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(SUPPORTING INFORMATION)

One-step fabrication of γ-Fe_2O_3/polyrhodanine magnetic nanoparticles using *in-situ* chemical oxidation polymerization and their antibacterial properties

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Supplementary study of the re-dissolved Fe ions from the magnetic polyrhodanine nanoparticles by UV-Vis spectroscopy

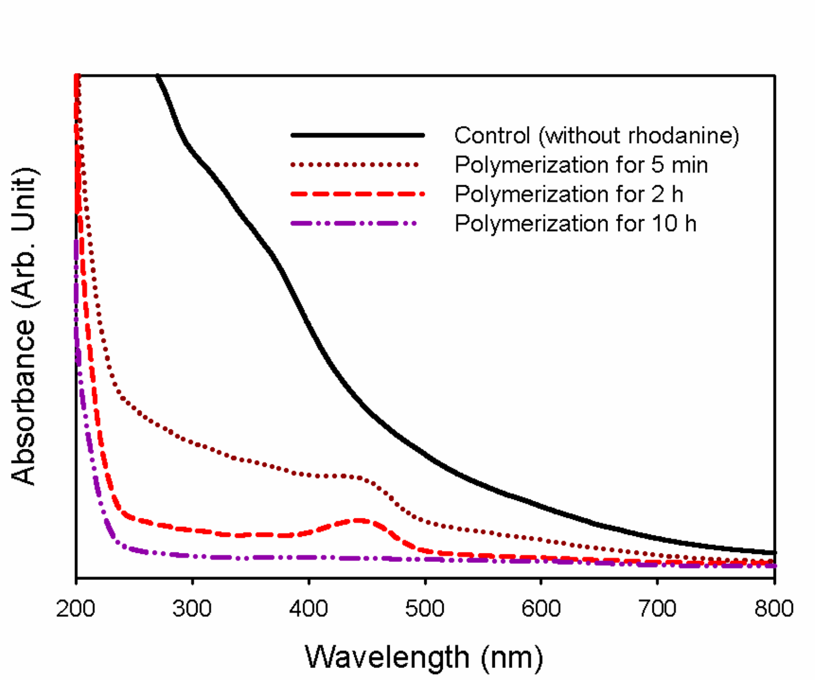

Figure S1 UV-Vis spectroscopy of the re-dissolved Fe ions from the surface of magnetic nanoparticles as a function of polymerization time in aqueous solution at 25 °C.

In aqueous solution, Fe ions can be re-dissolved out from the surface of synthesized magnetic nanoparticles. Especially, nanoscale magnetic particles have high surface reactivity, leading to the accelerated release of Fe ions. UV-Vis spectroscopy was used for this characterization in Figure S1. For the comparison, the control magnetic particles were synthesized without the rhodanine monomer and the γ-Fe_2O_3/polyrhodanine nanoparticles were prepared as a function of polymerization time after the reduction by $NaBH_4$. As can be seen in Figure S1, the peak of re-dissolved ions is observed near 370 nm in the control particles and the γ-Fe_2O_3/polyrhodanine after the polymerization time for 5 min and 2 h. In addition, the absorbance of Fe ion-bound rhodanine monomers also appears at 430 nm in the case of the magnetic polyrhodanine (polymerization for 5 min and 2 h). In general, rhodanine monomers have the n-π* transition absorption in the range of 360-390 nm.[1] Therefore, the red-shifted UV/Vis absorbance of rhodanine monomer indicates that the monomer is coordinated to the re-dissolved Fe ion or the iron oxide molecules.[2] The released ions entrapped by the surface-coordinated rhodanine monomers could be used as an oxidant for the chemical oxidation polymerization. As increasing the polymerization time, the absorbance peaks decreased and disappeared after the polymerization for 10 h because the monomers were consumed for the polymerization and the polymer shell protected the maghemite core from the oxidation.

[1] K. A. V'yunov, A. I. Ginak and E. G. Sochilin, *Journal of Applied Spectroscopy*, 1972, **16**, 1037-1042.

[2] J. K. H. Hui, Z. Yu and M. J. MacLachlan, *Angew. Chem. Int. Ed.,* 2007, **46**, 7980-7983.

Supplementary study on the formation of magnetic polyrhodanine nanoparticles using XPS characterization

Recently, the fabrication of gelatin-coated γ-Fe_2O_3 nanoparticles using $NaBH_4$ has been reported by Kinoshita group (*Jpn. J. Appl. Phys.*, **2008**, *47*, 1389-1392). On their preparation, $NaBH_4$ generated some alkaline condition for the synthesis of iron oxide and no effective reduction of Fe^{3+} to Fe^{2+} was observed even after injection of the strong reducing agent, $NaBH_4$. In addition, "reduction-oxidation routes" for the synthesis of γ-Fe_2O_3 nanoparticles was proposed by Zhang group (*Chem. Mater.*, **2002**, *14*, 1048-1052). The Fe ions were first reduced to Fe^0 atoms and then the Fe^0 atoms were easily oxidized to γ-Fe_2O_3 by air.

By combining upper two explanations, some hypothetic description could be applied to demonstrate our experimental procedure. In the preparation, the ferric ions could be reduced to Fe^0 atoms or Fe^{2+} ions using the strong reductant ($NaBH_4$) and oxidized to γ-Fe_2O_3 after the formation of intermediate Fe^0 and Fe_3O_4. In order to inspect the experimental procedure, we performed the additional experiments with *in-situ* characterization of synthesized iron oxide. For the characterization, XPS analysis was applied. The results were displayed in Figure S2 and Table S1.

Generally, in the Fe 2p XPS analysis, Fe^{3+} has a broad peak compared to Fe^{2+} and a satellite peak of Fe^{3+} is observed at approximately 8.0 eV higher than Fe $2p_{3/2}$ peak, whereas a satellite peak of Fe^{2+} is located at about 5.0~6.0 eV above Fe $2p_{3/2}$ peak.[1] Based on these references, the de-convoluted peaks are assigned and presented.

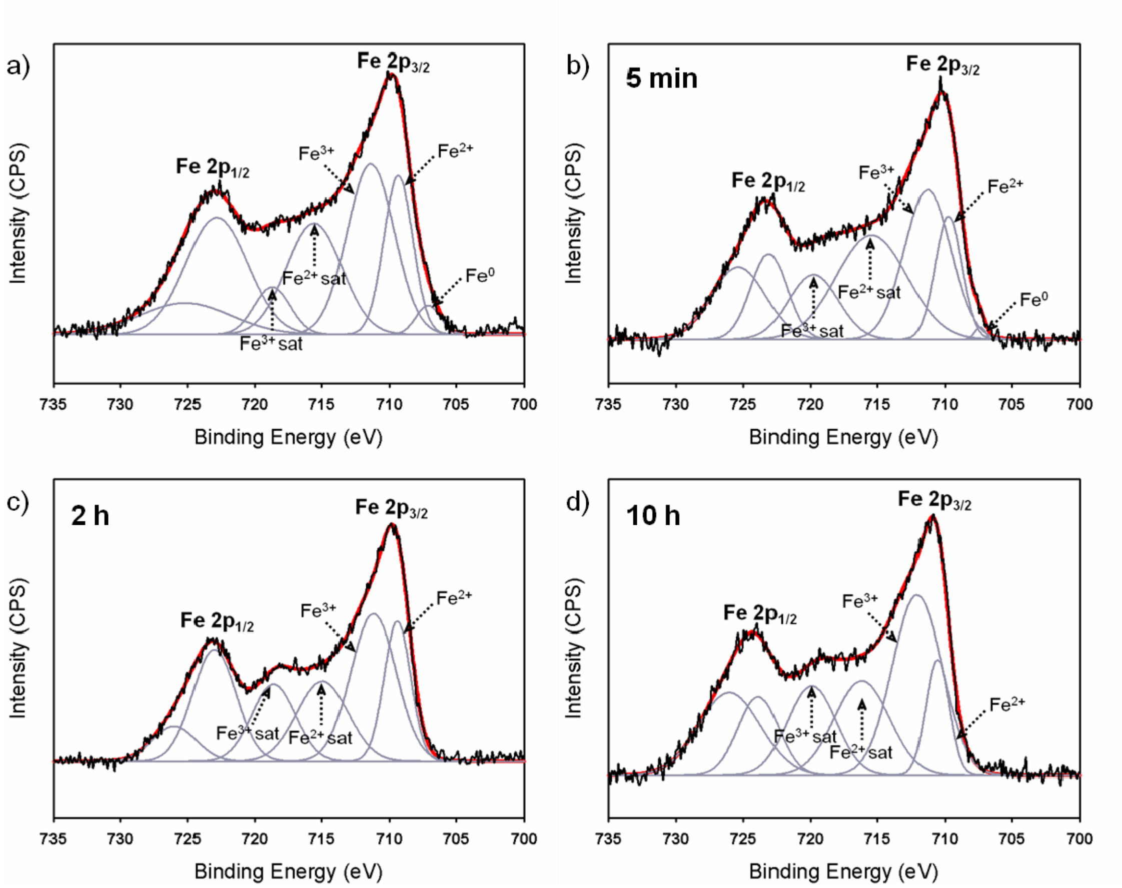

Figure S2. XPS spectra of obtained iron oxides with different reaction conditions of a) control experiment without rhodanine, reaction with rhodanine for b) 5 min, c) 2 h, and d) 10 h polymerization after injection of $NaBH_4$.

Table S1. Binding energy (eV) of de-convoluted Fe 2p lines in the synthesized iron oxides

Sample	Fe $2p_{3/2}$ (eV)	Fe^0 (eV)	Fe^{2+} (eV)	Fe^{3+} (eV)	Fe^{3+}/Fe^{2+} ratio[e]	Fe^{2+} Satellite (eV)	Fe^{3+} Satellite (eV)
Fe_3O_4	710.35±0.2[a]						
γ-Fe_2O_3	710.7±0.2[a]						
Fe^{2+}	709.3[b] (709.9)[c]						
Fe^{3+}	711.4[b] (710.8)[c]						
Control experiment without rhodanine[d]	710.15	707.09	709.33	711.38	1.74 : 1	715.59	718.70
5 min after injection of $NaBH_4$	710.75	707.43	709.73	711.29	2.11 : 1	715.44	719.77
2 h after injection of $NaBH_4$	710.55		709.40	711.18	1.79 : 1	714.96	718.60
10 h after injection of $NaBH_4$	710.75		710.55	712.06	3.33 : 1	716.17	719.90

[a] Literature value from reference 18 in the manuscript (*Thin Solid Films*, **2005**, *473*, 63-67). [b] Literature value from additional references (*J. Mater. Chem.*, **2005**, *15*, 4252-4257). [c] Literature value from additional references (*Chem. Mater.*, **2009**, *21* (20), 4880–4891). [d] Control experiment was performed for 5 min without rhodanine after the injection of $NaBH_4$. [e] The ratio of Fe^{3+}/Fe^{2+} was estimated from the relative areas of the Gaussian peaks under Fe^{3+} and Fe^{2+}.

We applied some hypothetic description for the demonstration of our experimental procedure. In the hypothesis, the ferric ions were reduced to Fe^0 atoms or Fe^{2+} ions using the strong reductant ($NaBH_4$) and rapidly oxidized to γ-Fe_2O_3 after the formation of intermediate Fe^0 and Fe_3O_4. Based on the hypothesis, we envisaged that three peaks of both intermediate states (Fe^0 and Fe^{2+}) and Fe^{3+} ions of γ-Fe_2O_3 might be detected at the initial reaction condition.

XPS spectra of each reaction condition are presented in Figure S2 and the related assigned-peaks are shown in Table S1. On the control experiment (without rhodanine, Figure S2a), Fe^0 state was detected near 707 eV, which originated from the reduction of ferric ions by $NaBH_4$. In addition, the assigned Fe $2p_{3/2}$ line (710.15 eV) matched well with that of magnetite (Fe_3O_4) and the ratio of Fe^{3+}/Fe^{2+} was 1.74:1 which was close to the reported magnetite value (1.84:1).[2] The result demonstrated that the obtained iron oxides from the reduction of ferric ions by $NaBH_4$ (reaction for 5 min without rhodanine) were magnetites with some mixtures of intermediate Fe^0 atoms. On the other hand, the synthesized iron oxides from our experimental procedure (with rhodanine at the reaction for 5 min after injection of $NaBH_4$, Figure S2b) had the binding energy of 710.75 eV, which could be assigned to the Fe $2p_{3/2}$ value of γ-Fe_2O_3 (maghemite). The ratio of Fe^{3+}/Fe^{2+} was 2.11:1 and some intermediate state of Fe^0 was also observed at 707 eV. Therefore, it could be concluded that the synthesized iron oxides at the initial condition with rhodanine consisted of mixture of magnetite and maghemite with some intermediates of Fe^0. These different characters of iron oxides from two comparative experiments might be attributed to the pH of reaction solution. In the presence of rhodanine molecules, protons were liberated from the amine groups of some rhodanine molecules due to the alkaline condition (which was caused by $NaBH_4$), which led to the decreased solution pH. Under our experimental condition, the pH of control solution was 8.7 and the solution pH with rhodanine molecules was 7.4. The oxidation of intermediates to γ-Fe_2O_3 (Fe^{3+}) was accelerated in more acidic condition. Thus, in the rhodanine solution, more intermediates were oxidized to Fe^{3+}, resulting in the increased relative amount of Fe^{3+} ions compared to the control reaction without rhodanine.

As the reaction proceeded, Fe^0 peak disappeared and only Fe^{2+} and Fe^{3+} states were detected in the XPS spectra because the magnetic nanoparticles were more oxidized (Figure S2c and Figure S2d). In the chemical oxidation polymerization, ferric ions were re-dissolved out from the surface of iron oxides nanoparticles and entrapped by the surface-bound rhodanine monomer. Afterwards, the re-dissolved ions were reduced to Fe^{2+} ions by oxidizing the rhodanine monomers for initiating the polymerization. Therefore, at the initial polymerization step (the reaction for 2 h after the injection of $NaBH_4$, Figure S2c), the binding energy of Fe 2p was little shifted to lower value getting close to Fe_3O_4 and the relative ratio of Fe^{3+}/Fe^{2+} was decreased to 1.79:1 due to the relatively increased amount of Fe^{2+}.

On the contrary, as the polymerization further proceeded, the relative amount of Fe^{3+} ions re-increased and the peak of Fe 2p line was shifted to higher value which could be assigned to Fe 2p of γ-Fe_2O_3 (Figure S2d). The relative ratio of Fe^{3+}/Fe^{2+} increased to 3.33:1 and the binding energy of Fe $2p_{3/2}$ was 710.75 eV, which was in good agreement with the reported value for γ-Fe_2O_3. This phenomenon could be explained by the lowered solution pH related to the polymerization. During the chemical oxidation polymerization, more oxidized rhodanine molecules led to more released protons with decreasing the solution pH (the solution pH was 5.2 at the end of polymerization). As a result, the oxidation reaction of Fe^{2+} to Fe^{3+} in the iron oxides was concurrently much more accelerated than the reduction reaction of Fe^{3+} to Fe^{2+} (which was dominant in the initiation polymerization step), resulting in the γ-Fe_2O_3 phases.

In addition, on the XPS spectrum of magnetic polyrhodanine nanoparticles at the end of polymerization (Figure S2d), the lack of shoulder around 709 eV supports that the Fe_3O_4 phase is in a very low concentration.[3] The assigned Fe $2p_{3/2}$ of Fe^{2+} value (710.55 eV) is rather to be close to that of Fe^{3+}, which also indicates that iron oxide is composed of mainly Fe^{3+} states. On the other hand, the shifted Fe $2p_{3/2}$ of Fe^{3+} peak to 712.06 eV can be ascribed to the sulfuric environment originated from the surface-bound polyrhodanine shell.[4]

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[1] a) P. Mills and J. L. Sullivan, *J. Phys. D: Appl. Phys.*, 1983, **16**, 723-740; b) A. Gupta, A. Kumar, U. V. Waghmare and M. S. Hegde, *Chem. Mater.*, 2009, **21**, 4880-4891; c) A. A. Tahir, K. G. U. Wijayantha, S. Saremi-Yarahmadi, M. Mazhar and V. McKee, *Chem. Mater.*, 2009, **21**, 3763-3772.

[2] T. Yamashita and P. Hayes, *Appl. Surf. Sci.*, 2008, **254**, 2441-2449.

[3] S. Huang, Y. Fan, Z. Cheng, D. Kong, P. Yang, Z. Quan, C. Zhang and J. Lin, *J. Phys. Chem. C*, 2009, **113**, 1775-1784.

[4] a) B. Yan, J. Tao, C. Pang, Z. Z. Z. Shen, C. H. A. Huan and T. Yu, *Langmuir*, 2008, **24**, 10569-10571; b) M. Xing, J. Zhang and F. Chen, *J. Phys. Chem. C*, 2009, **113**, 12848-12853; c) V. M. Bogatyrev, V. M. Gunko, M. V. Galaburda, M. V. Borysenko, V. A. Pokrovskiy, O. I. Oranska, E. V. Polshin, O. M. Korduban, R. Leboda and J. Skubiszewska-Zieba, *J. Colloid Interf. Sci.*, 2009, **338**, 376-388.

Supplementary study of X-ray photoelectron spectroscopy (XPS)

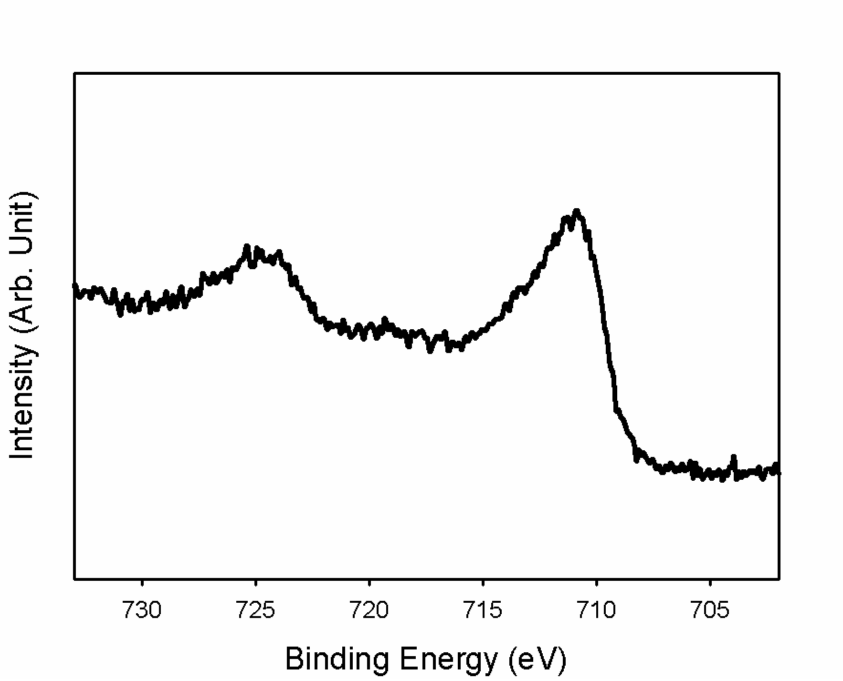

Figure S3 XPS spectrum of the maghemite/polyrhodanine nanoparticles.

Supplementary study of thermogravimetric analysis (TGA)

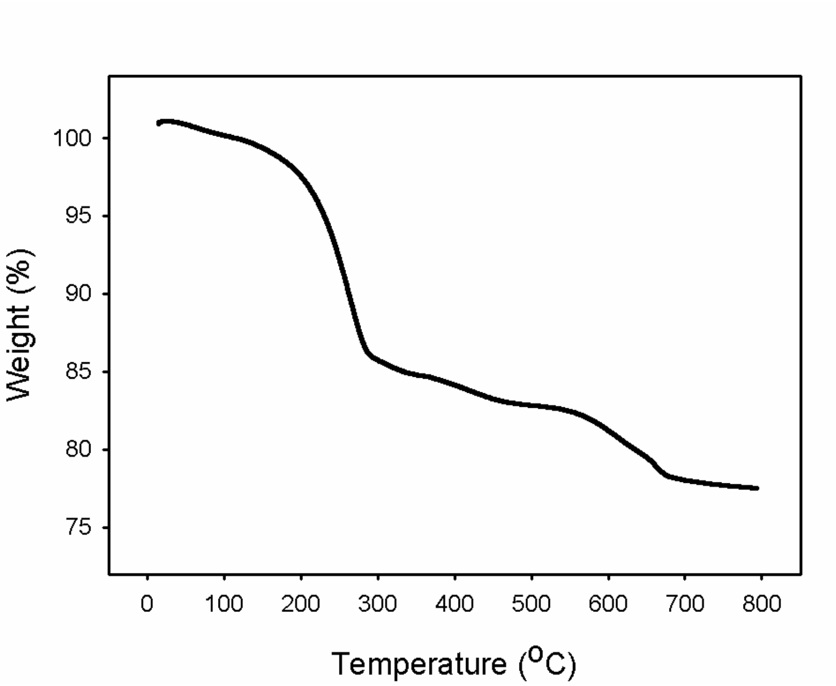

Figure S4 TGA graph of the maghemite/polyrhodanine nanoparticles.

Experimental details on the antibacterial test

For the antibacterial tests, 15 mg of the magnetic polyrhodanine nanoparticles was added into the 1 mL of each *E. coli* and *S. aureus* bacterial solution (10^5-10^6 CFU/mL), and then the solution was incubated at 37 °C by using a shaking incubator. During the incubation, small volumes were chosen as a function of contact time (min) from the bacterial test solution and cultured in LB agar plates. The LB agar plates were incubated at 37 °C for 24 h and the number of survival bacterial colonies was counted. For the recycled antibacterial test, the tested bacterial solution was placed into a magnetic field for 60 seconds and the supernatant was discarded in order to separate the magnetic polymer nanoparticles. The obtained magnetic particles were washed with distilled water and freshly bacterial solution was re-added for the recycle test. After 30 min, small volumes was chosen and cultured in LB agar plates. The same experimental procedure was repeated to obtain fifth recycle result.