

A ferromagnetic nanocrystallines containing copper as an efficient catalyst for photoinduced water oxidation

Xiaoqiang Du^a, Yong Ding^{*a,b}, Rui Xiang^a, Xu Xiang^b

^a Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China

^b State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology

* To whom correspondence should be addressed.

E-mail addresses: dingyong1@lzu.edu.cn

The preparing of Fe₂O₃ nanoparticles¹ and CuO nanoparticles²

Fe₂O₃ nanoparticles with size of 60 nm (Figure S8) and CuO nanoparticles were prepared according to published method.

Synthesis of [Ru(bpy)₃]Cl₂·6H₂O

Commercial RuCl₃·xH₂O is dried in an oven at 120 °C for 3 h. It is then finely ground in a mortar and returned to the oven for a further 1h prior to use. It is convenient to store the “dried” RuCl₃ at this temperature. “Dried” RuCl₃ (0.4 g, 1.93 mmol), 2, 2'-bipyridine (0.9 g, 5.76 mmol) and water (40 mL) are placed in a 100 mL flask fitted with a reflux condenser. Then sodium hypophosphite solution (2 mL) is added and the mixture heated at the boil for 30 min. During reflux, the initial green solution changes to brown and finally orange. It is filtered to remove traces of undissolved material and potassium chloride (12.6 g) added to the filtrate to precipitate the crude product. The solution and solid are then heated at the boil to give a deep red solution, which on cooling to room temperature yields beautiful, red plate-like crystals. These are filtered off, and air-dried. The yield is 0.9 g (63%). The product could be recrystallized from boiling water (~2.8 mL·g⁻¹) and then air dried.

Text of XPS analyses

The samples prepared for XPS analyses were processed according to the following procedure: first, catalyst powders were added on to an Al foil and pressed under high pressure to be a thin film and the thickness of the catalyst films was hundreds of nanometers. Then, the resulted samples were used for XPS tests.

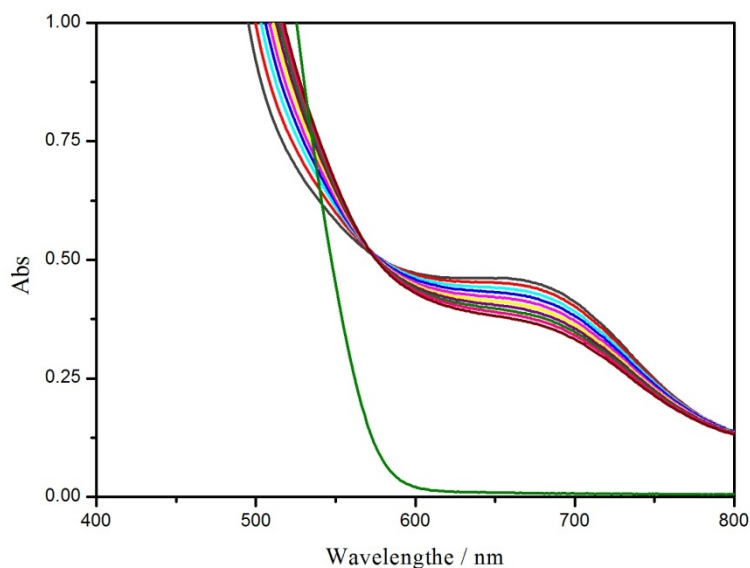


Figure S1. UV-vis spectral changes during the photocatalytic water oxidation with pH 8.0 buffer. The bottom green line shows the absorption of an aqueous borate buffer solution (pH = 8.0, 80 mM) containing $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (1.0 mM), $\text{Na}_2\text{S}_2\text{O}_8$ (5.0 mM) and CuFe_2O_4 (0.5 gL^{-1}). Other lines show the UV-vis spectral changes of the green reaction solution obtained by irradiating the initial reaction solution about 30 s.

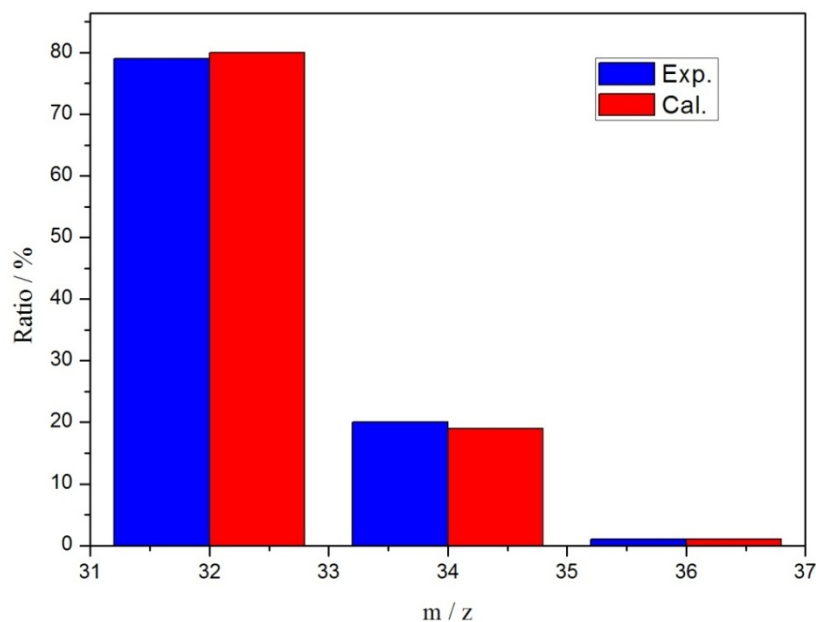


Figure S2. Observed and theoretical relative abundances of ^{18}O -labeled and unlabeled oxygen evolved during the photocatalytic oxidation of a buffer solution (4.5 mL) prepared with H_2^{18}O -enriched water (10.8% H_2^{18}O) containing CuFe_2O_4 (0.5 gL^{-1}), $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (1.0 mM) and $\text{Na}_2\text{S}_2\text{O}_8$ (5.0 mM) (blue, observed mass intensity; red, calculated values assuming that evolved O_2 results exclusively from water).



Figure S3. The picture of collecting CuFe_2O_4 by a magnet.

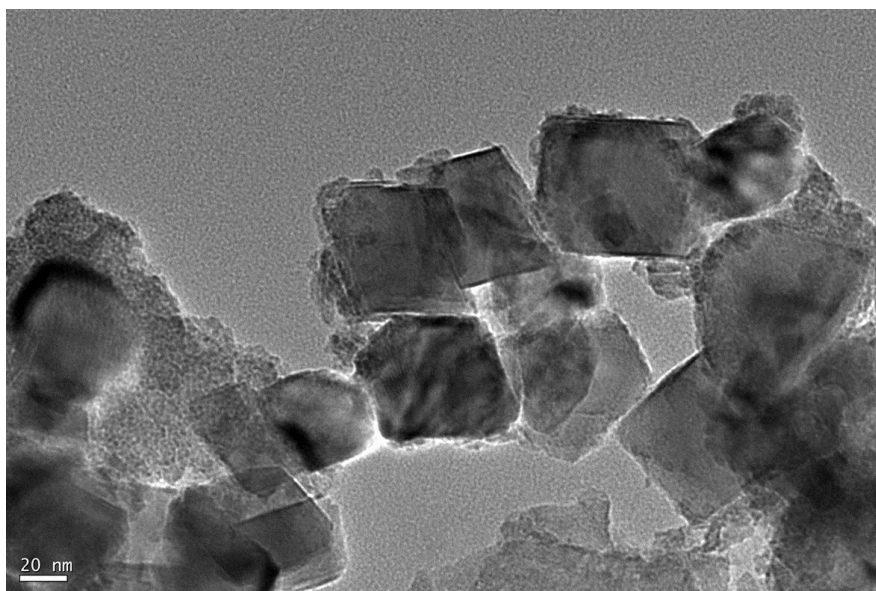


Figure S4. TEM of fresh CuFe_2O_4

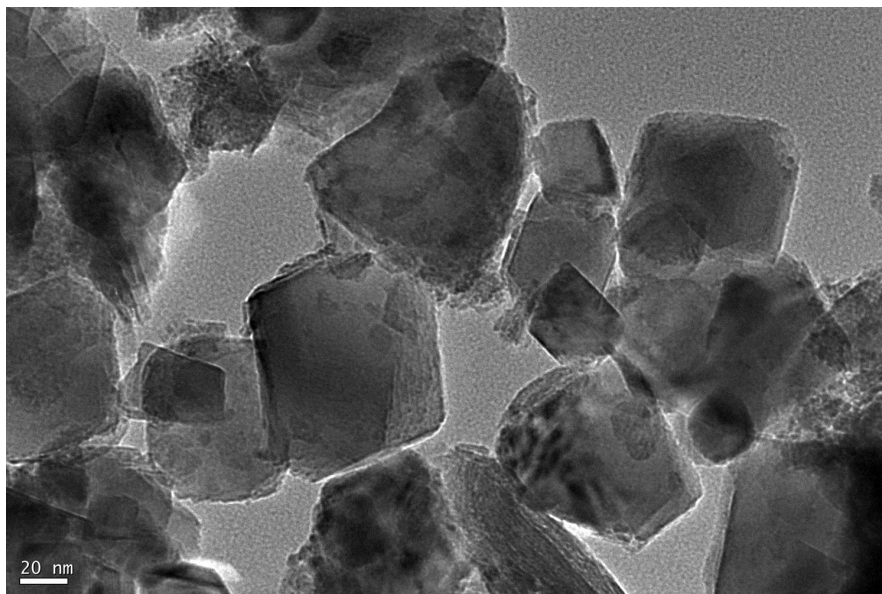


Figure S5. TEM of recovered CuFe_2O_4

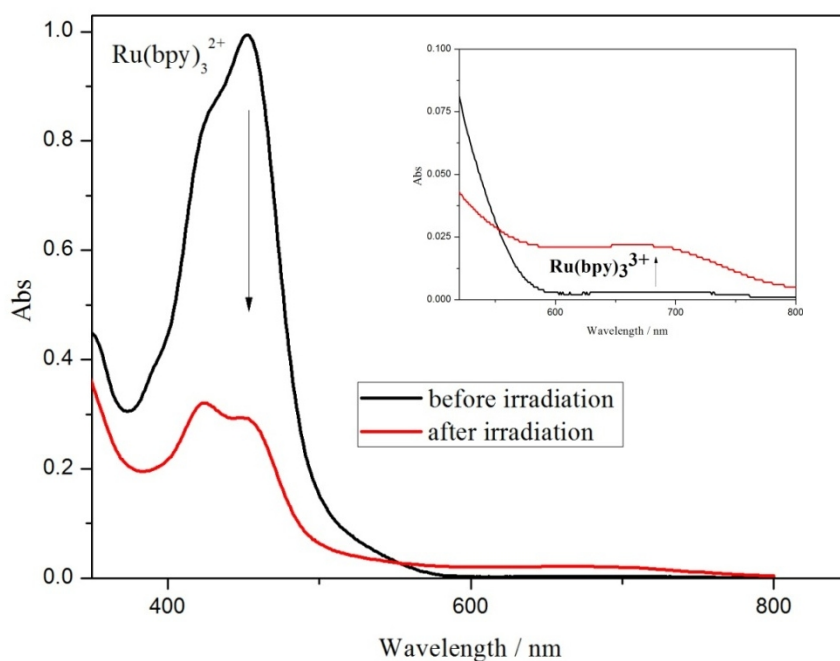


Figure S6. The absorbance spectra of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ solution (1.0 mM) containing $\text{Na}_2\text{S}_2\text{O}_8$ (5.0 mM) in an 80 mM NaBi (pH 8.0) buffer (black) before and (red) after visible light irradiation (> 420 nm). The absorption peaks at approximately 453 nm and 670 nm correspond to $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{bpy})_3^{3+}$, respectively. After visible light irradiation, the absorption peak corresponding to $\text{Ru}(\text{bpy})_3^{3+}$ increased because of photo-induced oxidation of $\text{Ru}(\text{bpy})_3^{2+}$ whereas the absorption peak of $\text{Ru}(\text{bpy})_3^{2+}$ decreased.

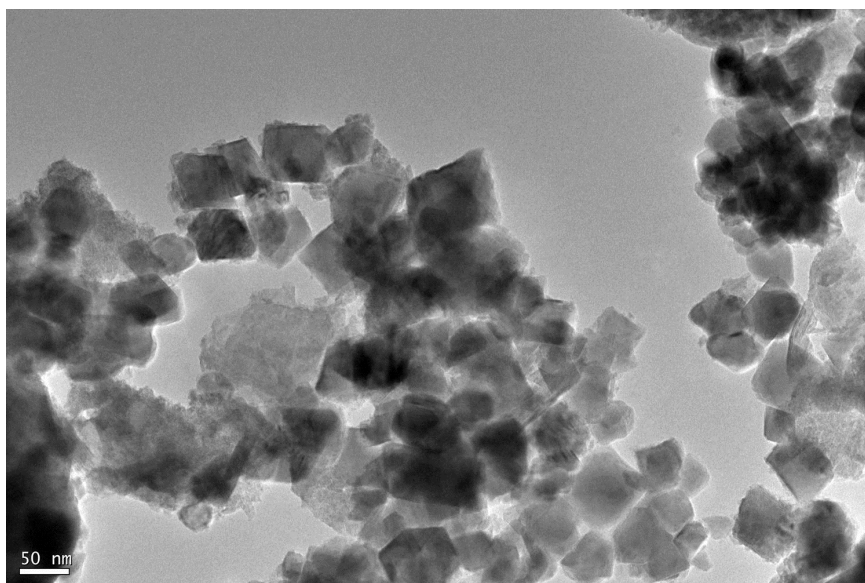


Figure S7. TEM of fresh CuFe_2O_4

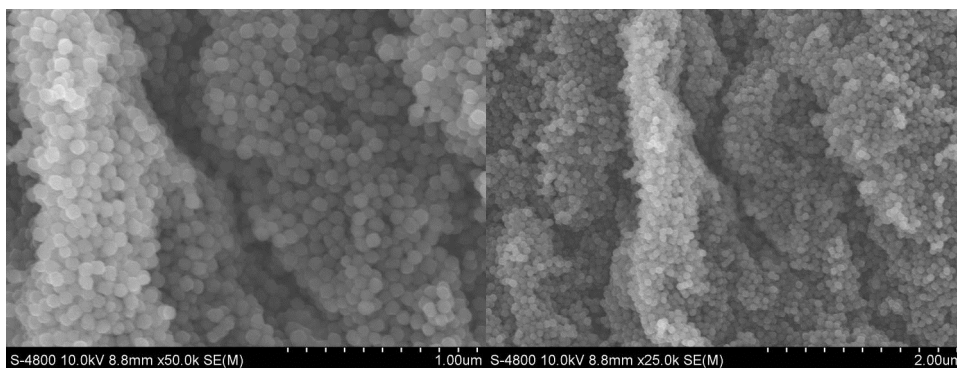


Figure S8. SEM images of Fe_2O_3 nanoparticles.

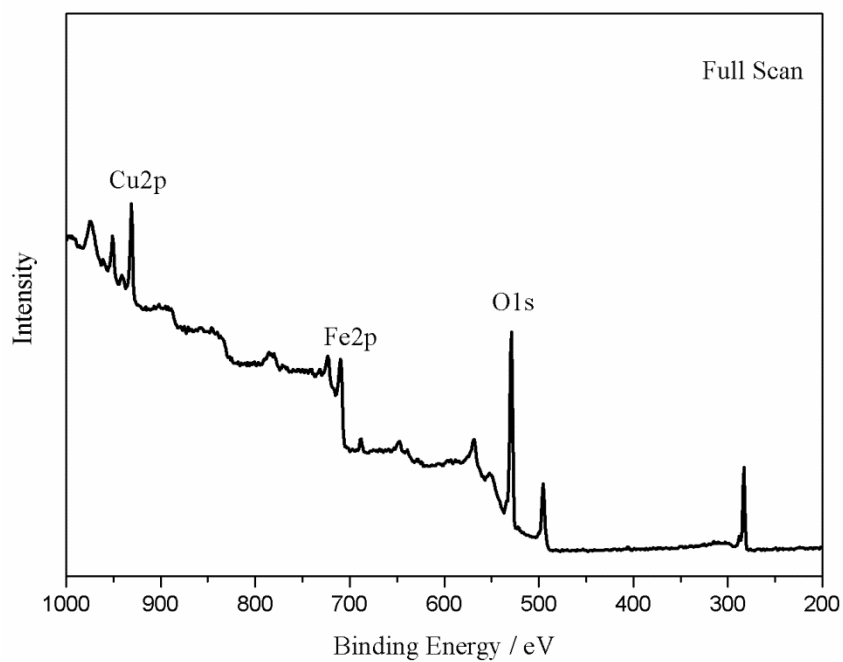


Figure S9. X-ray photoelectron spectrum of CuFe_2O_4 showing the all elements region peaks of CuFe_2O_4 .

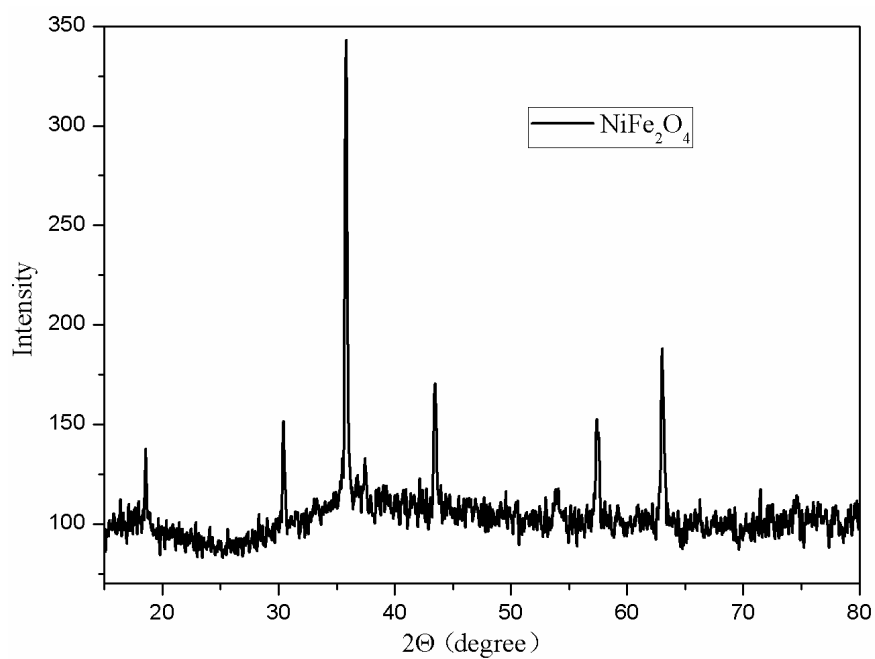


Figure S10. XRD of NiFe_2O_4

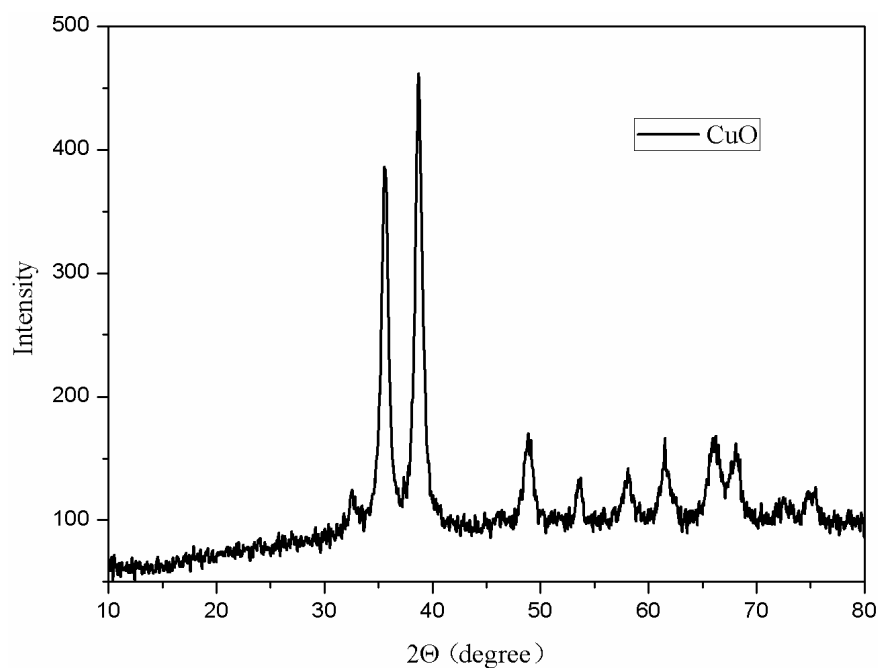


Figure S11.XRD of CuO

1. T. Raming, A. Winnubst, C. M. van Kats and A. Philipse, *J. Colloid Interface Sci.*, 2002, **249**, 346-350.
2. J. Zhu, D. Li, H. Chen, X. Yang, L. Lu and X. Wang, *Mater.Lett.*, 2004, **58**, 3324-3327.