



Cite this: *RSC Adv.*, 2018, 8, 2209

# Eco-friendly seeded Fe<sub>3</sub>O<sub>4</sub>-Ag nanocrystals: a new type of highly efficient and low cost catalyst for methylene blue reduction†

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Hybrid Fe<sub>3</sub>O<sub>4</sub>-Ag nanocrystals, a new type of highly efficient and reusable catalyst for methylene blue (MB) reduction, are fabricated by a novel seed deposition process. X-ray diffraction and Mössbauer spectroscopy results show that the developed iron oxides are in a pure magnetite Fe<sub>3</sub>O<sub>4</sub> phase. Upon manipulating the amount of Ag seeds capsuled on the modified surfaces of Fe<sub>3</sub>O<sub>4</sub> nanocrystals, the catalytic capacities on the reduction of MB can be precisely adjusted with a tunable fabrication cost control. The linear correlation of the reduced MB concentration *versus* reaction time catalyzed by our developed hybrid Fe<sub>3</sub>O<sub>4</sub>-Ag nanocrystals is coherent with pseudo first order kinetics. Importantly, with remarkable recyclability features, the hybrid Fe<sub>3</sub>O<sub>4</sub>-Ag nanocrystals can be easily separated by applying an external magnetic field. The tailored catalytic performances of the hybrid Fe<sub>3</sub>O<sub>4</sub>-Ag nanocrystals during MB reduction are attributed to the optimized dynamic electron transfer process, which dominates the electrochemical mechanism wherein the nucleophilic BH<sub>4</sub><sup>-</sup> ions donate electrons to electrophilic organic MB through Ag seeds in a regulated amount. Such developed hybrid Fe<sub>3</sub>O<sub>4</sub>-Ag nanocrystals pave the way towards the mass production of highly efficient and low cost catalysts for methylene blue reduction.

Received 14th October 2017  
 Accepted 3rd January 2018

DOI: 10.1039/c7ra11348j

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## 1. Introduction

Organic dyes with considerable coloring capacity are widely employed in the manufacturing of consumer products,

including textiles, paints, printing inks, cosmetics, plastics and paper.<sup>1-3</sup> However, the massive discharge of dye-containing effluents into the water environment have led to severe environmental issues, which have attracted extensive attention.<sup>4</sup> The immoderate release of wastewater containing organic dyes could impede sunlight penetration into water, thus reducing the photosynthetic reaction of plants and destroying the ecological balance of water bodies.<sup>5</sup> Most seriously, most of the organic dyes have toxic, carcinogenic and teratogenic properties, which will severely threaten the health of human beings.<sup>6</sup> For example, as an important basic dye used for printing calico, dyeing cotton and leather, methylene blue (MB), a heterocyclic aromatic dye, may cause various harmful effects such as eye burns, irritation to the gastro-intestinal tract and to the skin.<sup>7</sup>

There are many approaches, such as chemical oxidation, adsorption, photocatalytic degradation and catalytic reduction have been widely studied and exploited to decolorize and remove these organic dyes.<sup>8-10</sup> Among them, the photocatalytic degradation in the presence of semiconductor photocatalysts (*e.g.*, typically, ZnO and TiO<sub>2</sub>) and catalytic reduction of noble metal catalysts (*e.g.*, typically, Ag and Au) are two of the most common ways for the treatment of organic dyes.<sup>11-16</sup> Although semiconductor photocatalysts have many advantages such as nontoxicity, high photostability and relatively low cost, the photocatalytic efficiency for all these photocatalysts is still low, hindering them far away from the practical applications.

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† Electronic supplementary information (ESI) available: Pawley refinement and size distribution histogram of the XRD pattern of the pure Fe<sub>3</sub>O<sub>4</sub>; UV-Vis spectra of the as-prepared colloidal Ag solution and the Ag solution after immobilization on the Fe<sub>3</sub>O<sub>4</sub>@PEI-DTC nanocrystals after the magnetic separation; SEM images of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>-Ag 10 mg-10 mL, Fe<sub>3</sub>O<sub>4</sub>-Ag 10 mg-30 mL, Fe<sub>3</sub>O<sub>4</sub>-Ag 10 mg-50 mL, Fe<sub>3</sub>O<sub>4</sub>-Ag 10 mg-100 mL, Fe<sub>3</sub>O<sub>4</sub>-Ag 10 mg-150 mL, Fe<sub>3</sub>O<sub>4</sub>-Ag 5 mg-30 mL, Fe<sub>3</sub>O<sub>4</sub>-Ag 15 mg-30 mL and Fe<sub>3</sub>O<sub>4</sub>-Ag 20 mg-30 mL; XPS survey scan spectra of pure Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>-Ag 10 mg-10 mL, Fe<sub>3</sub>O<sub>4</sub>-Ag 10 mg-30 mL and Fe<sub>3</sub>O<sub>4</sub>-Ag 10 mg-150 mL; ZFC and FC curves of pure Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>-Ag 10 mg-150 mL; color variation of MB over time catalyzed by Fe<sub>3</sub>O<sub>4</sub>-Ag 10 mg-100 mL. See DOI: 10.1039/c7ra11348j

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Catalytic reduction of noble metal catalysts is one of the most effective methods for the treatment of organic dyes. Unfortunately, on one hand, noble metal nanocrystals tend to aggregate easily because of their high surface energy which originates from the high surface area to volume ratio.<sup>17</sup> On the other hand, noble metal catalysts encounter an obstacle that are difficult to be separated by the traditional methods such as centrifugation or filtration. To solve aforementioned two problems, immobilizing the noble metal nanocrystals onto the surface of the suitable magnetic nanocrystal supports has been a new trend, which may not only prevent aggregation of noble metal nanocrystals, but also be efficiently separated and recycled by an external magnetic field.<sup>18</sup>

Magnetite  $\text{Fe}_3\text{O}_4$  nanocrystals with the insoluble and superparamagnetic properties are the most popular “support materials” for catalysts due to the relatively high saturation magnetization and fast magnetic responsiveness.<sup>19–23</sup> In addition, noble metal nanoparticles have received considerable attention because of their facile and robust interaction with different molecules.<sup>24–27</sup> Compared with other noble metal nanocatalysts such as Au, Pt and Pd, Ag nanocrystals are cheaper and possess good chemical and physical properties, which can act as catalysts for the degradation of a variety of organic dye pollutants.<sup>28</sup> Recently, the considerable efforts have been devoted to the design and preparation of  $\text{Fe}_3\text{O}_4$ -Ag nanocrystals for the degradation of the MB. Xie *et al.* prepared  $\text{Fe}_3\text{O}_4$ @PDA-Ag microspheres and investigated the catalytic capabilities on the reduction of MB at different pH values.<sup>29</sup> Amir *et al.* synthesized  $\text{Fe}_3\text{O}_4$ @His@Ag and  $\text{Fe}_3\text{O}_4$ @HA@Ag nanocrystals, respectively, to catalyze the degradation of MB and studied the rate constants for the reduction of MB.<sup>30</sup> However, there are relatively few systematic studies devoted to the relation between the amount of silver seeds deposited on the surfaces of  $\text{Fe}_3\text{O}_4$  nanocrystals and catalytic capacities on the reduction of MB. Therefore, it is necessary to effectively control the amount of silver seeds adhered to the surfaces of  $\text{Fe}_3\text{O}_4$  nanocrystals.

In this work, the polyethyleneimine dithiocarbamate (PEI-DTC) were employed as polymers to prepare  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals by the seed deposition process. By adjusting the adding times of silver seeds or the additive amount of  $\text{Fe}_3\text{O}_4$  nanocrystals, we control the amount of silver seeds deposited on the modified surfaces of  $\text{Fe}_3\text{O}_4$  nanoparticles and investigate the effects of the amount of silver seeds on the catalytic capacities on the reduction of MB. In comparison with the previous results, the following features are evident: (1) the utilization of PEI-DTC polymers can enhance the adhesive force of the silver seeds on the surfaces of  $\text{Fe}_3\text{O}_4$  nanocrystals; (2) the silver seeds are uniformly deposited on the surfaces of the  $\text{Fe}_3\text{O}_4$  nanocrystals; (3)  $\text{Fe}_3\text{O}_4$  nanocrystals coated with the silver seeds instead of the continuous silver shell can avoid the decrease of the saturation magnetization ( $M_s$ ) of  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals to the most extent; (4)  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals not only exhibit excellent catalytic capacities on the reduction of MB, but also are easily separated and recycled by applying an external magnet field.

## 2. Experimental

### 2.1 Materials

The initial materials included iron(III) acetylacetonate ( $\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_3$ ), benzyl ether ( $\text{C}_{14}\text{H}_{14}\text{O}$ ), oleic acid ( $\text{C}_{18}\text{H}_{34}\text{O}_2$ ), polyethyleneimine (PEI, branched,  $M_w \approx 25\,000\text{ g mol}^{-1}$ ), potassium hydroxide (KOH), carbon disulfide ( $\text{CS}_2$ ), sodium citrate dihydrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ ), sodium borohydride ( $\text{NaBH}_4$ ) and silver nitrate ( $\text{AgNO}_3$ ). All chemical reagents in this experiment were used as received with no further purification.

### 2.2 Preparation of $\text{Fe}_3\text{O}_4$ nanocrystals

Rather than general nanomaterials or quantum dots synthesis,<sup>31–36</sup> in present work, the cubic  $\text{Fe}_3\text{O}_4$  nanocrystals were synthesized by the thermal decomposition method, which was described in our previous work.<sup>37</sup> Typically, 1.268 mL of  $\text{C}_{18}\text{H}_{34}\text{O}_2$  was added to a mixture of 706 mg of  $\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_3$  and 25 mL of  $\text{C}_{14}\text{H}_{14}\text{O}$ , which was heated to 300 °C and maintained for 2 h under an argon ambient. After being cooled down to room temperature, the solution was rinsed with a mixture of toluene and hexane and dried under vacuum overnight.

### 2.3 Preparation of $\text{Fe}_3\text{O}_4$ @PEI-DTC

This process involved two steps. The first step is the synthesis of PEI-DTC. In brief, 250 mg of PEI and 325 mg of KOH were dissolved in 25 mL methanol. After the mixture solution was degassed, 347.5  $\mu\text{L}$  of  $\text{CS}_2$  was added dropwise to the mixture solution. The second step is the synthesis of  $\text{Fe}_3\text{O}_4$ @PEI-DTC. The 10 mg of  $\text{Fe}_3\text{O}_4$  nanocrystals was well dispersed in 20 mL of methanol, and the obtained PEI-DTC solution was added drop by drop. After the reaction, mixture was kept at room temperature for 1 h, the resultant product was separated and collected with a magnet and subsequently put through 3 wash cycles with deionized water. The obtained  $\text{Fe}_3\text{O}_4$ @PEI-DTC nanocrystals were stored in 4 mL of deionized water.

### 2.4 Preparation of silver seeds

The silver seeds were prepared based on the work by Dasgupta *et al.*<sup>38</sup> Some experimental conditions were modified. 20 mL of 0.5 mM  $\text{NaBH}_4$  and 25 mL of 3.5 mM  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$  were mixed. The mixture was heated up to and kept at 60 °C under vigorous stirring for 0.5 h in the dark. Subsequently, 5 mL of 1 mM  $\text{AgNO}_3$  was injected drop by drop. The pH of the solution was adjusted to 10.8 by using 0.1 M NaOH while heating process was continued for another 20 min. Finally, the reaction mixture was allowed to cool down to room temperature and stored in the dark.

### 2.5 Preparation of $\text{Fe}_3\text{O}_4$ @PEI-DTC-Ag seeds nanocrystals

10 mL of silver seeds was added dropwise to obtain  $\text{Fe}_3\text{O}_4$ @PEI-DTC nanocrystals dispersed in deionized water under ultrasonic treatment. After 2 h of sonication, the  $\text{Fe}_3\text{O}_4$ @PEI-DTC-Ag seeds nanocrystals were washed three times with the deionized water and finally dispersed in 4 mL of deionized water, named as  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-10 mL. The experiment was carried out



under the same conditions as  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-10 mL. But the addition of the silver seeds was changed to 30, 50, 100 and 150 mL (10 mL each time), named as  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-30 mL,  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-50 mL,  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-100 mL and  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-150 mL, respectively. Furthermore, to study the effect of the concentration of  $\text{Fe}_3\text{O}_4$  nanocrystals on the quantity of silver seeds deposited on the surface of  $\text{Fe}_3\text{O}_4$  nanocrystals, the volume of the silver seeds was fixed in 30 mL, but the mass of the cubic  $\text{Fe}_3\text{O}_4$  nanocrystals was adjusted to 1, 5, 15 and 20 mg, which were named as  $\text{Fe}_3\text{O}_4$ -Ag 1 mg-30 mL,  $\text{Fe}_3\text{O}_4$ -Ag 5 mg-30 mL,  $\text{Fe}_3\text{O}_4$ -Ag 15 mg-30 mL and  $\text{Fe}_3\text{O}_4$ -Ag 20 mg-30 mL, respectively. Fig. 1 shows schematic illustration of the synthesis of  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals.

## 2.6 Application of the $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals for catalytic reduction of MB

The catalytic reduction of MB by the  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals in the presence of  $\text{NaBH}_4$  was performed to explore the catalytic activity and the reusability of the  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals. 1 mg of  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals was added to 2 mL of MB aqueous solution ( $\text{pH} = 5.8$ ,  $40 \text{ mg L}^{-1}$ ). Subsequently, 0.1 mL of  $\text{NaBH}_4$  aqueous solution (0.1 M, freshly prepared each time before use) was injected into the solution under mechanical agitation. MB with blue color could be gradually reduced to colorless, and the catalytic process was monitored by measuring the absorbance changes of MB at 660 nm with a UV-Vis absorbance spectroscopy. To study the recyclability of the  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals, the used samples were separated from the reaction solution using a magnet after the catalytic reduction, and were first rinsed with 2 mL of 1.5 mM  $\text{NaBH}_4$  aqueous solution and then washed three times with ethanol and deionized water. As is described above, the procedure for catalytic reduction of MB was repeated four times.

## 2.7 Characterization methods

Structure characterization of the as-synthesized samples was carried out on a Rigaku D/Max-2500 copper rotating-anode X-

ray diffractometer (XRD) using  $\text{CuK}\alpha$  radiation (40 kV, 200 mA). The Mössbauer spectrum was collected on a FAST Comtec Mössbauer system at room temperature, using a source of  $^{57}\text{Co(Pd)}$  and a conventional constant acceleration mode. The isomer shift and velocity were given relative to that of  $\alpha\text{-Fe}$  and the spectrum was fitted with Lorentzian lines *via* the least square method. Detailed structure of the obtained samples were characterized by a JEOL JSM-7800F field-emission scanning electron microscopy (FESEM) at an acceleration voltage of 20 kV and a JEOL 2100 transmission electron microscope (TEM) operating at 200 kV. X-ray photoelectron spectrum was measured with Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectroscopy (XPS). Magnetic properties were taken by a Quantum Design MPMS3 superconducting quantum interference device (SQUID) magnetometer. Ultraviolet-visible spectroscopy (UV-Vis) absorbance spectra were recorded on a Shimadzu UV 3600 spectrophotometer in the range of 350–800 nm.

## 3. Results and discussion

### 3.1 Structure of $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals

Fig. 2a and b presents XRD patterns of the pure  $\text{Fe}_3\text{O}_4$  nanocrystals and the  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals with the different addition quantities of the silver seed colloids ( $\text{Fe}_3\text{O}_4$ -Ag 10 mg-10 mL,  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-30 mL,  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-50 mL,  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-100 mL and  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-150 mL) and the different addition quantities of the  $\text{Fe}_3\text{O}_4$  nanocrystals ( $\text{Fe}_3\text{O}_4$ -Ag 5 mg-30 mL,  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-30 mL,  $\text{Fe}_3\text{O}_4$ -Ag 15 mg-30 mL and  $\text{Fe}_3\text{O}_4$ -Ag 20 mg-30 mL), respectively. As for the pure  $\text{Fe}_3\text{O}_4$  nanocrystals, all of the diffraction peaks can be indexed to the cubic spinel structured  $\text{Fe}_3\text{O}_4$  (JCPDS card no. 65-3107) and no trace of other impurities is detected.<sup>39</sup> Pawley refinement is selected to consider asymmetry correction to the whole diffraction peaks of pure  $\text{Fe}_3\text{O}_4$  nanocrystals (shown in Fig. S1†). The residual  $R_{\text{wp}}$  of the sample is 10.93%, which is in good agreement with the standard pattern of the magnetite  $\text{Fe}_3\text{O}_4$ .

Because the crystal structures of the magnetite  $\text{Fe}_3\text{O}_4$  and the maghemite  $\gamma\text{-Fe}_2\text{O}_3$  almost possess the same lattice constant

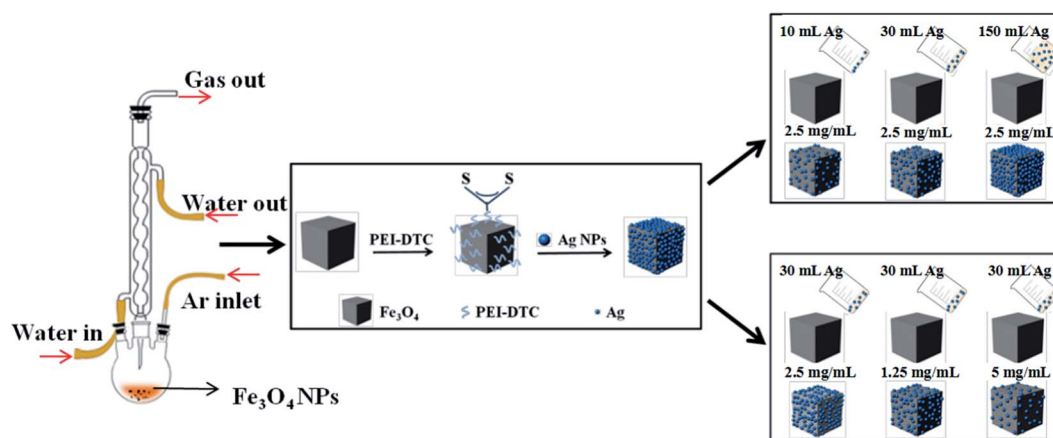


Fig. 1 Schematic illustration of the synthesis of  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals.



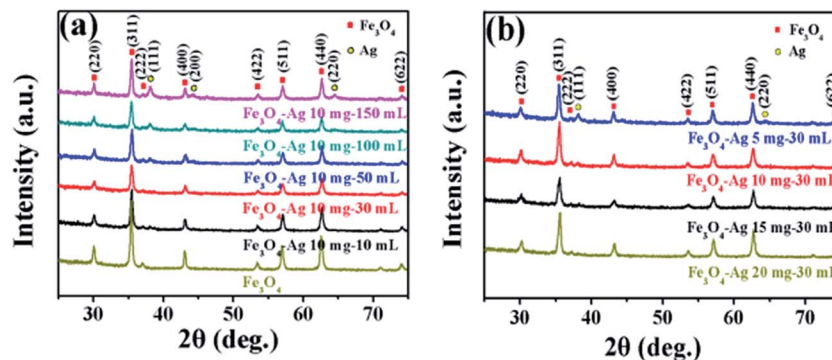


Fig. 2 XRD patterns of pure  $\text{Fe}_3\text{O}_4$  nanocrystals and  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals with different addition quantities of the silver seed colloids ( $\text{Fe}_3\text{O}_4$ -Ag 10 mg-10 mL,  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-30 mL,  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-50 mL,  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-100 mL and  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-150 mL) (a) and the different addition quantities of the  $\text{Fe}_3\text{O}_4$  nanocrystals ( $\text{Fe}_3\text{O}_4$ -Ag 5 mg-30 mL,  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-30 mL,  $\text{Fe}_3\text{O}_4$ -Ag 15 mg-30 mL and  $\text{Fe}_3\text{O}_4$ -Ag 20 mg-30 mL) (b).

and atomic arrangement, they have similar XRD patterns.<sup>40</sup> In order to confirm that the formed phase is the magnetite  $\text{Fe}_3\text{O}_4$  and not the maghemite  $\gamma\text{-Fe}_2\text{O}_3$ , the further characterization was used before attaching silver seeds to  $\text{Fe}_3\text{O}_4$  nanocrystals. Mössbauer spectrum is an effective method to differentiate magnetite  $\text{Fe}_3\text{O}_4$  from maghemite  $\gamma\text{-Fe}_2\text{O}_3$ . Mössbauer spectrum and the fitting curves of pure  $\text{Fe}_3\text{O}_4$  nanocrystals are presented in Fig. 3, and the fitted Mössbauer parameters are listed in Table 1. The spectrum is fitted using two sextets. The acute and strong lines of the magnetic

sextets show a double six-peak structure and testifies the presence of magnetite  $\text{Fe}_3\text{O}_4$ . The hyperfine field is 49.3 and 46.1 T, and the value of isomer shift is 0.230 and 0.600  $\text{mm s}^{-1}$ , which correspond to  $\text{Fe}^{3+}$  ions at site A (tetrahedral interstitial site) and  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions at site B (octahedral interstitial site), respectively. The result is in agreement with the result obtained by Zhang *et al.*<sup>41</sup>

For all the samples coated with silver seeds, besides the characteristic diffraction peaks corresponding to the  $\text{Fe}_3\text{O}_4$ , there also exist other three diffraction peaks indexed to the cubic Ag phase (JCPDS card no. 04-0783),<sup>42</sup> which preliminarily illustrates that the silver seeds have attached to  $\text{Fe}_3\text{O}_4$  surfaces. Fig. S2† displays UV-Vis absorption spectra of the as-prepared colloidal Ag solution (red curve line) and the Ag solution after immobilization on the  $\text{Fe}_3\text{O}_4$ @PEI-DTC nanocrystals after the magnetic separation (black curve line). The characteristic UV-Vis peak of the as-prepared colloidal Ag solution is observed at 403 nm.<sup>38</sup> A broad full width at half maximum suggests the polydispersity of the silver seeds.<sup>43</sup> The UV-Vis peak of the Ag solution after depositing onto the  $\text{Fe}_3\text{O}_4$ @PEI-DTC nanocrystals disappears, which indicates that almost all of the silver seeds are adsorbed effectively on the surfaces of the  $\text{Fe}_3\text{O}_4$ @PEI-DTC nanocrystals.

With the increase of the adding times of Ag seeds or the decrease of the additive amount of  $\text{Fe}_3\text{O}_4$  nanocrystals, there is no obvious variation in the peak positions. But there is a noticeable enhancement in the intensity of Ag diffraction peaks, which indicates that the amount of Ag seeds deposited onto the surfaces of  $\text{Fe}_3\text{O}_4$  nanoparticles can be adjusted by changing the adding times of Ag seeds or the additive amount of  $\text{Fe}_3\text{O}_4$  nanocrystals.

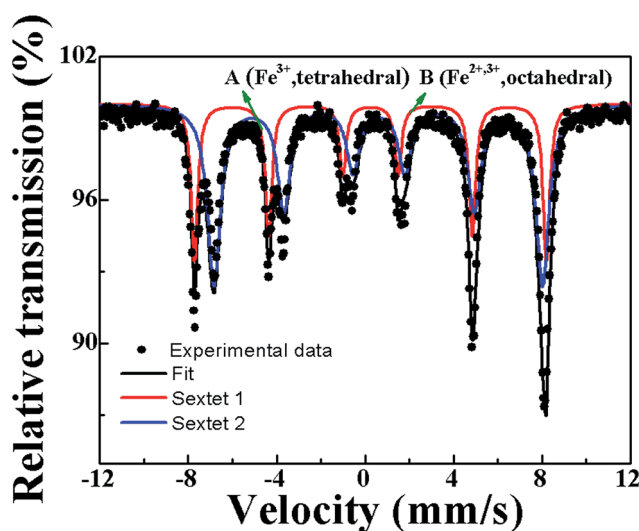


Fig. 3 Mössbauer spectra of pure  $\text{Fe}_3\text{O}_4$  nanocrystals.

Table 1 Mössbauer spectrum parameters of pure  $\text{Fe}_3\text{O}_4$  nanocrystals: IS is the isomer shift, QS is the quadrupole splitting, HIN is the hyperfine field, HWHM is the half width at half maximum and AREA is the relative absorption area

Composition	IS ( $\text{mm s}^{-1}$ )	QS ( $\text{mm s}^{-1}$ )	HIN (T)	HWHM ( $\text{mm s}^{-1}$ )	AREA (%)
A	0.230	0.034	49.3	0.179	34.1
B	0.600	0.002	46.1	0.355	65.9



### 3.2 Morphology of Fe<sub>3</sub>O<sub>4</sub>-Ag seeds nanocrystals

The morphology and detailed structure of the samples were characterized by SEM and TEM. Fig. 4 and S3<sup>†</sup> show typical low-magnification TEM and SEM images of the pure Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>-Ag 10 mg-10 mL, Fe<sub>3</sub>O<sub>4</sub>-Ag 10 mg-30 mL, Fe<sub>3</sub>O<sub>4</sub>-Ag 10 mg-50 mL, Fe<sub>3</sub>O<sub>4</sub>-Ag 10 mg-100 mL and Fe<sub>3</sub>O<sub>4</sub>-Ag 10 mg-150 mL nanocrystals. The shape of the pure Fe<sub>3</sub>O<sub>4</sub> nanocrystals is cubic and the average particle size is about 50 nm. Histogram of the pure Fe<sub>3</sub>O<sub>4</sub> nanocrystals from SEM image of Fig. S3a is shown in Fig. S4,<sup>†</sup> which indicates that the Fe<sub>3</sub>O<sub>4</sub> nanocrystals have a narrow distribution of particle size. As is shown in Fig. 4b, silver seeds with average particle diameter of about 7 nm are uniformly located on the surfaces of Fe<sub>3</sub>O<sub>4</sub> nanocrystals for the Fe<sub>3</sub>O<sub>4</sub>-Ag 10 mg-10 mL. The inset of Fig. 4b is the corresponding high-resolution TEM (HRTEM) image, which shows that the distinct lattice fringes with interplanar spacings of 0.290 and

0.235 nm well match the *d*-values indexed as the (220) plane of Fe<sub>3</sub>O<sub>4</sub> and the (111) plane of Ag, respectively.<sup>44,45</sup> A close observation reveals that the thin PEI-DTC shell layers with the thickness of about 2 nm form around the Fe<sub>3</sub>O<sub>4</sub> nanocrystals. Selected area electron diffraction (SAED) pattern of Fe<sub>3</sub>O<sub>4</sub>-Ag 10 mg-100 mL is presented in the inset of Fig. 4e. The bright and discrete diffraction spots can be assigned to the diffractions of either Fe<sub>3</sub>O<sub>4</sub> nanocrystals or silver seeds, and this result is consistent with that of the XRD pattern of Fe<sub>3</sub>O<sub>4</sub>-Ag 10 mg-100 mL. HRTEM and SAED results confirm the coexistence of Fe<sub>3</sub>O<sub>4</sub> and Ag.<sup>46</sup> In addition, with the increase of adding times of silver seeds, the amount of the silver seeds deposited on the surfaces of Fe<sub>3</sub>O<sub>4</sub> nanocrystals significantly increases (Fig. 4c-f), which can be verified by their corresponding SEM images of Fig. S3.<sup>†</sup> Although the silver seeds are difficult to be distinguished in SEM images due to the small silver seeds sizes, the

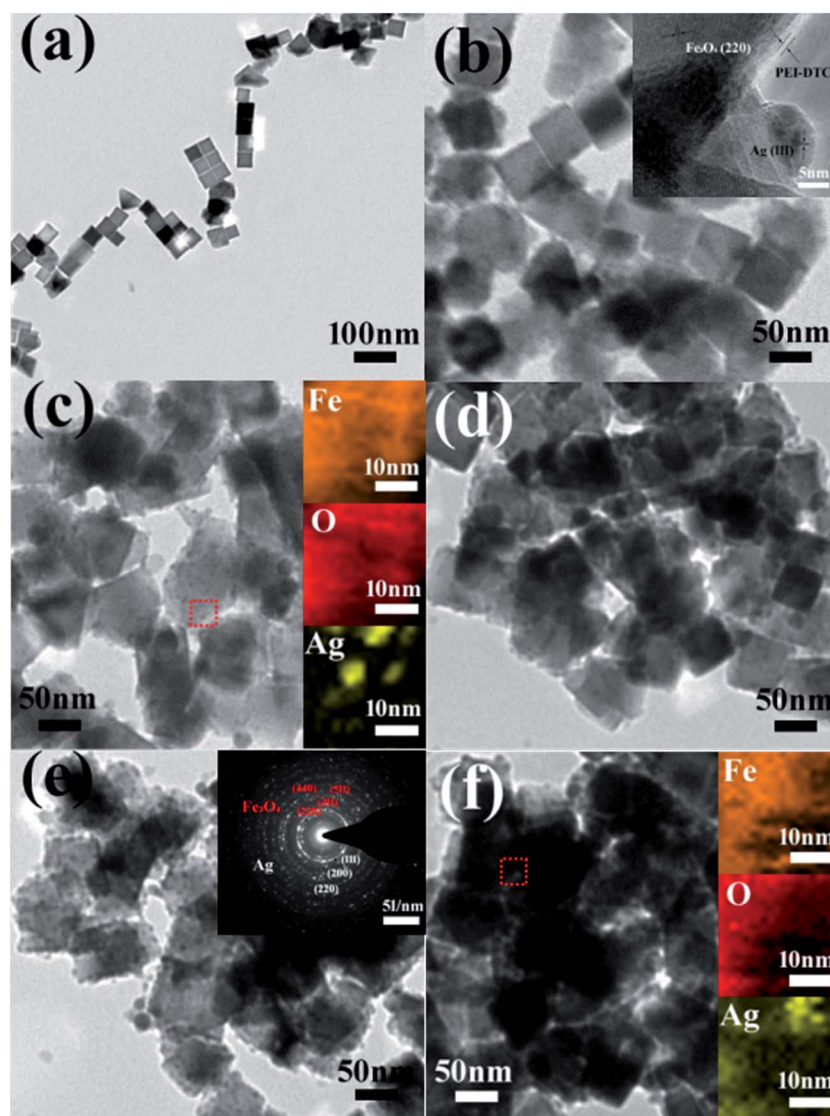


Fig. 4 TEM images of pure Fe<sub>3</sub>O<sub>4</sub> (a), Fe<sub>3</sub>O<sub>4</sub>-Ag 10 mg-10 mL with HRTEM image (inset) (b), Fe<sub>3</sub>O<sub>4</sub>-Ag 10 mg-30 mL (c), Fe<sub>3</sub>O<sub>4</sub>-Ag 10 mg-50 mL (d), Fe<sub>3</sub>O<sub>4</sub>-Ag 10 mg-100 mL with SAED pattern (inset) (e) and Fe<sub>3</sub>O<sub>4</sub>-Ag 10 mg-150 mL (f). The insets of (c) and (f) are EDS elemental mapping images (Fe, O and Ag) of corresponding red dash line square.



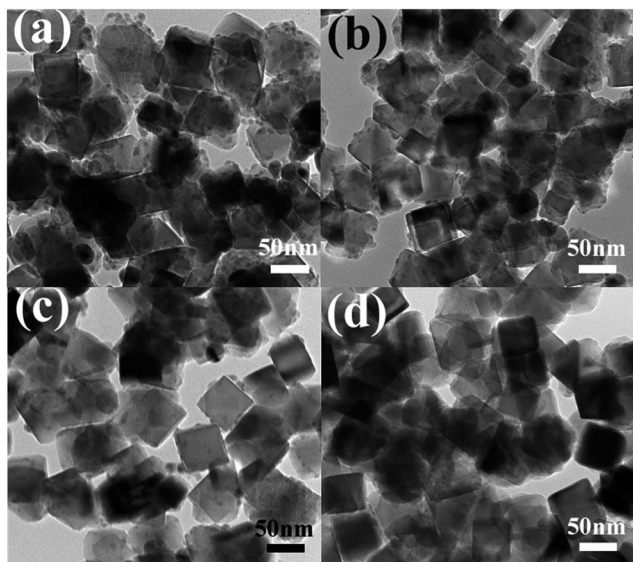


Fig. 5 TEM images of  $\text{Fe}_3\text{O}_4$ -Ag 5 mg-30 mL (a),  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-30 mL (b),  $\text{Fe}_3\text{O}_4$ -Ag 15 mg-30 mL (c) and  $\text{Fe}_3\text{O}_4$ -Ag 20 mg-30 mL (d).

corresponding energy-dispersive spectroscopy (EDS) spectra (insets in Fig. S3†) demonstrate that Ag peaks increase when increasing the adding times of silver seeds. Similar results were

observed by Zhong *et al.*<sup>47</sup> EDS-mappings were applied to analyze the distributions of Fe, O and Ag atoms. The insets of Fig. 4c and f are the EDS elemental mapping images (Fe, O and Ag) of the corresponding red dash line square for  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-30 mL and  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-150 mL nanocrystals, respectively. The EDS maps not only impress us directly that the silver seeds are uniformly deposited on the surfaces of  $\text{Fe}_3\text{O}_4$  nanoparticles, but further illustrate that the number of silver seeds on the  $\text{Fe}_3\text{O}_4$  surfaces may be adjusted by changing the adding times of silver seeds.

TEM and SEM images of the  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals with the different addition quantities of the  $\text{Fe}_3\text{O}_4$  nanocrystals ( $\text{Fe}_3\text{O}_4$ -Ag 5 mg-30 mL,  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-30 mL,  $\text{Fe}_3\text{O}_4$ -Ag 15 mg-30 mL and  $\text{Fe}_3\text{O}_4$ -Ag 20 mg-30 mL) are exhibited in Fig. 5 and S5.† It can be seen from Fig. 5 and S5,† the amount of silver seeds adhered to the surfaces of  $\text{Fe}_3\text{O}_4$  nanocrystals decreases with the increase in the addition amount of the  $\text{Fe}_3\text{O}_4$  nanocrystals. These results suggest that both the adding times of silver seeds and the additive quantity of  $\text{Fe}_3\text{O}_4$  nanocrystals play critical roles in adjusting the amount of silver seeds attached on the  $\text{Fe}_3\text{O}_4$  surfaces.

### 3.3 XPS studies of $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals

Surface analysis of the pure  $\text{Fe}_3\text{O}_4$  nanocrystals and the  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals ( $\text{Fe}_3\text{O}_4$ -Ag 10 mg-10 mL,  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-

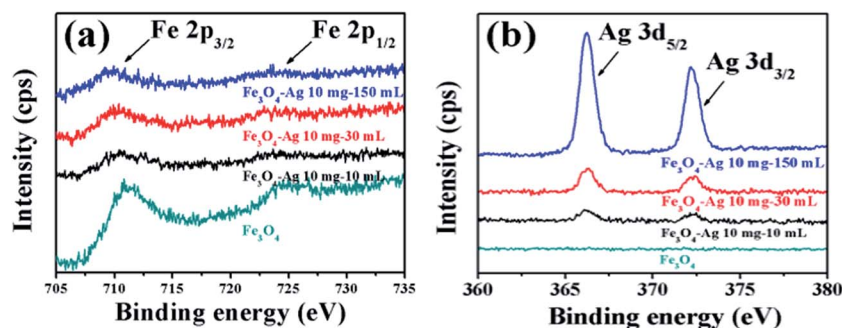


Fig. 6 High resolution XPS scans of Fe 2p (a) and Ag 3d (b) for pure  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-10 mL,  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-30 mL and  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-150 mL.

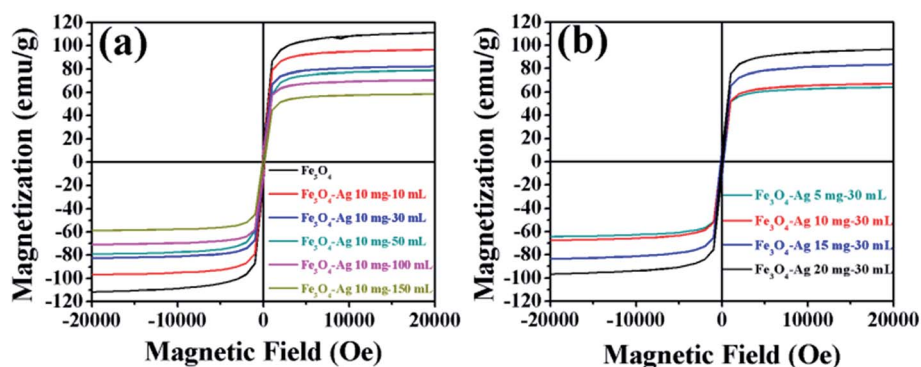


Fig. 7 Magnetic hysteresis ( $M-H$ ) loops of pure  $\text{Fe}_3\text{O}_4$  nanocrystals and  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals with the different addition quantities of the silver seed colloids ( $\text{Fe}_3\text{O}_4$ -Ag 10 mg-10 mL,  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-30 mL,  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-50 mL,  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-100 mL and  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-150 mL) (a) and the different addition quantities of the  $\text{Fe}_3\text{O}_4$  nanocrystals ( $\text{Fe}_3\text{O}_4$ -Ag 5 mg-30 mL,  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-30 mL,  $\text{Fe}_3\text{O}_4$ -Ag 15 mg-30 mL and  $\text{Fe}_3\text{O}_4$ -Ag 20 mg-30 mL) (b).



30 mL and  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-150 mL) was carried out using XPS (Fig. 6 and S6†). With the exception of Fe, O, Ag and C peaks, no impurities are observed from the XPS survey scan spectra in Fig. S6.† The high resolution XPS spectrum of Fe 2p for the pure  $\text{Fe}_3\text{O}_4$  nanocrystals shows two contributions, Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub> (resulting from the spin-orbit splitting), locating at respectively 711.2 and 724.5 eV (Fig. 6a), which can be assigned to magnetite  $\text{Fe}_3\text{O}_4$ .<sup>48,49</sup> In addition, the core level binding energy observed for Ag 3d<sub>5/2</sub> and Ag 3d<sub>3/2</sub> of the  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-10 mL nanoparticles locates at 367.4 and 373.4 eV with a spin-orbit splitting of 6 eV between Ag 3d<sub>5/2</sub> and Ag 3d<sub>3/2</sub> (Fig. 6b), which matches well with the standard reference XPS spectrum of metallic Ag.<sup>50</sup> It should be pointed out that the increase of adding times of silver seeds deposited onto the surfaces of

$\text{Fe}_3\text{O}_4$  nanocrystals results in the shift of the Fe 2p peaks to lower binding energy and the simultaneously opposing changes of Ag 3d peaks, which demonstrates an electronic exchange interaction between  $\text{Fe}_3\text{O}_4$  nanocrystals and Ag seeds.<sup>51</sup> Another interesting finding is that the intensity of Fe 2p peaks become weaker, whereas that of Ag 3d peaks become stronger with the increase of the adding times of Ag seeds, indicating the increase in the number of silver seeds on the  $\text{Fe}_3\text{O}_4$  surfaces.<sup>52</sup>

### 3.4 Magnetism of $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals

The effects of the number of silver seeds deposited on the surfaces of the magnetic properties of  $\text{Fe}_3\text{O}_4$  nanocrystals were also investigated. Fig. 7a and b show the magnetization *versus*

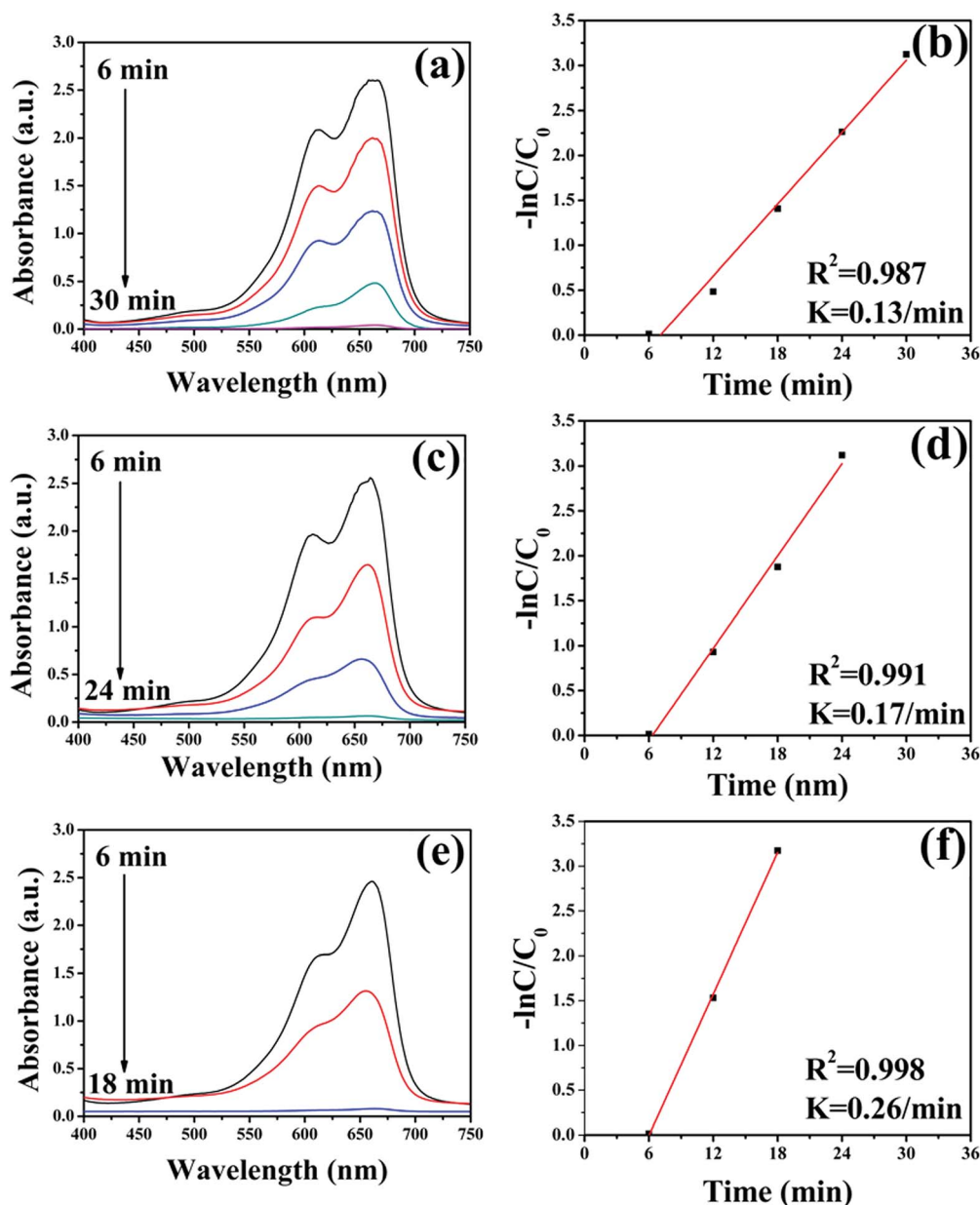


Fig. 8 UV-Vis absorption spectra of MB aqueous solution after reduction catalyzed by  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-10 mL (a),  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-50 mL (c) and  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-100 mL (e). (b), (d) and (f) is the corresponding  $-\ln(C/C_0)$  versus reaction time plots.



magnetic field ( $M-H$ ) loops of the pure  $\text{Fe}_3\text{O}_4$  nanocrystals and the  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals with the different addition quantities of the silver seed colloids and the different addition quantities of the  $\text{Fe}_3\text{O}_4$  nanocrystals, respectively. All the samples exhibit the superparamagnetic behavior without the obvious observation of the coercivity and the remanence. Magnetic saturation ( $M_s$ ) value of the pure  $\text{Fe}_3\text{O}_4$  nanocrystals is  $110.5 \text{ emu g}^{-1}$ . It is noticed that the  $M_s$  value linearly decreases with the increase of the addition quantity of the silver seed colloids or the decrease of the addition quantity of the  $\text{Fe}_3\text{O}_4$  nanocrystals. The decrease of  $M_s$  value may be attributed to the increase of the mass owing to the adherence of silver seeds on the surfaces of the  $\text{Fe}_3\text{O}_4$  nanocrystals<sup>53</sup> or the interaction between  $\text{Fe}_3\text{O}_4$  nanocrystals and silver seeds.<sup>54</sup> Even if  $M_s$  value decreases to  $59.1 \text{ emu g}^{-1}$  for the  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-150 mL and  $63.6 \text{ emu g}^{-1}$  for  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-30 mL, the samples still have the strong magnetic responsiveness and can be magnetically separated easily from aqueous solution by imparting an external magnetic field, which renders them economic and reusable for various applications.

The temperature-dependent magnetization ( $M-T$ ) of pure  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4$ -150 mL Ag was measured under zero-field-cooled (ZFC) and 1000 Oe field-cooled (FC) conditions (Fig. S7†). The magnetic characterization was carried out in the temperature range of 10 K to 300 K. In the ZFC process, the samples were cooled down from room temperature to 10 K in the absence of an external magnetic field, and the magnetic data were acquired during the warming run in a constant external field (1000 Oe). In the FC measurements, the samples were initially cooled down to 10 K in the presence of 1000 Oe

magnetic field and the FC data were recorded during the warm-up cycle in the same magnetic field. Typical ZFC-FC magnetization curves of superparamagnetic results are observed. From the maximum of the ZFC curve, the blocking temperature ( $T_B$ ) of pure  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-150 mL is 112 and 99 K, respectively. Generally,  $T_B$  value is determined by the particle size and the magnetic interaction between the particles.<sup>55,56</sup> It is rational to eliminate the contribution of the  $\text{Fe}_3\text{O}_4$  particle size to the shift of the peak of the ZFC magnetization curve in our experiment. Therefore, it is apparent that the silver seeds attached on the  $\text{Fe}_3\text{O}_4$  surface disrupt the magnetic coupling between adjacent  $\text{Fe}_3\text{O}_4$  nanocrystals and lead to the slight decrease of  $T_B$  value.<sup>57</sup>

### 3.5 Catalytic studies of $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals

The application in the field of catalysis is an important applied aspect of nanomaterials.<sup>58-63</sup> To investigate the catalytic performance of the  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals to organic dyes, the MB was chosen as a core sample. The changes in UV-Vis absorption spectra of MB aqueous solution over time catalyzed by the different  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals are shown in Fig. 8. The intensity of the typical absorption peaks at 665 nm shows a decreasing trend and disappears completely after 30, 24 and 18 min for  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-10 mL,  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-50 mL and  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-100 mL, respectively.<sup>64</sup> This indicates the catalytic reduction and the complete removing of MB has been achieved by the  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals, which can be verified by the color variation of MB over time from blue to colorless (Fig. S8†). The pseudo first order kinetics was applied

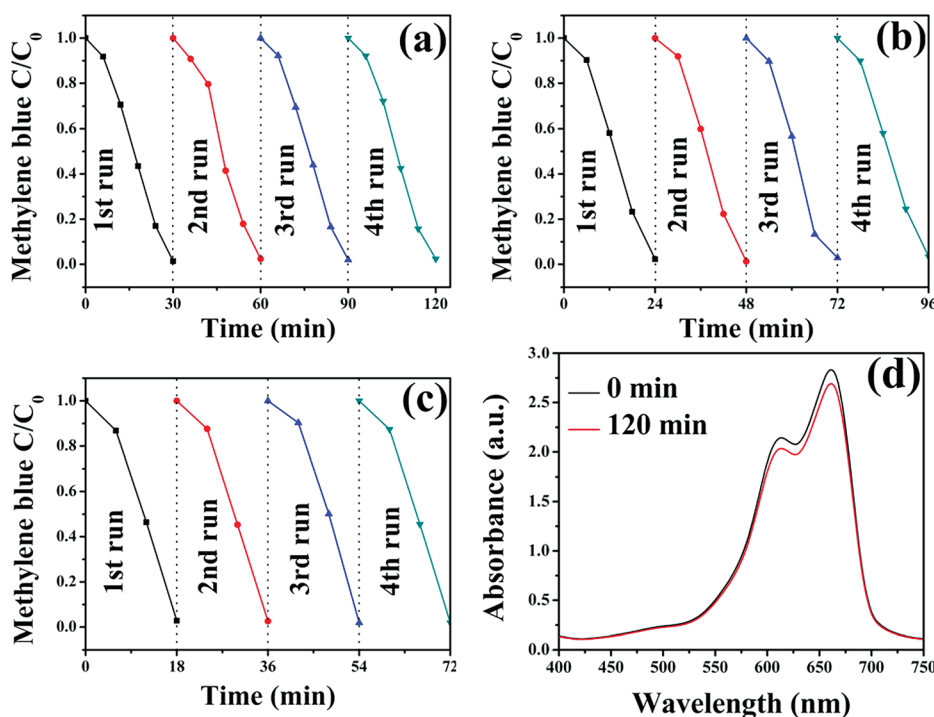


Fig. 9 Four cycles of removal of MB over  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-10 mL (a),  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-50 mL (b) and  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-100 mL (c). UV-Vis absorption spectra of MB aqueous solution catalyzed by the pure  $\text{Fe}_3\text{O}_4$  nanocrystals (d).



to study the rate constants of MB.<sup>65</sup> The concentration of MB at time  $t$  is denoted as  $C$ , and the initial concentration of MB at  $t = 0$  is regarded as  $C_0$ . The  $C/C_0$  is obtained from the relative intensity of absorption. The linear relationship of  $\ln(C/C_0)$  versus reaction time represents that the reduction of MB by the  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals matches well with the pseudo first order kinetics. The correlation coefficients  $R^2$  are all higher than 0.9 and the rate constants of MB are  $0.13 \text{ min}^{-1}$ ,  $0.17 \text{ min}^{-1}$  and  $0.26 \text{ min}^{-1}$  for  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-10 mL,  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-50 mL and  $\text{Fe}_3\text{O}_4$ -Ag 10 mg-100 mL, respectively. It is worthy to note that the calculated rate constant is much higher than those previously reported values for the degradation of MB by using semiconductor photocatalysts,<sup>66–68</sup> moreover, the rate constant for the  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals is significantly higher than the previous works by utilizing noble metal catalysts.<sup>69–71</sup>

It can be noticed that the time required to catalytic reduce decreases with the increase of the amount of silver seeds deposited on the  $\text{Fe}_3\text{O}_4$  surfaces. It is generally accepted that the catalytic reaction of silver nanocrystals occurs through electron transfer.<sup>72</sup> The electrochemical mechanism that the nucleophilic  $\text{BH}_4^-$  ions donate electrons to electrophilic organic MB through silver seeds is proposed. Therefore, the increase of the number of silver seeds immobilized on the surfaces of  $\text{Fe}_3\text{O}_4$  nanocrystals supplies more opportunities to the catalytic reaction of MB, resulting in the increase of reduction rate of MB.

In order to test the reusability of the  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals, the catalytic reaction experiments of MB with the same sample were repeated for four times. As is shown in Fig. 9, the catalytic reaction ability of all the samples maintains almost consistent even after at least four circles, which demonstrates that these  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals can serve as recyclable catalysts for organic dyes. For the purpose of comparison, it can be observed that no significant change occurred in the reduction of MB even after 120 min in the presence of the pure  $\text{Fe}_3\text{O}_4$  nanocrystals only (Fig. 9d).

## 4. Conclusions

In this study, magnetically retrievable  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals were successfully synthesized through a novel seed deposition process. XRD, TEM and SEM results indicate that the adding times of silver seeds or the additive amount of  $\text{Fe}_3\text{O}_4$  nanocrystals is essential to control the number of silver seeds deposited on the modified surfaces of  $\text{Fe}_3\text{O}_4$  nanocrystals. The increase of the number of silver seeds attached to the  $\text{Fe}_3\text{O}_4$  nanocrystals surfaces results in the shift of the Fe 2p peaks to lower binding energy and the simultaneously opposing changes of Ag 3d peaks due to the enhancement of the electronic exchange interaction between  $\text{Fe}_3\text{O}_4$  nanocrystals and Ag seeds. Although the silver seeds decrease the  $M_s$  value and  $T_B$  value,  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals can be easily separated by applying a magnetic field. The time required to catalytic reduce to MB decreases with the increase of the amount of silver seeds deposited on the  $\text{Fe}_3\text{O}_4$  surfaces. The catalytic reaction ability of  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals is almost consistent even after at least four circles, demonstrating that the  $\text{Fe}_3\text{O}_4$ -Ag seeds nanocrystals can serve as recyclable catalysts for MB. Therefore, this newly synthesized  $\text{Fe}_3\text{O}_4$ -Ag seeds

nanocrystals can be promising nanocatalysts for the reduction of the organic dyes during the wastewater treatment.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Numbers 21676115, 51609100, 61575080, 61405072, 61675090 and 21546013); Program for the development of Science and Technology of Jilin Province (Grant Numbers 20160101287JC, 20150520015JH, 20150519024JH and 20140519003JH); and Technology of Education Department of Jilin Province (Grant Number JJKH20170374KJ).

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