Supplementary information

Pt coupled $ZnFe_2O_4$ nanocrystals as a breakthrough photocatalyst for Fenton-like processes – photodegradation treatments from hours to seconds

*Kuan-Ting Lee,[a] Xui-Fang Chuah,[a,b] Yu-Chieh Cheng,[a] and Shih-Yuan Lu [a]**

[a] Department of Chemical Engineering, National Tsing Hua University, Hsinchu, 30013, TAIWAN; E-mail: SYLu@mx.nthu.edu.tw

[b] Department of Chemical Engineering, Universiti Tunku Abdul Rahman, Kuala Lumpur, 53300, Malaysia.

*Email : *SYLu@mx.nthu.edu.tw*

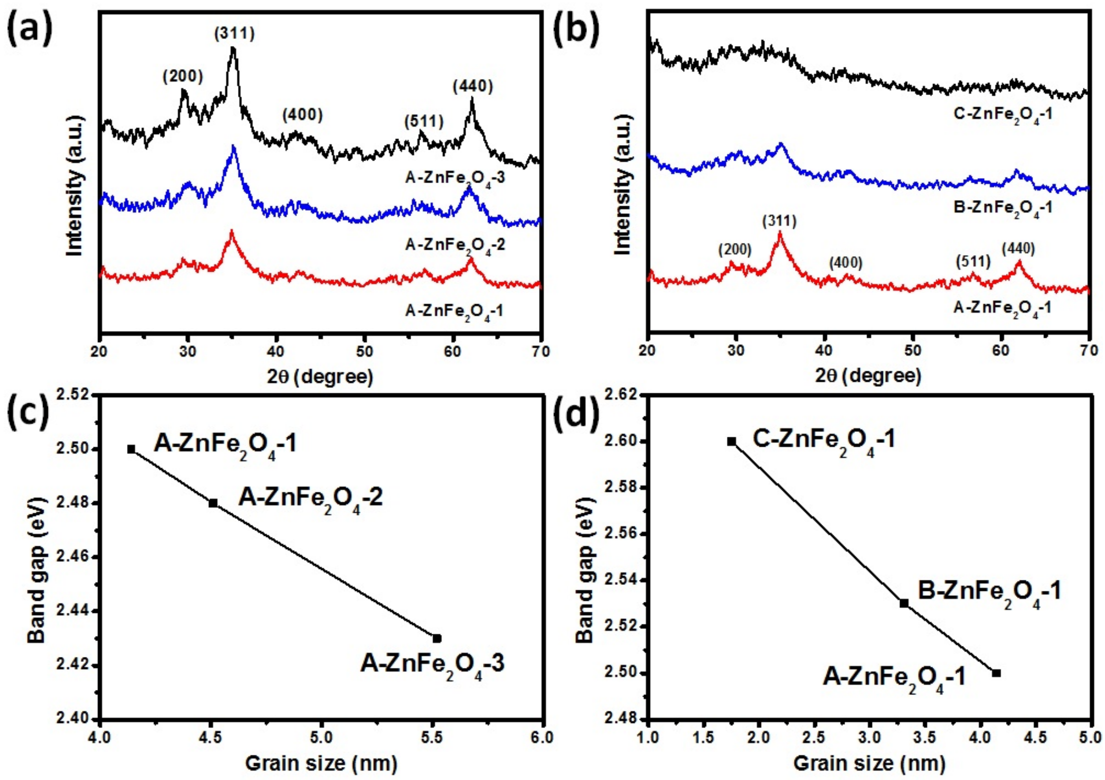

Fig. S1 (a) XRD patterns of samples A-$ZnFe_2O_4$-1, A-$ZnFe_2O_4$-2, and A-$ZnFe_2O_4$-3. (b) XRD patterns of samples A-$ZnFe_2O_4$-1, B-$ZnFe_2O_4$-1, and C-$ZnFe_2O_4$-1. (c) Band gaps vs. grain size for samples A-$ZnFe_2O_4$-1, A-$ZnFe_2O_4$-2, and A-$ZnFe_2O_4$-3. (d) Band gaps vs. grain size for samples A-$ZnFe_2O_4$-1, B-$ZnFe_2O_4$-1, and C-$ZnFe_2O_4$-1.

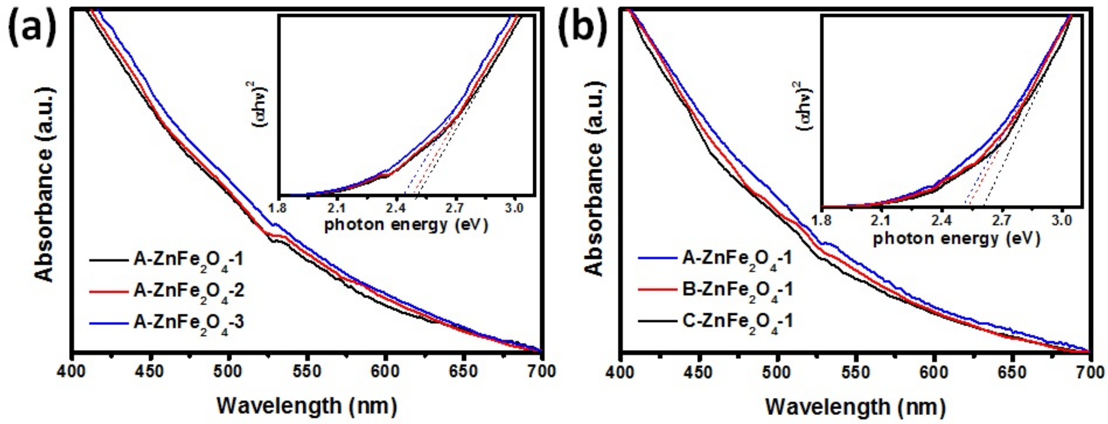

Fig. S2 The band gap energy, *E*g, of the $ZnFe_2O_4$ NCs can be determined by the equation $(\alpha h\nu)^{1/n} = B(h\nu - Eg)$, where α is the absorption coefficient, hν the photon energy, n a value that depends on the nature of the transition (1/2 for direct band gap materials such as $ZnFe_2O_4$), and B a constant. (a) UV-visible absorption spectra of samples A-$ZnFe_2O_4$-1, A-$ZnFe_2O_4$-2, and A-$ZnFe_2O_4$-3. Inset shows $(\alpha h\nu)^2$ vs. photon energy plot from which band gaps are determined. (b) UV-visible absorption spectra of samples A-$ZnFe_2O_4$-1, B-$ZnFe_2O_4$-1, and C-$ZnFe_2O_4$-1. Inset shows corresponding $(\alpha h\nu)^2$ vs. photon energy plot.

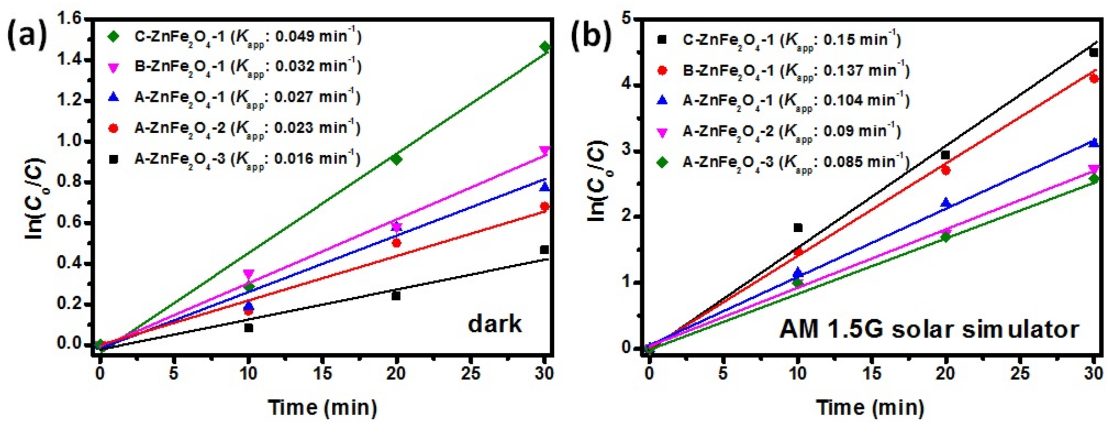

Fig. S3 $\ln(C_0/C)$ vs. time curves for all five $ZnFe_2O_4$ samples (a) in dark and (b) illuminated with simulated sun light. The K_{app} values were determined as the slopes of the regressed lines.

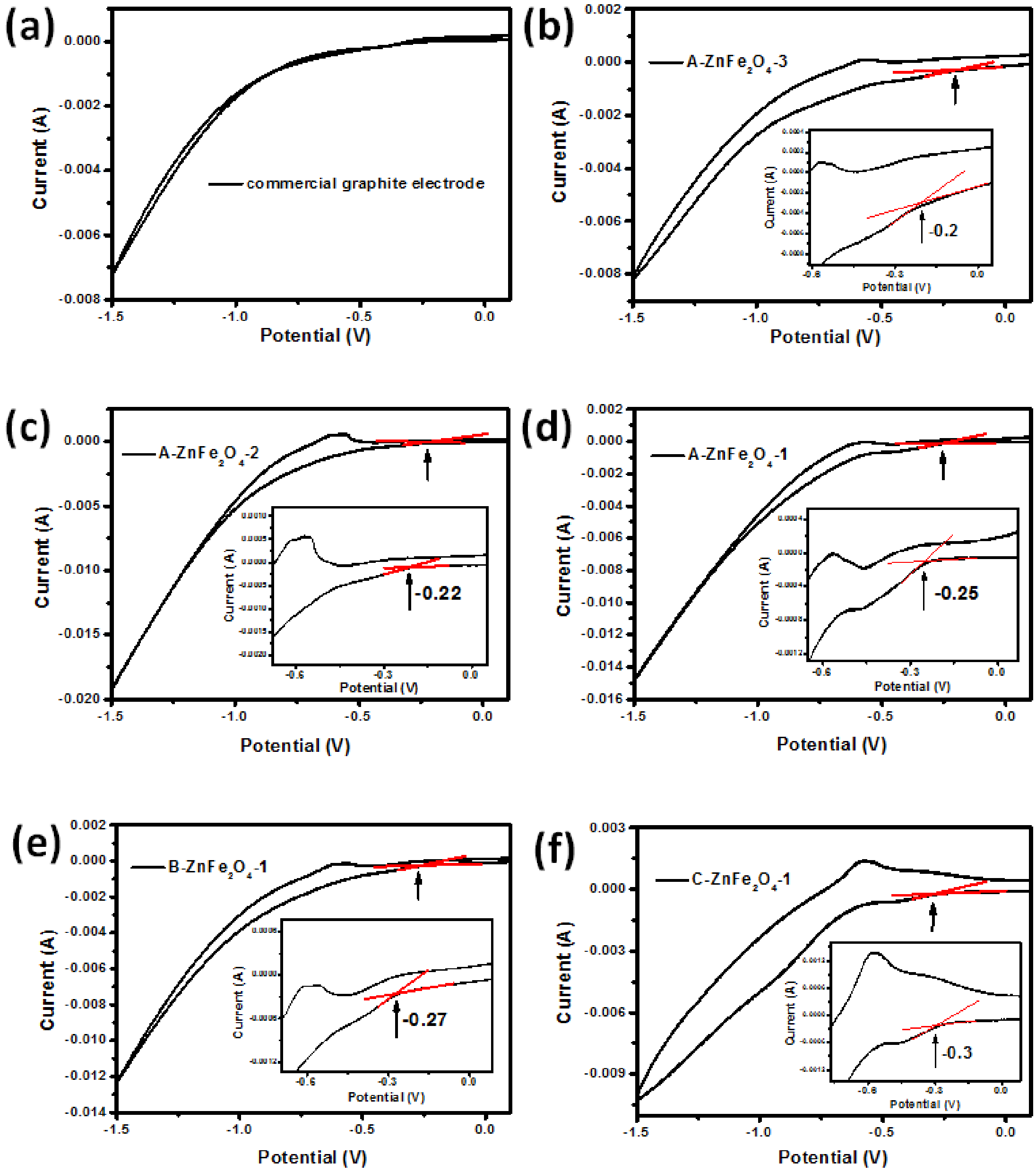

Fig. S4 Cycling voltammograms recorded for (a) commercial graphite electrode, samples (b) A-$ZnFe_2O_4$-3, (c) A-$ZnFe_2O_4$-2, (d) A-$ZnFe_2O_4$-1, (e) B-$ZnFe_2O_4$-1, and (f) C-$ZnFe_2O_4$-1. Insets show locally enlarged CVs for determination of onset reduction potentials.

Experimental determination of conduction band positions of $ZnFe_2O_4$ NCs:

Here, we determine the conduction band positions of $ZnFe_2O_4$ NCs with cyclic voltammetry analyses. The working electrode was prepared by drop-casting ethanolic suspension of $ZnFe_2O_4$ NCs onto a graphite electrode followed by drying at 60 °C. The counter electrode was Pt coil and Ag/AgCl served as the reference electrode. The cyclic voltammograms were recorded in an electrolyte of 0.1 M

Na_2SO_4(aq) with a negative scan starting from 0.5 to −1.5 V and then back to 0.5 V at a scan rate of 100 mV/s. The LUMO potential (E_{LUMO}) of electroactive materials can be estimated from the onset reduction potential (E_{red}), according to the following equation[S1,S2]

$$E_{LUMO} = -(E_{red} + 4.71)\ \text{eV}\ . \qquad (1)$$

Here, the onset reduction potential is referenced to the Ag/AgCl electrode. The value of 4.71 represents the difference between the vacuum level potential of the normal hydrogen electrode (NHE) and the potential of the Ag/AgCl electrode versus NHE.[S3,S4] We started from 0.5 V and proceeded with a negative potential scan from 0.5 to −1.5 V and then back to 0.5 V. The onset reduction potential of sample C-$ZnFe_2O_4$-1 was thus determined to be −0.30 V as shown in Fig. S4(f). A commercial graphite electrode was taken as a control, and no reduction peak can be identified under the same testing condition, as shown in Fig. S4(a). The results of relevant band structure data were summarized in Table 1.

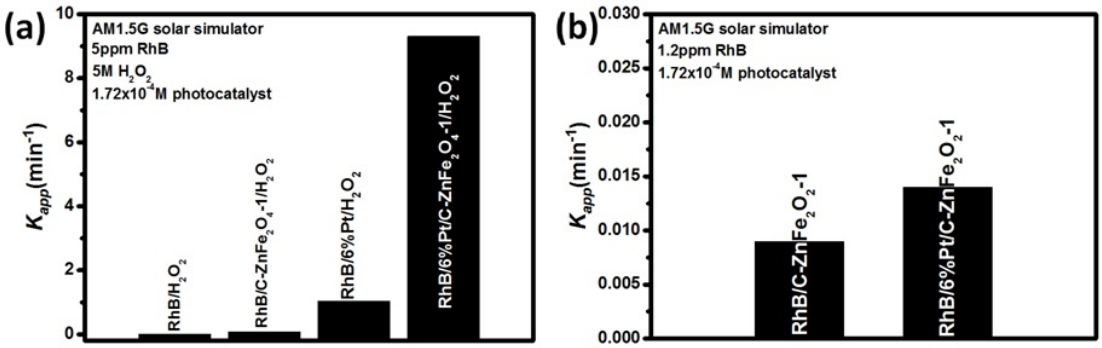

Fig. S5 Comparison of K_{app} values collected from cases of (a) RhB/H_2O_2 (0.007 min^{-1}), RhB/C-$ZnFe_2O_4$-1/H_2O_2 (0.08), RhB/6%Pt/H_2O_2 (1.04), RhB/6%Pt/C-$ZnFe_2O_4$-1/H_2O_2 (9.31) and (b) RhB/C-$ZnFe_2O_4$-1 (0.009) and RhB/6%Pt/C-$ZnFe_2O_4$-1 (0.014).

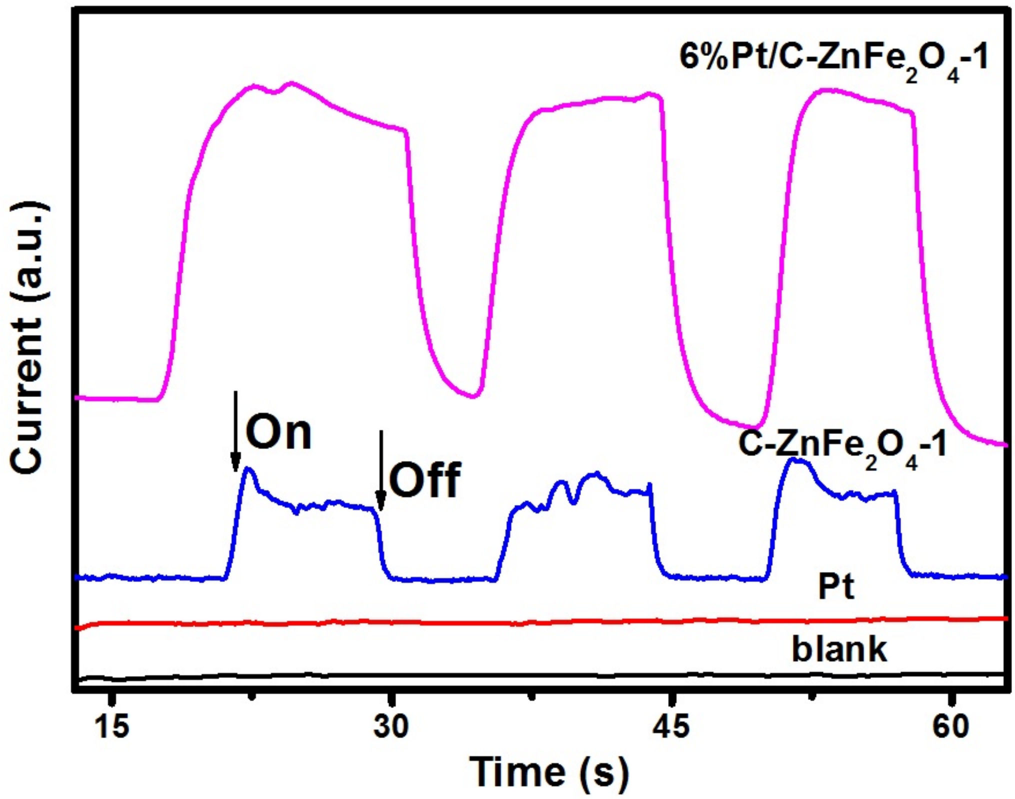

Fig. S6 Photocurrent response curves of blank (no catalyst deposited), Pt NCs, C-$ZnFe_2O_4$-1 NCs, and 6%Pt/C-$ZnFe_2O_4$-1 NCs.

Photocurrent measurement

The tested catalysts were loaded onto porous FTO glass by drop-casting to serve as the working electrode. The porous FTO glass (PFTO) was prepared following the procedures developed in our previous work. [S5] Ethanol was used as the solvent to suspend the tested catalyst for the drop-casting operation. An amount of 0.0023 mg catalyst was loaded onto the PFTO, which was then dried in a vacuum oven at 60°C for 6 h to afford the working electrode. The area of the electrode was controlled to be 2×0.5 cm^2. A 2 W white LED was used as the light source (λ> 425 nm), placed 2 cm away from the electrode. Amperometric I-t curves were recorded on an electrochemical workstation (CHI6275D, CH Instruments Inc.) in a two-electrode system with a commercial FTO glass serving as the counter electrode and 0.01 M Na_2SO_4 aquous solution as the electrolyte.

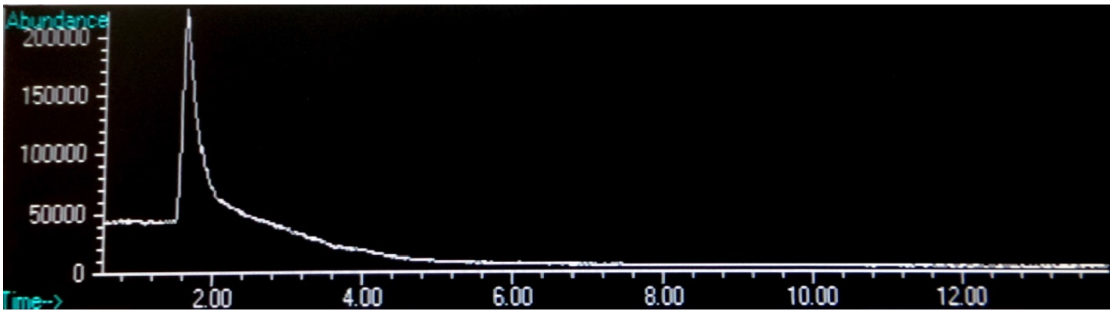

Fig. S7 GC/MS (Hewlett Packard 5890 series II) measurement result of RhB solution after treatment with 6%Pt/C-$ZnFe_2O_4$-1 NCs under simulated sun light.

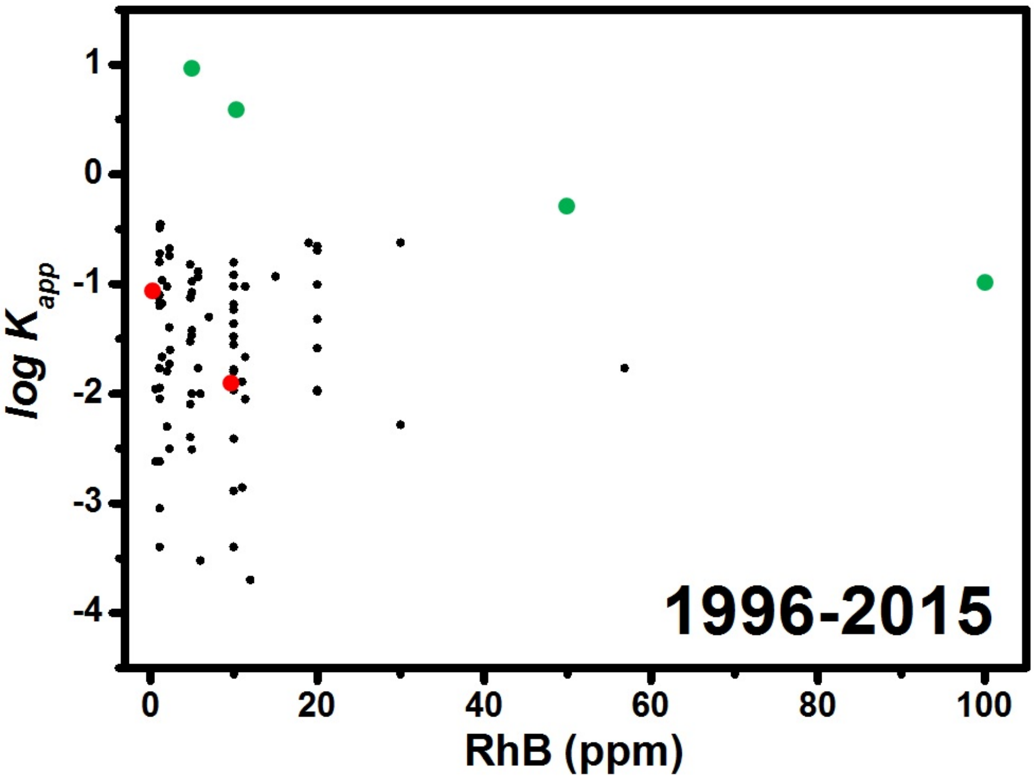

Fig. S8 log(K_{app}) vs. RhB concentration from literature collected over the past two decades. [our work - green dots, literature using solar simulator for light source – red dots, literature using light sources other than simulated sun light – black dots.

References:

[S1] K. G. Deepa, J. Nagaraju, Mater. Sci. Eng. B, 2012, 177, 1023-1028.
[S2] K. T. Lee, S. Y. Lu, J. Phys. Chem. C, 2014, 118, 14457-14463.
[S3] C. Karunakaran, J. Jayabharathi, K. Jayamoorthy, K. B. Devi, Sens. Actuators B, 2012, 168, 263-270.
[S4] S. H. Chang, M. Y. Chiang, C. C. Chiang, F. W. Yuan, C. Y. Chen, B. C. Chiu, T. L. Kao, C. H. Lai, H. Y. Tuan, Energy Environ. Sci. 2011, 4, 4929-4932.

[S5] K.T. Lee, S.Y. Lu, J. Mater. Chem., 2012, 22, 16259-16268.
[S5] Y. Huang, W. Ma, J. Li, M. Cheng, J. Zhao, J. Phys. Chem. B, 2003, 107, 9409-9414.
[S6] X. Tao, W. Ma, T. Zhang, J. Zhao, Chem. Eur. J., 2002, 8, 1321-1326.
[S7] S. Horikoshi, A. Saitou, H. Hidaka, Environ. Sci. Technol., 2003, 37, 5813-5822.
[S8] S. Horikoshi, H. Hidaka, Environ. Sci. Technol., 2002, 36, 1357-1366.
[S9] S. Horikoshi, H. Hidaka, Environ. Sci. Technol., 2002, 36, 5229-5237.
[S10] F. Chen, J. Zhao, H. Hidaka, International Journal of Photoenergy, 2003, 05, 209-217.
[S11] S. Wang, P. Liu, X. Wang, X. Fu, Langmuir, 2005, 21, 11969-11973.
[S12] J. Yang, C. Chen, H. Ji, W. Ma, J. Zhao, J. Phys. Chem. B, 2005, 109, 21900-21907.
[S13] É. Gavilan, T. Doussineau, A.E. Mansouri, M. Smaïhi, S. Balme, J.M. Janot, C. R. Chimie, 2005, 8, 1946-1953.
[S14] J. Li, W. Ma, Y. Huang, X. Tao, J. Zhao, Y. Xu, Applied Catalysis B: Environmental, 2004, 48, 17-24.
[S15] J. Zhao, T. Wu, K. Wu, K. Oikawa, H. Hidaka, N. Serpone, Environ. Sci. Technol, 1998, 32, 2394-2400.
[S16] T. Wu, G. Liu, J. Zhao, J. Phys. Chem. B, 1998, 102, 5845-5851.
[S17] B. Xin, Z. Ren, H. Hu, X. Zhang, C. Dong, K. Shi, L. Jing, H. Fu, Applied Surface Science, 2005, 252, 2050-2055.
[S18] Y.S. Na, D.H. Kim, C.H. Lee, S.W. Lee, Y.S. Park, Y.K. Oh, S.H. Park, S.K. Song, Korean J. Chem. Eng., 2004, 21, 430-435.
[S19] M. Hu, Y. Xu, Chemosphere. 2004, 54, 431-434.
[S20] H. Park, W. Choi, J. Phys. Chem. B, 2005, 109, 11667-11674.
[S21] C. Chen, W. Zhao, P. Lei, J. Zhao, N. Serpone, Chem. Eur. J., 2004, 10, 1956-1965.
[S22] Y. Lei, J. Sun, C. Yang, K. Deng, D. Wang, J. Porphyrins Phthalocyanines, 2005, 9, 537-543.
[S23] C. Zhang, Y. Zhu, Chem. Mater., 2005, 17, 3537-3545.
[S24] M. Cheng, W. Ma, J. Li, Y. Huang, J. Zhao, Environ. Sci. Technol., 2004, 38, 1569-1575.
[S25] H. Fu, C. Pan, W. Yao, Y. Zhu, J. Phys. Chem. B, 2005, 109, 22432-22439.
[S26] Z.T. Yu, Z.L. Liao, Y.S. Jiang, G.H. Li, J.S. Chen, Chem. Eur. J., 2005, 11, 2642-2650.
[S27] S.K. Zheng, T.M. Wang, W.C. Hao, R. Shen, Vacuum, 2002, 65, 155-159.
[S28] F. Chen, J. Zhao, H. Hidaka, Res. Chem. Intermed., 2003, 29, 733-748.
[S29] X. Tao, J. Su, J. Chen, J. Zhao, Chem. Commun., 2005, 36, 4607-4609.
[S30] W.C. Hao, K. Zheng, C. Wang, T.M. Wang, Journal of Materials Science Letters, 2002, 21, 1627-1629.

[S31] L. Liang, Y. Yulin, L. Xinrong, F. Ruiqing, S. Yan, L. Shuo, Z. Lingyun, F. Xiao, T. Pengxiao, X. Rui, Z. Wenzhi, W. Yazhen, Ma Liqun, Applied Surface Science, 2013, 265, 36-40.
[S32] L. Shi, L. Liang, J. Ma, F. Wang, J. Sun, Catal. Sci. Technol., 2014, 4, 758-765.
[S33] X. Li, Y. Hou, Q. Zhao, L. Wang, Journal of Colloid and Interface Science, 2011, 358, 102-108.
[S34] D. Liu, W. Cui, J. Lin, Y. Xue, Y. Huang, J. Li, J. Zhang, Z. Liu, C. Tang, Catalysis Communications, 2014, 57, 9-13.
[S35] D. Zhao, C. Chen, Y. Wang, W. Ma, J. Zhao, T. Rajh, L. Zang, Environ. Sci. Technol., 2008, 42, 308-314.
[S36] H. Cao, Y. Xiao, Y. Lu, J. Yin, B. Li, S. Wu, X. Wu, Nano Res., 2013, 3, 863-873.
[S37] J. Zhang, Z. Zhu, Y. Tang, X. Feng, J. Mater. Chem. A, 2013, 1 3752-3756.
[S38] X. Zhao, J. Zhang, B. Wang, A. Zada, M. Humayun, Materials, 2015, 8, 2043-2053.
[S39] J. Ma, J. Ding, L. Yu, L. Li, Y. Kong, S. Komarneni, Applied Clay Science, 2015, 109-110, 76-82.
[S40] L. Li, B. Yan, Journal of Alloys and Compounds, 2009, 476, 624-628.
[S41] W. Yin, W. Wang, L. Zhou, S. Sun, L. Zhang, Journal of Hazardous Materials, 2010, 173, 194-199.
[S42] Q. Wang, C. Chen, D. Zhao, W. Ma, J. Zhao, Langmuir, 2008, 24, 7338-7345.
[S43] L. Zhang, W. Wang, Z. Chen, L. Zhou, H. Xua, W. Zhu, J. Mater. Chem., 2007, 17, 2526-2532.
[S44] T. Zhao, J. Zai, M. Xu, Q. Zou, Y. Su, K. Wang, X. Qian, CrystEngComm, 2011, 13, 4010-4017.
[S45] J. Hong, C.C. Wu, S. Lu, Y. Cui, International Conference on Environmental Science and Information Application Technology, 2009, 301, 627-630.
[S46] Y. He, J. Cai, T. Li, Y. Wu, H. Lin, L. Zhao, M. Luo, Chemical Engineering Journal, 2013, 215-216, 721-730.
[S47] Z. Wu, L. Chen, C. Xing, D. Jiang, J. Xie, M. Chen, Dalton Trans., 2013, 42, 12980-12988.
[S48] Y. Lv, L. Yu, H. Huang, Y. Feng, D. Chen, X. Xie, Nanotechnology, 2012, 23, 065402-065409.
[S49] T.H. Xie, X. Sun, J. Lin, J. Phys. Chem. C, 2008, 112, 9753-9759.
[S50] S. Guo, G. Zhang, J.C. Yu, Journal of Colloid and Interface Science, 2015, 448, 460-466.
[S51] X. Cheng, X. Yu, Z. Xing, L. Yang, International Journal of Photoenergy, 2012, 2012, 1-6.
[S52] K. Jia, J. Deng, H. Zang, J. Han, H. Arandiyan,H. Dai, Applied Catalysis B:

Environmental, 2015, 165, 285-295.
[S53] W. Chen, G.R. Duan, T.Y. Liu, S.M. Chen, X.H. Liu, Materials Science in Semiconductor Processing, 2015, 35, 45-54.
[S54] R. Zhang, H. Cui, X. Yang, H. Tang, H. Liu, Y. Li, Micro & Nano Letters, 2012, 7, 1285-1288.
[S55] Y. Su, C. Ding, Y. Dang, H. Wang, L. Ye, X. Jin, H. Xie, C. Liu, Applied Surface Science, 2015, 346, 311-316.
[S56] G. Liao, S. Chen, X. Quan, H. Yu, H. Zhao, J. Mater. Chem., 2012, 22, 2721-2726.
[S57] J. Zhang, Z. Xiong, X.S. Zhao, J. Mater. Chem., 2011, 21, 3634-3640.
[S58] T. Ghosh, K.Y. Cho, K. Ullah, V. Nikam, C.Y. Park, Z.D. Meng, W.C. Oh, Journal of Industrial and Engineering Chemistry, 2013, 19, 797-805.
[S59] K. Wang, J. Xu, X. Hua, N. Li, M. Chen, F. Teng, Y. Zhu, W. Yao, Journal of Molecular Catalysis A: Chemical, 2014, 393, 302-308.
[S60] W. Teng, X. Li, Q. Zhao, J. Zhao, D. Zhang, Applied Catalysis B: Environmental, 2012, 125, 538-545.
[S61] L. Shi, L. Liang, J. Ma, F. Wang, J. Sun, Catal. Sci. Technol., 2014, 4, 758-765.
[S62] S.Y. Pung, W.P. Lee, A. Aziz, International Journal of Inorganic Chemistry, 2012, 2012, 1-9.
[S63] W. Ren, Z. Ai, F. Jia, L. Zhang, X. Fan, Z. Zou, Applied Catalysis B: Environmental, 2007, 69, 138-144.
[S64] Y. Cui, Z. Ding, P. Liu, M. Antonietti, X. Fu, X. Wang, Phys. Chem. Chem. Phys., 2012, 14, 1455-1462.
[S65] H. Zhong, Y. Shaogui, J. Yongming, S. Cheng, Journal of Environmental Sciences, 2009, 21, 268-272.
[S66] L. Shi, C. Yang, X. Su, J. Wang, F. Xiao, J. Fan, C. Feng, H. Sun, Ceramics International, 2014, 40, 5103-5106.
[S67] X. Hao, J. Zhao, Y. Zhao, D. Ma, Y. Lu, J. Guo, Q. Zeng, Chemical Engineering Journal, 2013, 229, 134-143.
[S68] P.Q. Wang, Y. Bai, J.Y. Liu, Z. Fan, Y.Q. Hu, Micro & Nano Letters, 2012. 7, 876-879.
[S69] H. Liu, J. Yang, J. Liang, Y. Huang, C. Tang, J. Am. Ceram. Soc., 2008, 91, 1287-1291.
[S70] T.B. Li, G. Chen, C. Zhou, Z.Y. Shen, R.C. Jin, J.X. Sun, Dalton Trans., 2011, 40, 6751-6758.
[S71] W. Gao, M. Wang, C. Ran, J. Ding, J. Deng, Y. Li, IEEE International Conference on Nanotechnology, 2013, 978, 274-279.
[S72] X. Wang, X. Wan, W. Li, X. Chen, Micro & Nano Letters., 2014, 9, 376-381.
[S73] H. Huang, X. Gu, J. Zhou, K. Ji, H. Liu, Y. Feng, Catalysis Communications, 2009,

11, 58-61.
[S74] H. Fu, S. Zhang, T. Xu, Y. Zhu, J. Chen, Environ. Sci. Technol., 2008, 42, 2085-2091.
[S75] L. Zhang, Y. He, Y. Wu, T. Wu, Materials Science and Engineering B, 2011, 176, 1497-1504.
[S76] N. Liu, X. Ou, F. Zhang, C. Wang, J. Xu, International Conference on Bioinformatics and Biomedical Engineering – ICBBE, 2011, 978, 1-4.
[S77] L. Yang, J. Dong, J.Y. Xing, Y. Dang, X.Z. Zhou, W.L. Wang, Y. Zhang, International Conference on Bioinformatics and Biomedical Engineering – ICBBE, 2011, 978, 3167-3169.
[S78] Z. Zhang, W. Wang, M. Shang, W. Yin, Catalysis Communications, 2010, 11, 982-986.
[S79] J. Xu, L. Li, C. Guo, Y. Zhang, International Conference on Bioinformatics and Biomedical Engineering – ICBBE, 2011, 978, 1-4.
[S80] L. Kong, Z. Jiang, T. Xiao, L. Lu, M.O. Jones, P.P. Edwards, Chem. Commun., 2011, 47, 5512-5514.
[S81] D. Lu, Y. Zhang, S. Lin, L. Wang, C. Wang, Journal of Alloys and Compounds, 2013, 579, 33-342.
[S82] L. Zhang, Y. He, P. Ye, Y. Wu, T. Wu, Journal of Alloys and Compounds, 2013, 549, 105-113
[S83] K.T. Lee, S.Y. Lu, J. Mater. Chem. A, 2015, 3, 12259-12267.