimized pH.

2.2.4. Effect of the concentration of MnO₂/Au-NPs nanocomposite
The effect of the concentration of MnO₂/Au-NPs nanocomposite for the degradation of MB was studied and the result was given in Fig. 4D. It was evident from Fig. 4D that the degradation efficiency was increased with increasing the concentration of MnO₂/Au-NPs nanocomposite (MB (6.25 mg/L), pH = 3.0, room temperature and all other experimental conditions were the same). When the concentration of MnO₂/Au-NPs nanocomposite was higher than 0.14 mmol/L, MB was almost completely degraded (99.5%). To realize the degradation of MB in an efficient and saving manner, we chose 0.14 mmol/L as the appropriate dosage for the next-step experiment.

2.3. Enhanced oxidative degradation for MB
Finally, 0.14 mmol/L MnO₂/Au-NPs nanocomposite with the molar ratio at 160:1 of MnO₂ to HAuCl₄ was used for the
degradation of 6.25 mg/L MB at pH 3.0 for 60 min. Under the optimal experimental condition (mentioned above), the oxidation activity of MnO₂/Au-NPs nanocomposite with commercial MnO₂ powders and MnO₂ nanosheets were compared. It could be seen from Fig. 5a, for commercial MnO₂ powders, the blue color of the reaction mixture almost remained unchanged after 60 min, and the degradation efficiency of MB of which was low to 4.3%. For the same amount of MnO₂ nanosheets, the blue color of the reaction mixture faded to light-blue and the degradation efficiency of MB was to 74.2% after 60 min (Fig. 5b). While, with the presence of Au-NPs in-situ generation on the surface of MnO₂ nanosheets, the blue color of the mixture faded much more quickly. After 60 min, the colorless solution was observed, and the absorbance at 664 nm diminished. Finally, about 98.9% of MB was degraded (Fig. 5c). From this result, we

![UV–vis spectra of MB at different time intervals](image)

Fig. 5 – UV–vis spectra of MB at different time intervals with the presence of (a) 0.14 mmol/L of commercial MnO₂ powders; (b) 0.14 mmol/L of MnO₂ nanosheets; (c) 0.14 mmol/L of MnO₂/Au-NPs nanocomposite; (d) the degradation efficiency with commercial MnO₂ powders, MnO₂ nanosheets and MnO₂/Au-NPs nanocomposite, respectively. Error bars indicate standard deviations (n = 3). Inset: Photographs of the supernatant of the mixture at 0 and 60 min. All experiments were carried out at the optimal condition. UV–vis: ultraviolet-visible.

<table>
<thead>
<tr>
<th>Degradation material</th>
<th>Initial concentration of MB (mg/L)</th>
<th>Dosage of material (g/L)</th>
<th>Degradation efficiency (%) (reaction time)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO₂ coated with montmorillonite (Zhu et al., 2010)</td>
<td>100</td>
<td>2.5</td>
<td>90 (700 min)</td>
</tr>
<tr>
<td>Mn₃O₄ (UV/H₂O₂ AOP) (Wang et al., 2015)</td>
<td>10</td>
<td>0.4</td>
<td>70 (180 min)</td>
</tr>
<tr>
<td>Acid-treated MnO₂ (Das and Bhattacharyya, 2015)</td>
<td>1</td>
<td>2.5</td>
<td>97.7 (300 min)</td>
</tr>
<tr>
<td>β-MnO₂ (H₂O₂) (Zheng et al., 2015)</td>
<td>10</td>
<td>0.133</td>
<td>85 (120 min)</td>
</tr>
<tr>
<td>PEDOT/GO/MnO₂ (Zhang et al., 2015a, 2015b)</td>
<td>20</td>
<td>0.4</td>
<td>80 (60 min)</td>
</tr>
<tr>
<td>MnO₂/Au-NPs nanocomposite (this work)</td>
<td>6.5</td>
<td>0.012</td>
<td>98.9 (60 min)</td>
</tr>
</tbody>
</table>

UV: ultraviolet; AOP: advanced oxidation process; PEDOT: poly(3,4-ethylenedioxythiophene); GO: graphene oxide.
noticed that as one kind of two-dimensional materials, the MnO₂ nanosheets with large surface area exhibited better performance than commercial MnO₂ powders, so whether the decolorization of MB was caused by oxidative degradation or just by simple adsorption was carefully checked. As shown in our control experiment, when the decolorization of MB was achieved by MnO₂/Au-NPs nanocomposite, large amount of reducing agent was then added to the suspension to totally decompose MnO₂ nanosheets into Mn²⁺. After this process, the final solution was almost colorless, indicating the oxidation rather than simply physical adsorption plays a dominant role in the decolorization of MB (Appendix A Fig. S5), which was consistent with many reports previously (Ge and Qu, 2003; Kuan et al., 2011; Zhao et al., 2013). The comparison of degradation efficiencies of MB with three kinds of MnO₂ materials was further illustrated in Fig. 5d, the MnO₂/Au-NPs nanocomposite showed the enhanced oxidative degradation towards MB with higher efficiency than commercial MnO₂ powders and MnO₂ nanosheets clearly. More than that, from Table 3, it could be found out that MnO₂/Au-NPs nanocomposite exhibited great superiority over some other materials reported previously, as higher degradation efficiency could arrive in shorter time even with smaller concentration of initial materials and lower concentration ratio of initial materials to MB. This advantage might be attributed to the following three points: (1) the Au-NPs on MnO₂ nanosheets are ultra-small size, uniformly-dispersed, high surface-to-volume ratios which are beneficial to the reaction process; (2) the existence of certain content of Au⁺⁺ species and oxygen vacancies at the surface of MnO₂ nanosheets represents highly active sites towards oxidation reactions; (3) MnO₂ nanosheet is a kind of semi-conductor material, the embedded Au-NPs facilitate electron transfer between MnO₂ nanosheets and Au-NPs during the oxidation period by synergistic and/or interfacial effect (Gorlin et al., 2014). All of these properties validate the application of MnO₂/Au-NPs for direct, simple and convenient removal of organic dyes from wastewater in a simple and convenient fashion.

3. Conclusions

By taking the advantage of the synergistic effect and interfacial effect of MnO₂ nanosheets and Au-NPs, a simple and effective strategy to degrade the dye MB directly has been developed in this study. The in-situ generation of Au-NPs on the surface of MnO₂ nanosheets was tried for the first time, and the synthesized Au-NPs with ultra-small size, uniform distribution facilitated the oxidation degradation process of MB and enhanced the degradation efficiency. The highest activity for the degradation of MB achieved to 98.9% for MnO₂/Au-NPs within 60 min, which was obviously better than commercial MnO₂ powders (4.3%) and MnO₂ nanosheets (74.2%). Thus this study is very promising to be used for further application in environmental treatment. Moreover, the improved oxidative degradation of dye with MnO₂ assisted by noble metal nanoparticles in this study could be extended to other metal oxide as a universal strategy.

The average valence of Mn was calculated by Eq. (2):

$$\Delta E = 7.88 - 0.85n$$  
where \( n \) (2 ≤ \( n \) ≤ 4) is the average oxidation state of Mn atoms (Gao et al., 2010).

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 21277048 and 21505046), the China Postdoctoral Science Foundation (No. 2016 M590336) and the “Chenguang Program” funded by Shanghai Education Development Foundation and Shanghai Municipal Education Commission (No. 15CG21).

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2017.03.003.

REFERENCES


