Eco-friendlyseeded Fe_3O_4-Ag nanocrystals: a new type of highly efficient and low cost catalyst for methylene blue reduction

Y. Liu,[a,b,1] Y. Y. Zhang,[a,b] Q. W. Kou,[a,b] Y. Chen,[a,b] D. L. Han,[c,1] D. D. Wang,[d] Z. Y. Lu,[e] L. Chen,[a,b] J. H. Yang[a,b,*] and S. Xing[f,*]

[a] *College of Physics, Jilin Normal University, Siping 136000, China*

[b] *Key Laboratory of Functional Materials Physics and Chemistry of the Ministry of Education, Jilin Normal University, Changchun 130103, China*

[c] *School of Materials Science and Engineering, Changchun University of Science and Technology, Changchun 130022, China*

[d] *Technology Development Department, GLOBALFOUNDRIES (Singapore) Pte. Ltd., 60 Woodlands Industrial Park D, Street 2, Singapore 738406, Singapore*

[e] *School of Environment and Safety Engineering, Jiangsu University, Zhenjiang 212013, China*

[f] *United Microelect Corp. Ltd., 3 Pasir Ris Dr 12, Singapore 519528, Singapore*

Abstract

Hybrid Fe_3O_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_3O_4 phase. Upon manipulating the amount of Ag seeds capsuled on the modified surfaces of Fe_3O_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_3O_4-Ag nanocrystals is coherent with the pseudo first order kinetics. Importantly, with remarkable recyclability features, the hybrid Fe_3O_4-Ag nanocrystals can be easily separated by applying an external magnetic field. The tailored catalytic performances of the hybrid Fe_3O_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_3O_4-Ag nanocrystals pave the way towards the mass production of highly efficient and low cost catalyst for methylene blue reduction.

Keywords: Fe_3O_4-Ag nanocrystals; Magnetic properties; Catalytic reduction; Methylene blue.

*Corresponding author: J. H. Yang, S. Xing

E-mail address: jhyang1@jlnu.edu.cn (J. H. Yang), Scott_Xing@UMC.com (S. Xing)

Tel.: +86 434 3294566; fax: +86 434 3294566.

[1] The authors have the equal contribution to the manuscript.

Fig. S1

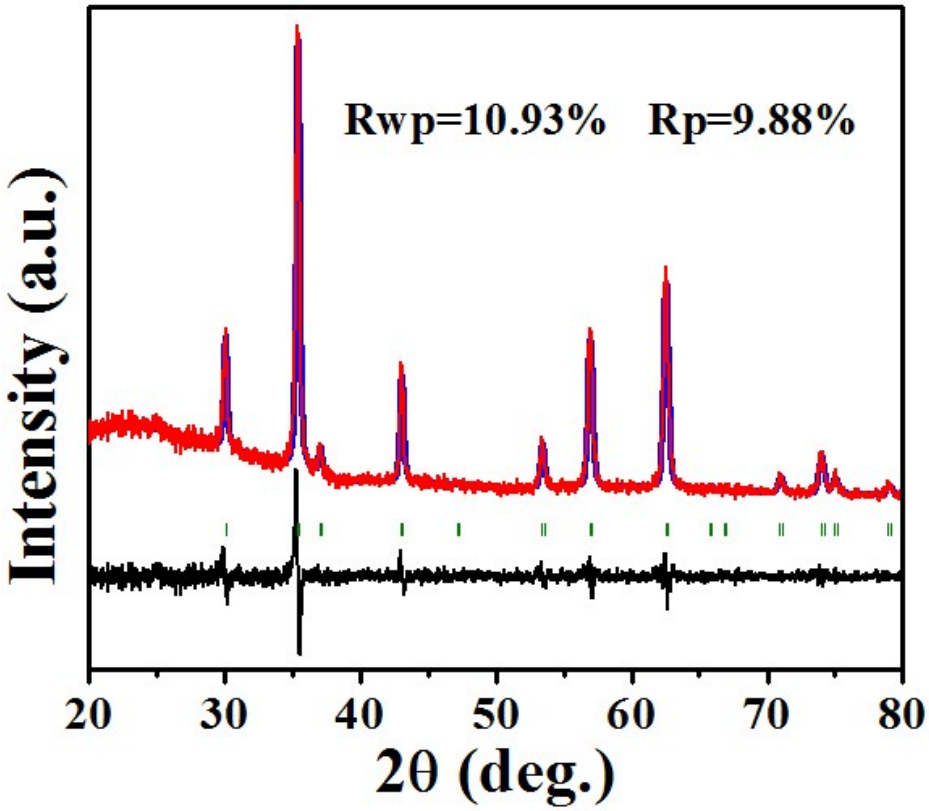

Fig. S1 Pawley refinement of the XRD pattern of the pure Fe_3O_4. Red dots, blue lines and olive bars represent the experimental data, the calculated data and the peak position of the sample, respectively. The bottom line in black shows the different experimental–calculated data.

Fig. S2

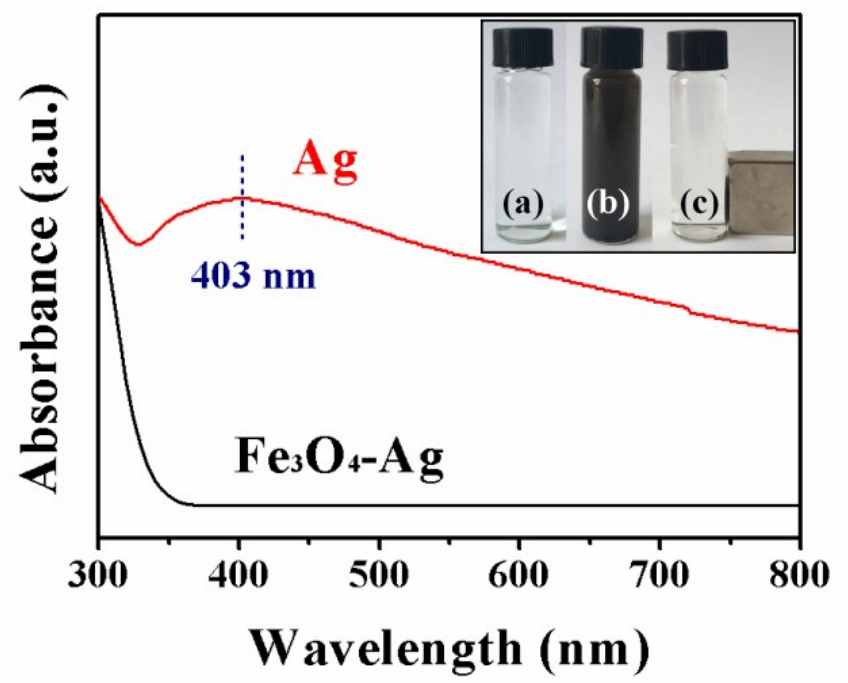

Fig. S2 UV-vis spectra of the as-prepared colloidal Ag solution (red curve line) and the Ag solution after immobilization on the Fe_3O_4@PEI-DTC nanocrystals after the magnetic separation (black curve line). Inset shows the photographs of the colloidal Ag solution (a), reaction solution (b), and after magnetic separation (c).

Fig. S3

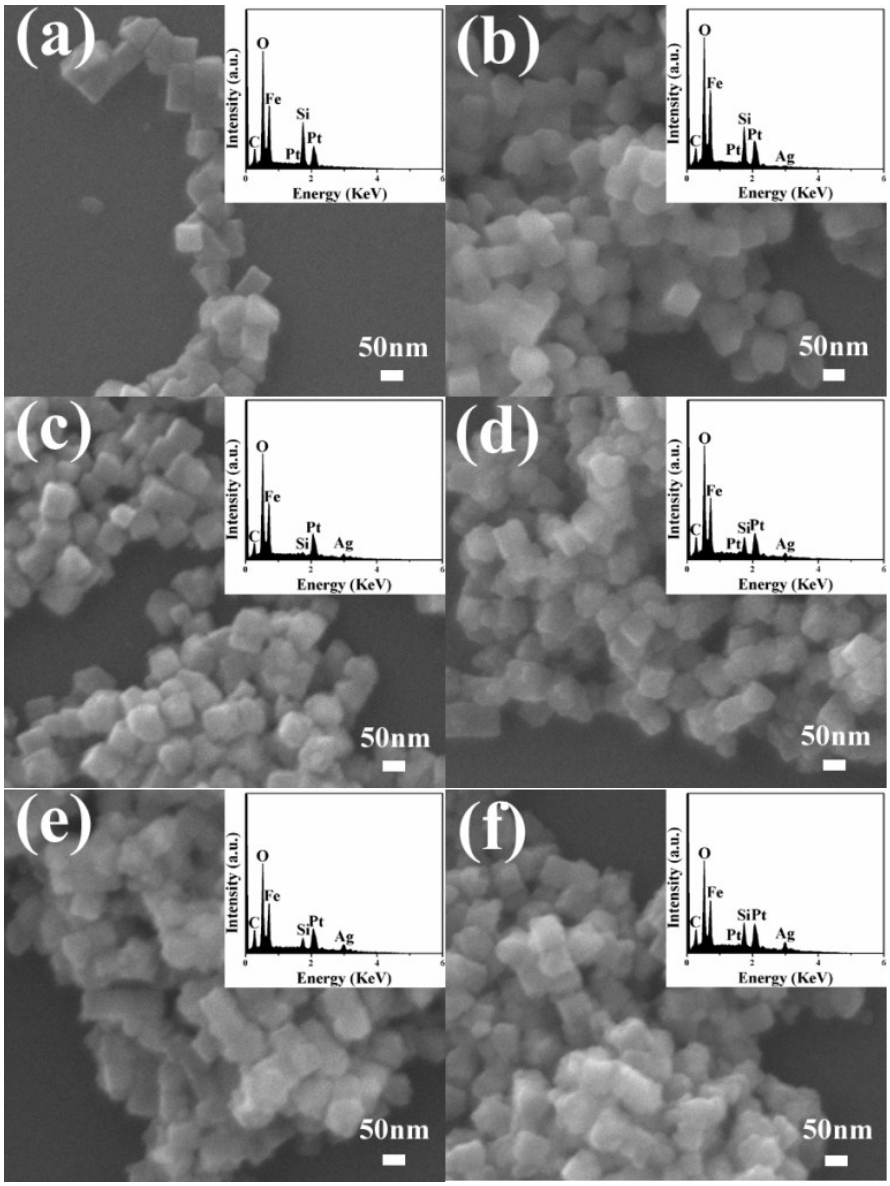

Fig. S3 SEM images of Fe_3O_4 (a), Fe_3O_4-Ag 10 mg-10 mL (b), Fe_3O_4-Ag 10 mg-30 mL (c), Fe_3O_4-Ag 10 mg-50 mL (d), Fe_3O_4-Ag 10 mg-100 mL (e) and Fe_3O_4-Ag 10 mg-150 mL (f). The insets are the corresponding energy-dispersive spectroscopy (EDS) spectra.

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

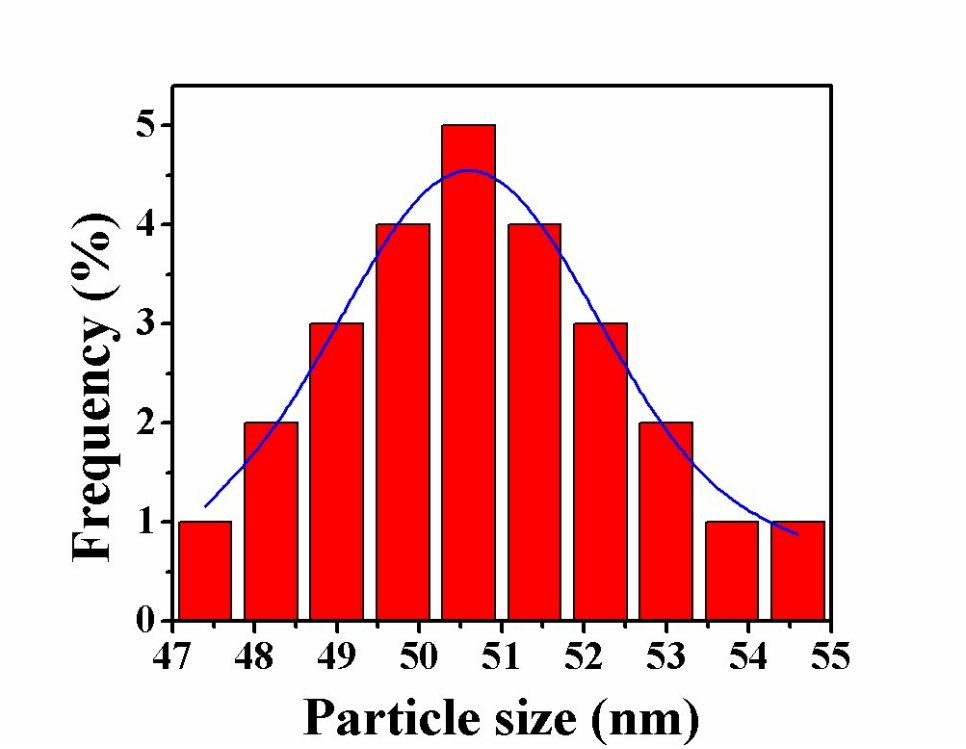

Fig. S4 Histogram of pure Fe_3O_4 nanocrystals from SEM image of Fig. S2 (a).

Fig. S5

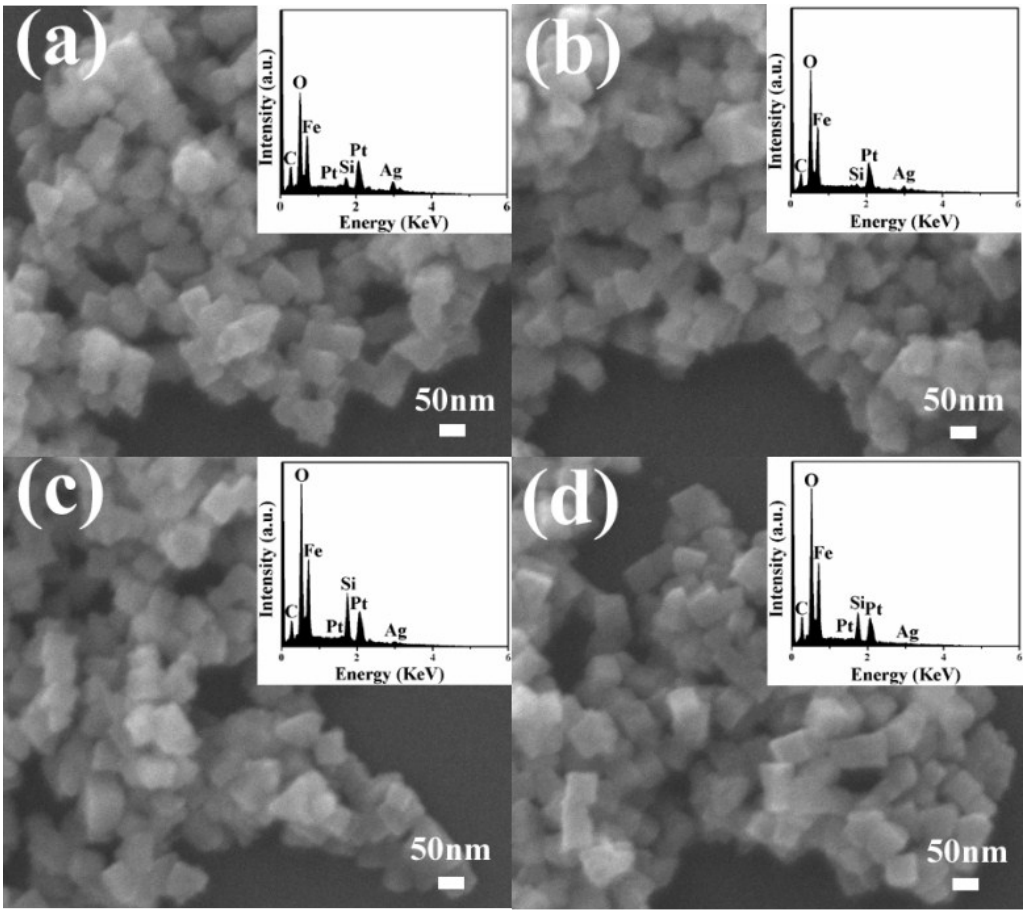

Fig. S5 SEM images of Fe_3O_4-Ag 5 mg-30 mL (a), Fe_3O_4-Ag 10 mg-30 mL (b), Fe_3O_4-Ag 15 mg-30 mL (c) and Fe_3O_4-Ag 20 mg-30 mL (d). Insets are the corresponding energy-dispersive spectroscopy (EDS) spectra.

Fig. S6

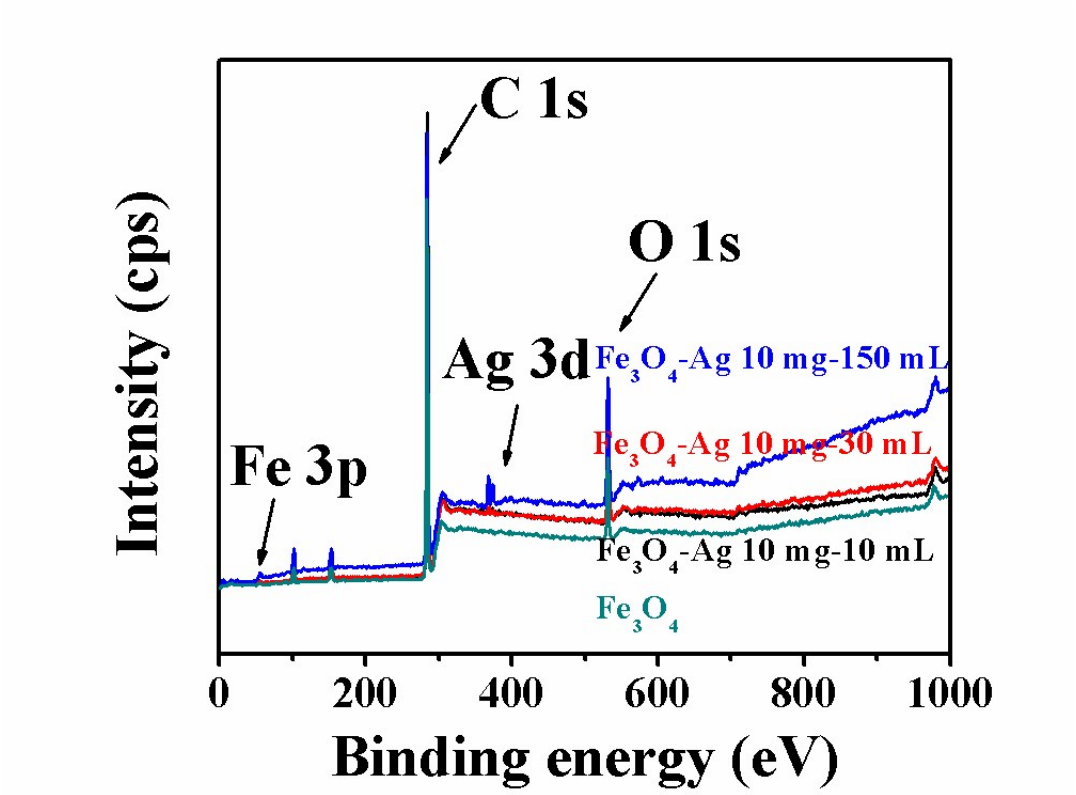

Fig. S6 XPS survey scan spectra of pure Fe_3O_4, Fe_3O_4-Ag 10 mg-10 mL, Fe_3O_4-Ag 10 mg-30 mL and Fe_3O_4-Ag 10 mg-150 mL.

Fig. S7

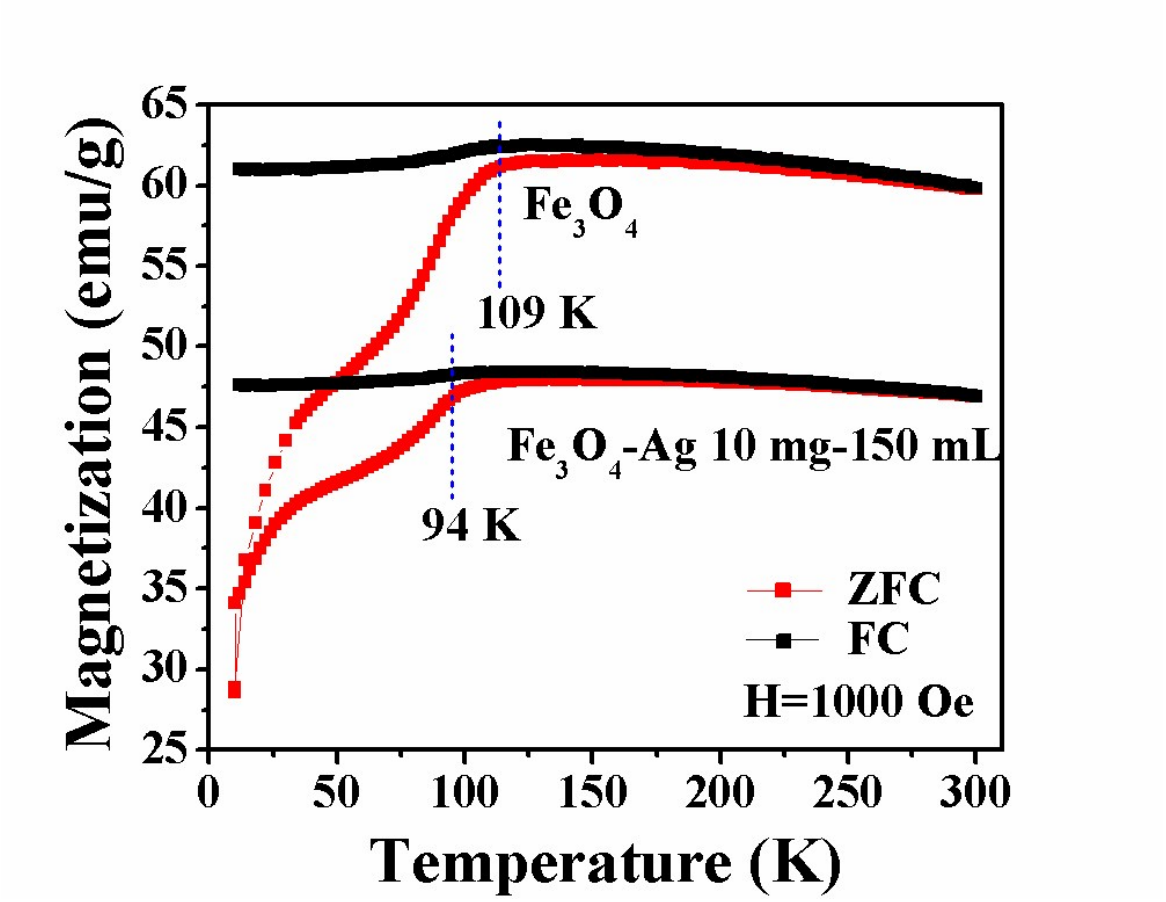

Fig. S7 ZFC and FC curves of pure Fe_3O_4 and Fe_3O_4-Ag 10 mg-150 mL under an applied field of 1000 Oe.

Fig. S8

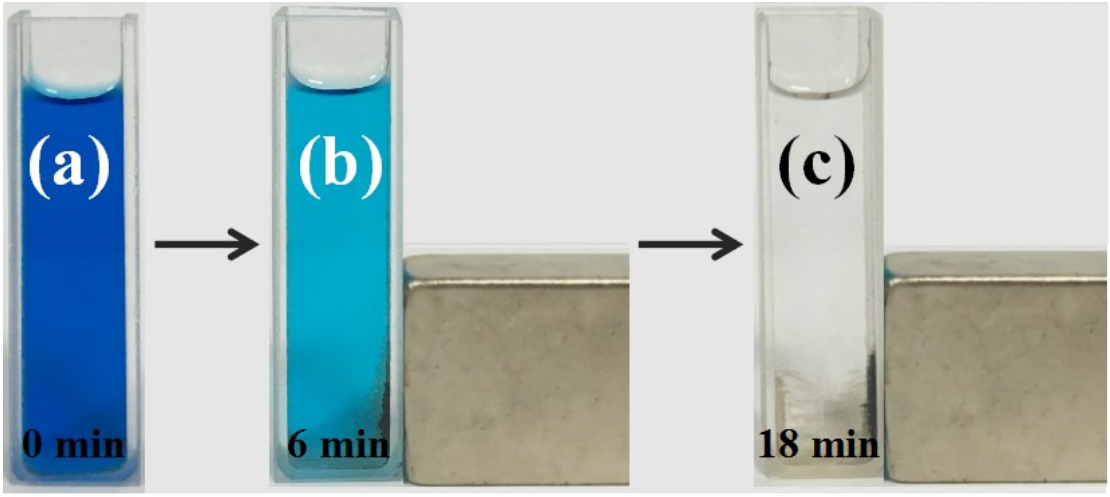

Fig. S8 Color variation of MB over time catalyzed by Fe_3O_4-Ag 10 mg-100 mL.