Eco-friendlyseeded Fe$_3$O$_4$-Ag nanocrystals: a new type of highly efficient and low cost catalyst for methylene blue reduction

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Abstract

Hybrid Fe$_3$O$_4$-Ag nanocrystals, a new type of highly efficient and reusable catalysts for methylene blue (MB) reduction, are fabricated by a novel seed deposition process. X-ray diffraction and Mössbauer spectroscopy results elaborate that the developed iron oxides are in pure magnetite Fe$_3$O$_4$ phase. Upon manipulating the amount of Ag seeds capsuled on the modified surfaces of Fe$_3$O$_4$ 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$_3$O$_4$-Ag nanocrystals is coherent with the pseudo first order kinetics. Importantly, with remarkable recyclability features, the hybrid Fe$_3$O$_4$-Ag nanocrystals can be easily separated by applying an external magnetic field. The tailored catalytic performances of the hybrid Fe$_3$O$_4$-Ag nanocrystals during MB reduction are attributed to the optimized dynamic electron transfer process, which dominates the electrochemical mechanism wherein the nucleophilic BH$_4^-$ ions donate electrons to electrophilic organic MB through Ag seeds with a regulated amount. Such developed hybrid Fe$_3$O$_4$-Ag nanocrystals pave the way towards the mass production of highly efficient and low cost catalyst for methylene blue reduction.

Keywords: Fe$_3$O$_4$-Ag nanocrystals; Magnetic properties; Catalytic reduction; Methylene blue.

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1 The authors have the equal contribution to the manuscript.
Fig. S1 Pawley refinement of the XRD pattern of the pure Fe$_3$O$_4$. Red dots, blue lines and olive bars represent the experimental data, the calculated data and the peak position of the sample, respectively. The bottom line in black shows the different experimental–calculated data.
Fig. S2 UV-vis spectra of the as-prepared colloidal Ag solution (red curve line) and the Ag solution after immobilization on the Fe₃O₄@PEI-DTC nanocrystals after the magnetic separation (black curve line). Inset shows the photographs of the colloidal Ag solution (a), reaction solution (b), and after magnetic separation (c).
Fig. S3

Fig. S3 SEM images of Fe$_3$O$_4$ (a), Fe$_3$O$_4$-Ag 10 mg-10 mL (b), Fe$_3$O$_4$-Ag 10 mg-30 mL (c), Fe$_3$O$_4$-Ag 10 mg-50 mL (d), Fe$_3$O$_4$-Ag 10 mg-100 mL (e) and Fe$_3$O$_4$-Ag 10 mg-150 mL (f). The insets are the corresponding energy-dispersive spectroscopy (EDS) spectra.

As can be seen from the insets of Fig. S2, Fe, O and Ag elements can be found in all samples and no impurity is detected within the detection limit. Si peaks come from the supporting Si substrates. Pt peaks are derived from the platinum layer sputtered onto the surface of the sample in order to avoid the charging of the sample surface and enhance the signal to noise ratio for electron microscopy analysis.
Fig. S4

Fig. S4 Histogram of pure Fe$_3$O$_4$ nanocrystals from SEM image of Fig. S2 (a).
Fig. S5 SEM images of Fe$_3$O$_4$-Ag 5 mg-30 mL (a), Fe$_3$O$_4$-Ag 10 mg-30 mL (b), Fe$_3$O$_4$-Ag 15 mg-30 mL (c) and Fe$_3$O$_4$-Ag 20 mg-30 mL (d). Insets are the corresponding energy-dispersive spectroscopy (EDS) spectra.
Fig. S6 XPS survey scan spectra of pure Fe$_3$O$_4$, Fe$_3$O$_4$-Ag 10 mg-10 mL, Fe$_3$O$_4$-Ag 10 mg-30 mL and Fe$_3$O$_4$-Ag 10 mg-150 mL.
Fig. S7 ZFC and FC curves of pure Fe$_3$O$_4$ and Fe$_3$O$_4$-Ag 10 mg-150 mL under an applied field of 1000 Oe.
Fig. S8

Fig. S8 Color variation of MB over time catalyzed by Fe$_3$O$_4$-Ag 10 mg-100 mL.