

Supporting Information

Surface Plasmon-Enhanced Nanozyme-Based Fenton Process for Visible-Light-Driven Aqueous Ammonia Oxidation

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1. Experimental

1.1 Preparation of ZIF-8.

A methanolic solution (500 mL) of zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 7.4350 g, 25 mmol) was added into a methanolic solution (500 mL) of 2-methylimidazole (2.0520 g, 25 mmol) and triethylamine (3.2675 g, 36 mmol) in 2 min with ultrasonication at ambient temperature, giving a turbid solution. The turbid solution was allowed to stand for 4 h and then centrifuged to give a white solid, which was washed for five times with methanol and then dried at 80 °C for 4 h to afford ZIF-8.¹

1.2 Preparation of functionalized porous carbon.

The ZIF-8 sample (4.0 g) was transferred into a ceramic boat and placed into a temperature-programmed furnace under H_2 flow, heated from room temperature to 1000 °C in 3 h, and then kept at 1000 °C for 10 h and cooled down to room temperature. The resultant black material was washed several times with a HCl (5 vol% in water) solution, followed by washing with plenty of distilled water and dried at 80 °C for 12 h to afford ZIF-8-derived 3D hierarchically porous carbon, denoted as PC. Subsequently, the functionalized PC were fabricated by a surface oxidation in 1.0 M acidic ammonia persulfate solution at 100 °C for 12 h to obtain the functionalized carbon matrix for loading iron oxides. The carboxy lgroups on the functionalized PC surface for the α -FeOOH and AuNPs immobilization and increases the surface hydrophilicity for enhancing their miscibility in aqueous solution. Functionalized PC were washed with deionized water by using iterative cycles of centrifugation (10,000 rpm for 10 min), decantation and DI water washing. Excessively-washed

functionalized PC were dried at 80 °C in a vacuum oven, and stored at room temperature, named as FPC.

1.3 Preparation of α -FeOOH–FPC.

α -FeOOH–FPC was prepared by a hydrothermal method. Typically, 0.5 g of hydrophilic FPC, 4 mmol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 20 mmol of urea were dispersed in 40 mL of deionized water by ultrasonication. The mixture was transferred into a 50 mL of Teflon-lined autoclave after 30 min ultrasonication, followed by the hydrothermal reaction for 12 h at 100 °C. Finally, the obtained powders were washed with water and ethanol for several times, then freeze-dried overnight, named as α -FeOOH–FPC.

1.4 Preparation of AuNPs.

Briefly, a 250 mL aqueous solution consisting of 1 mM HAuCl_4 was brought to a vigorous boil with stirring in a round-bottom flask fitted with a reflux condenser, and then 38.8 mM trisodium citrate (25 mL) was added rapidly to the solution. The solution was boiled for another 15 min, during which time its color changed from pale yellow to deep red. The solution was cooled to room temperature with continuous stirring.

1.5 H_2O_2 analytical methods

H_2O_2 was tested with a colorimetric reaction involving horseradish peroxidase (HRP) and 2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonate acid) (diammonium salt, ABTS²⁻).²

The H_2O_2 concentration was determined by flow-injection chemiluminescence

method.³ Typically, 0.65 mM of luminol solution was composed of 0.1 M of Na₂CO₃ (adjusting pH to 10.15 using 2 M of HCl and placing for 24 h), and then CoCl₂ (0.06 mM of Co²⁺) was added into above solution. The luminol solution and sample were injected in chemiluminescence system (MIP-B) simultaneously through the flow injection apparatus (IFISD). Finally, the chemiluminescent signal was recorded to determine H₂O₂ concentration.

1.6 TAN, NO₃-N and NO₂-N analytical methods

TAN test method: Under alkaline conditions, ammonia ions react with hypochlorite and sodium salicylate to form a color-developing complex. The whole reaction is carried out under the catalysis of sodium nitroprusside, colorimetric determination at 630 nm.

NO₃-N test method: Nitrate ions are reduced to nitrite ions by cadmium column in the environment of pH 7.80-7.85. Under acidic conditions, it is diazo-coupled with p-aminobenzenesulfonamide to form a diazonium salt, which is coupled with N-(1-naphthyl)-ethylenediamine dihydrochloride (C₁₂H₁₄N₂.2 HCL) to form a pink color complex. The colorimetric determination is carried out at 630 nm. The result obtained by the method is the sum of NO₃-N and NO₂-N.

NO₂-N test method: In the acidic medium, the nitrite and the sulfonamide are undergone the diazo reaction, and the product is coupled with N-(1-naphthyl) ethylenediamine dihydrochloride to form a red dye, and then the absorbance is measured at a wavelength of 550 nm.

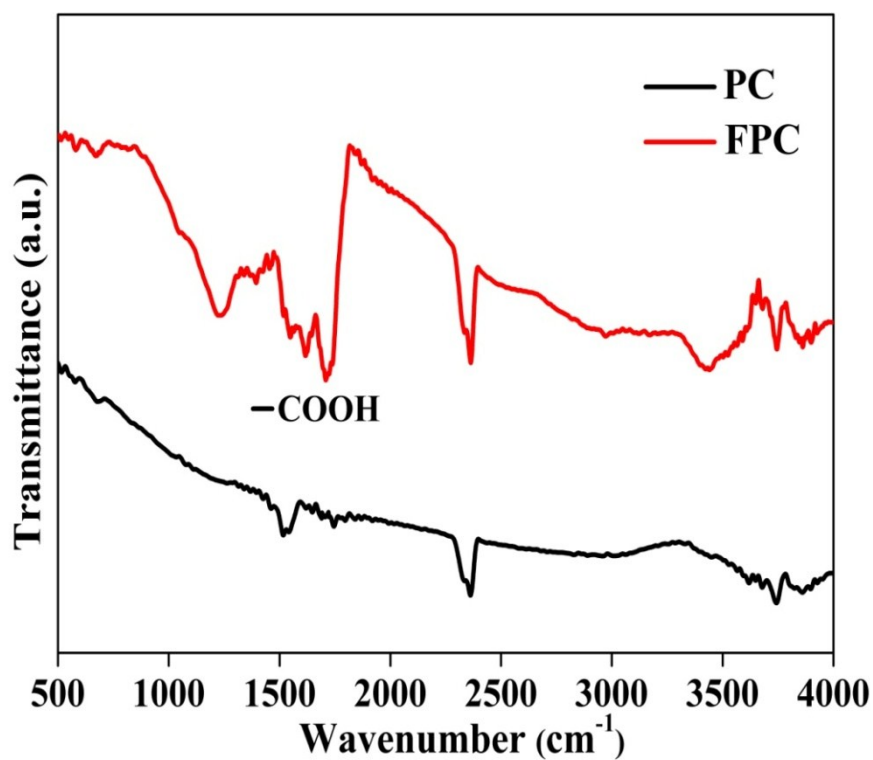


Figure S1. FT-IR spectra of porous carbon (PC) and functionalized porous carbon (FPC), an obvious band is present at 1720 cm^{-1} after wet oxidation assigned to the stretching vibration of carboxylic groups.

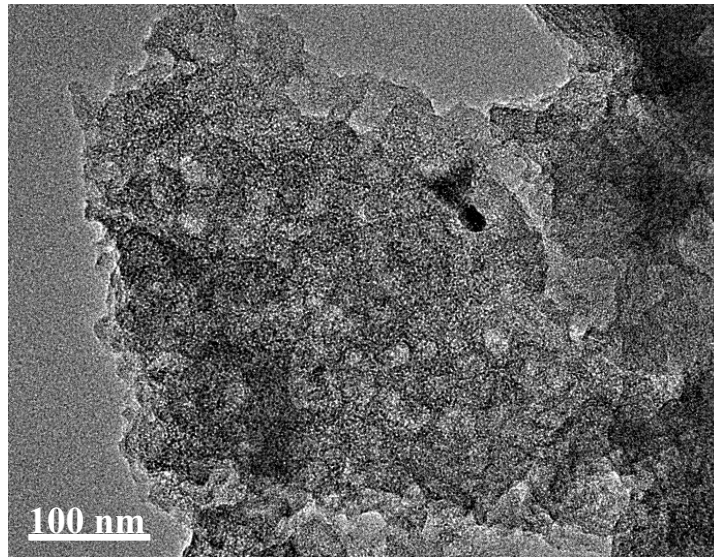


Figure S2. TEM image of pure FPC.

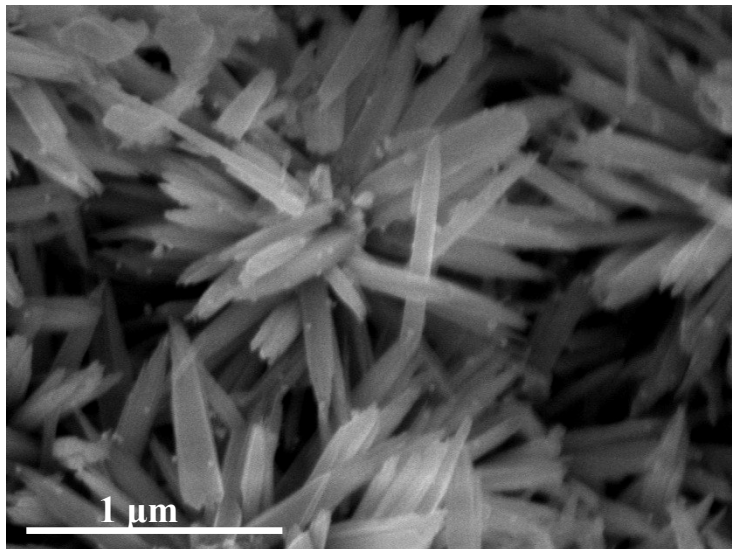


Figure S3. SEM image of α -FeOOH-FPC.

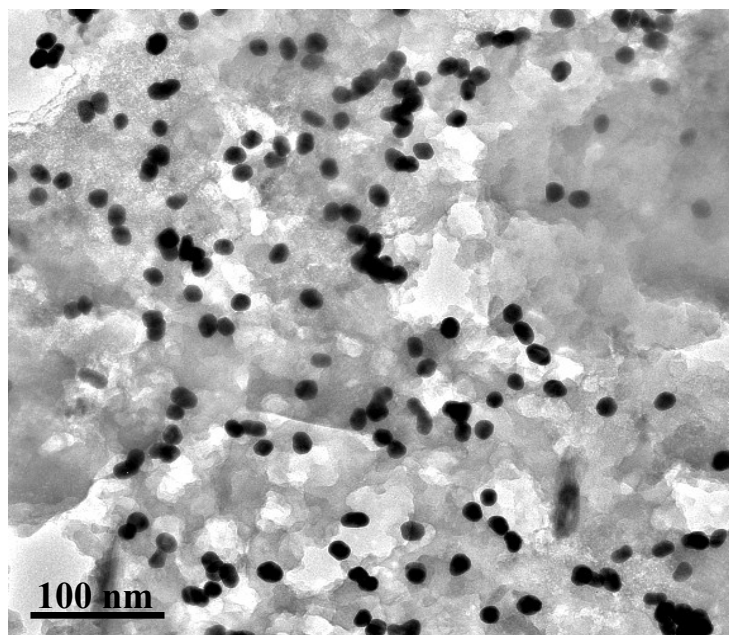


Figure S4. TEM image of Au-FPC.

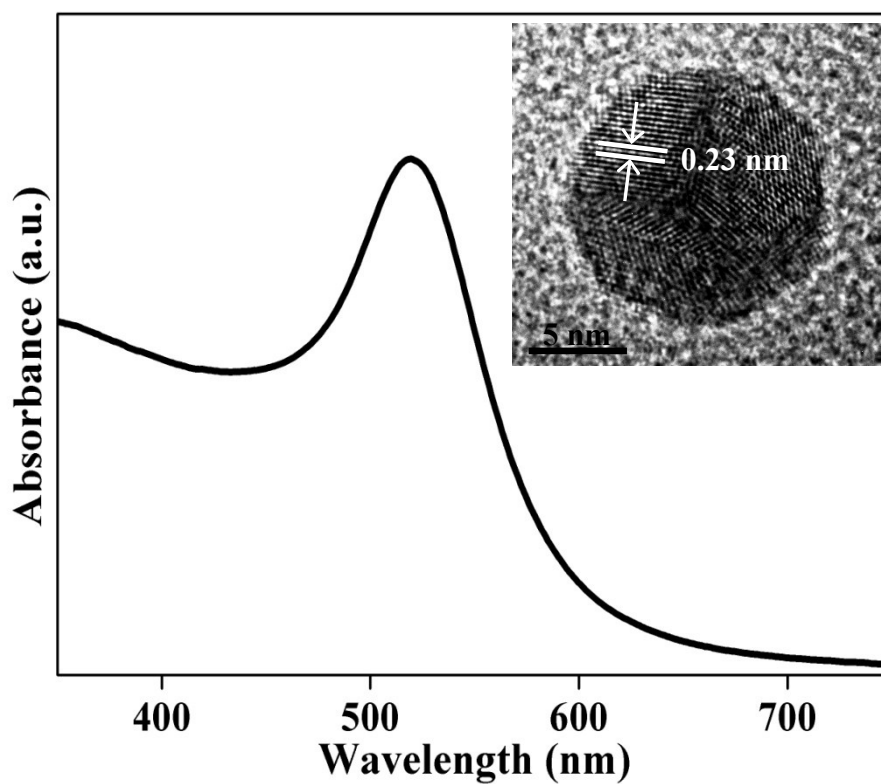


Figure S5. Absorption spectrum of the citrate-capped AuNPs (~13 nm). Inset is the photograph of synthesized AuNRs.

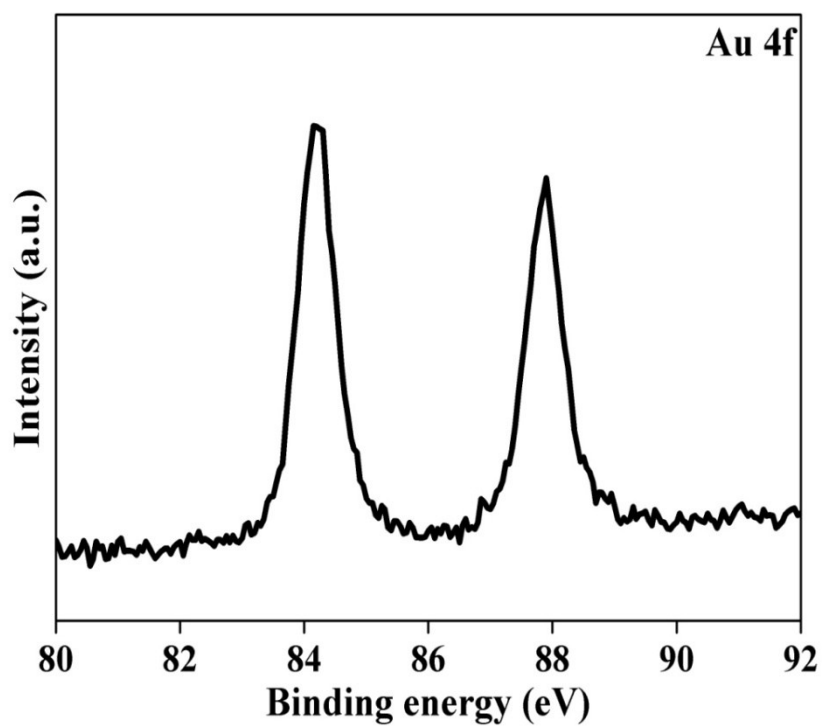


Figure S6. High resolution XPS spectra of Au 4f of the Au/ α -FeOOH-FPC

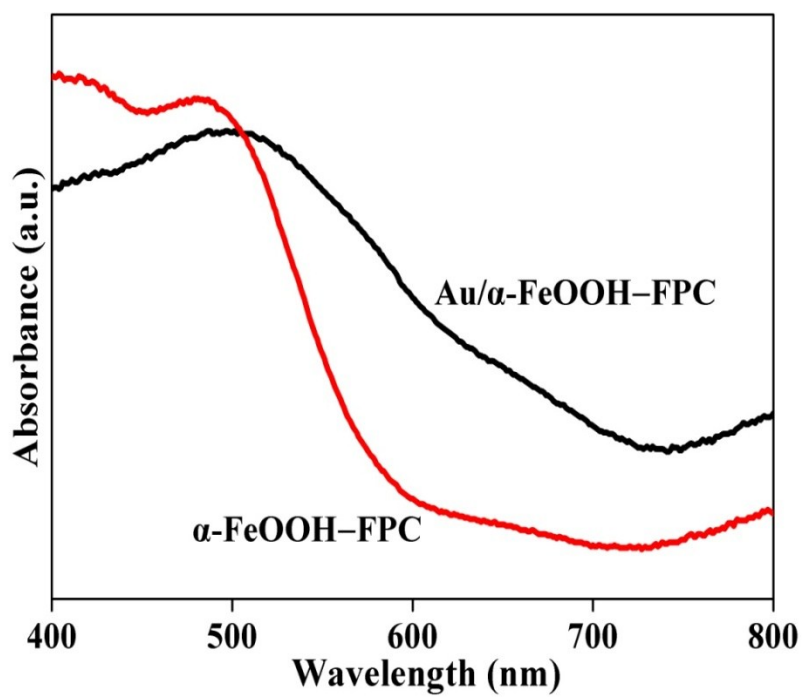


Figure S7. UV-vis diffuse reflection spectra of the of α -FeOOH-FPC and Au/ α -FeOOH-FPC.

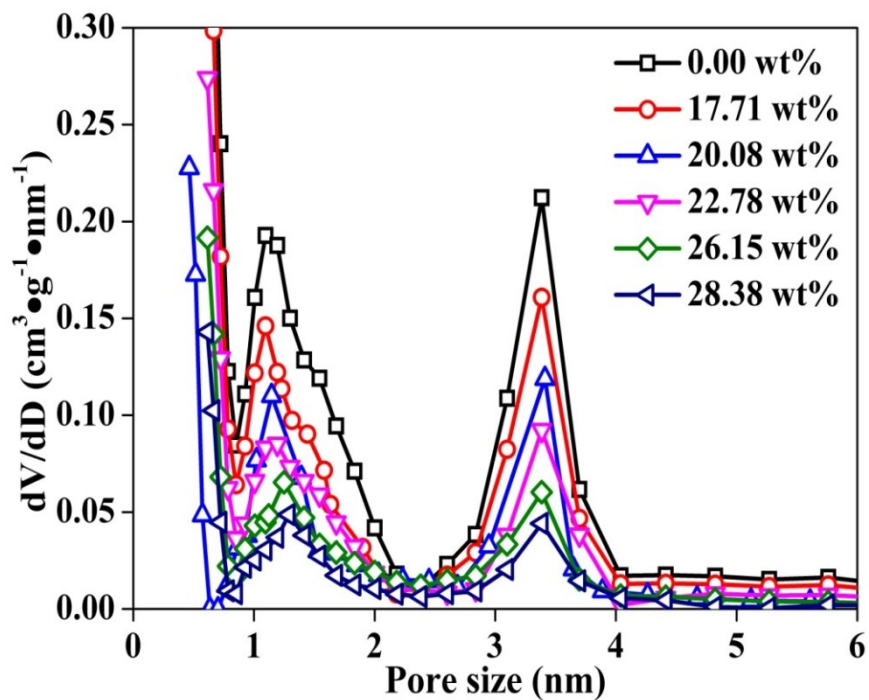


Figure S8. Pore size distributions of the Au/ α -FeOOH-FPC with the different Fe³⁺ (wt%) loading.

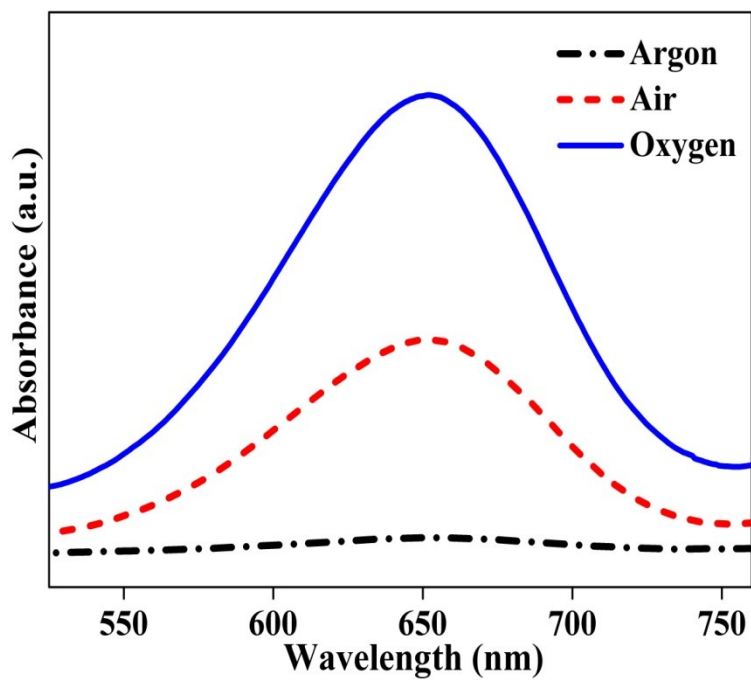


Figure S9. Absorption spectrum of the Au-FPC under different atmosphere.

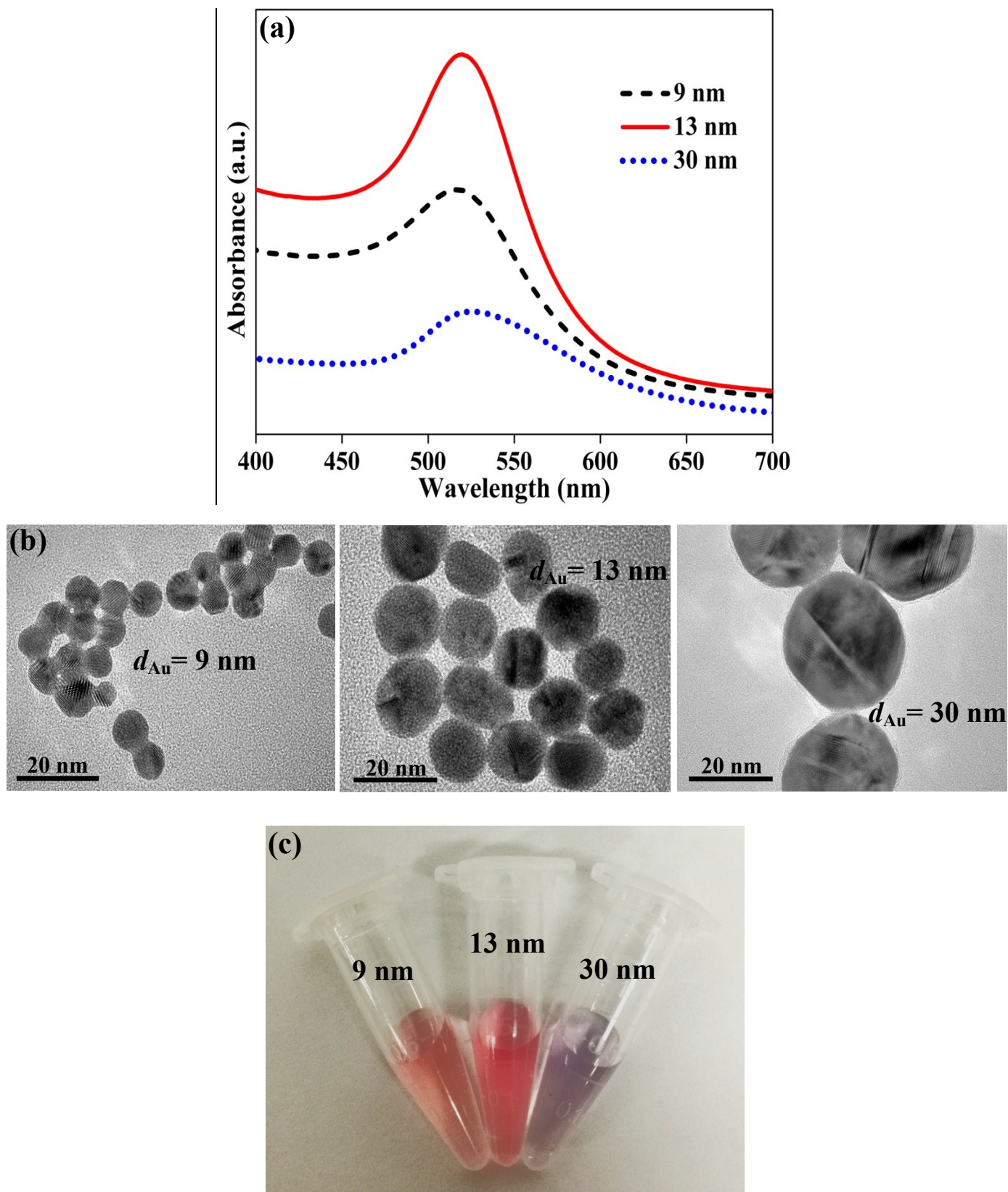


Figure S10. (a) UV-visible absorption spectra, (b) SEM images and (c) digital photos of AuNPs

with the different sizes.

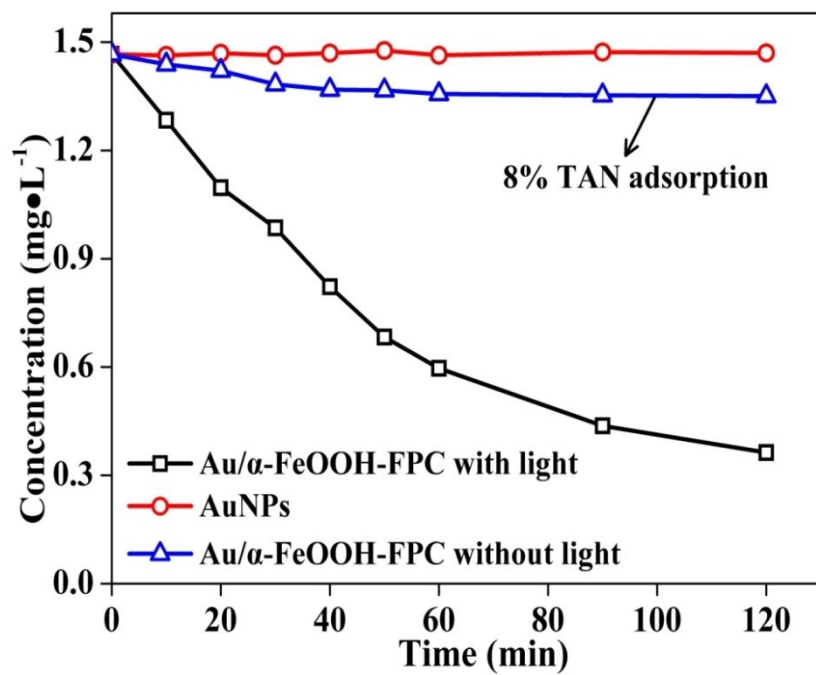


Figure S11. Changes of TAN concentrations by AuNPs and Au/α-FeOOH-FPC with and without visible-light irradiation.

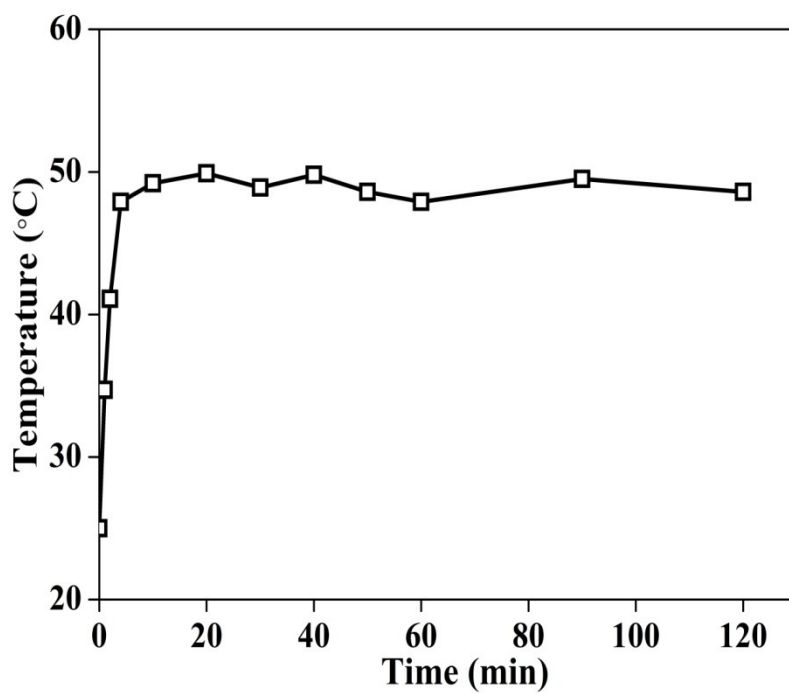


Figure S12. Time profile of temperature of reaction solution within 120 min.

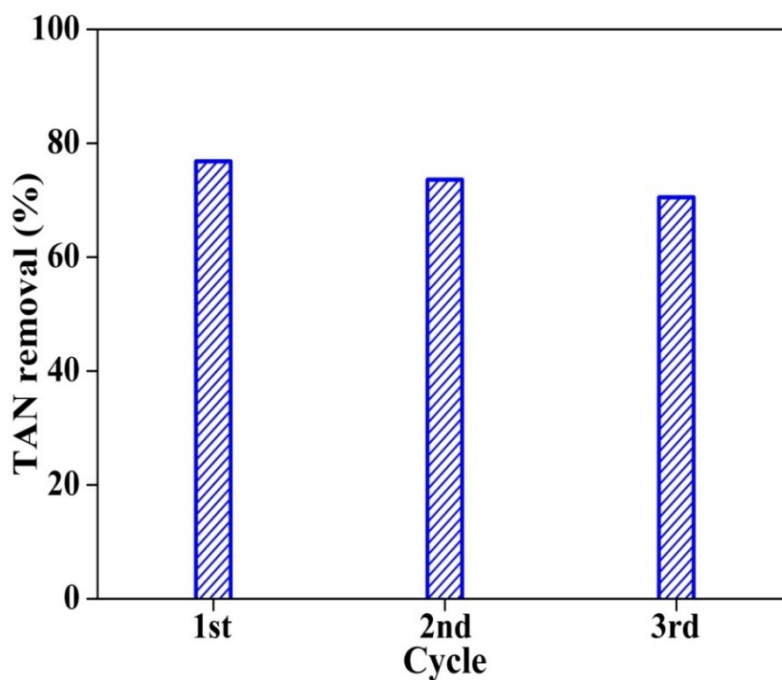


Figure S13. Cycling runs for the TAN removal with Au/ α -FeOOH–FPC catalyst under light irradiation.

The durability and stability is an important aspect for evaluating a heterogeneous Fenton catalyst. Figure S13 shows the reusability of Au/ α -FeOOH–FPC catalysts with successive three tests for TAN removal under the photo-assistance. There was only a limited loss of catalytic activity during the cycle tests, and the results of all the three cycles showed more than 70% of TAN removal within 120 min. These results indicated that the Au/ α -FeOOH–FPC catalysts possess sufficient stability for TAN removal in the surface plasmon-enhanced nanozyme-Fenton reaction.

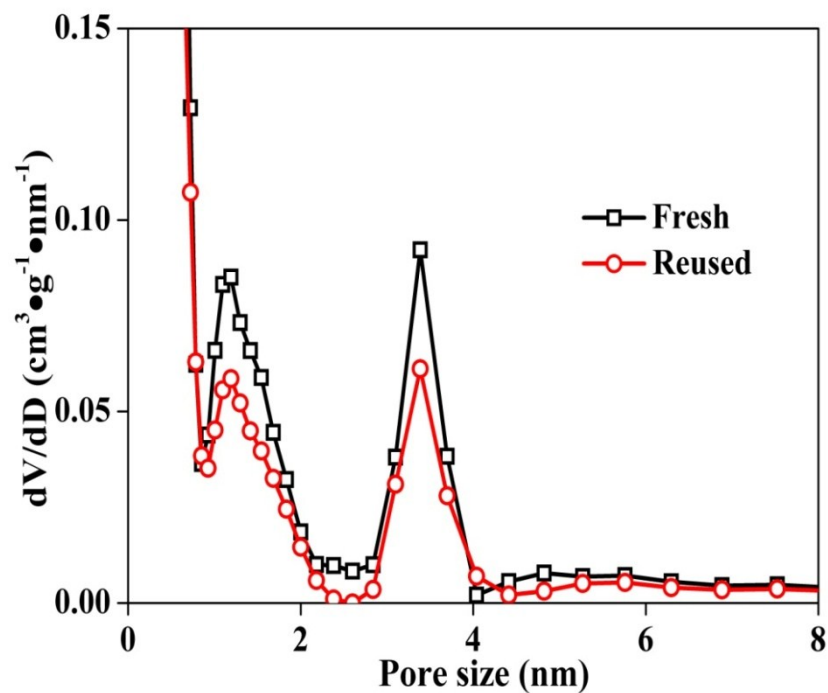


Figure S14. Pore size distributions of the fresh and reused Au/ α -FeOOH-APC.

References

- 1 A. J. Amali, J. K. Sun, Q. Xu, *Chem. Commun.* 2014, **50**, 1519–1522.
- 2 W. J. Luo, C. F. Zhu, S. Su, D. Li, Y. He, Q. Huang, C. H. Fan, *ACS Nano*, 2010, **4**, 7451–7458.
- 3 Y. M. Liu, S. Chen, X. Quan, H. T. Yu, H. M. Zhao, Y. B. Zhang, *Environ. Sci. Technol.* 2015, **49**, 13528–13533.