

Supporting Information

Synthesis of Graphene Quantum Dots Stabilized Gold Nanoparticles and Its Application

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1. General data

All commercial materials were used without further purification, unless indicated. The deionized water was prepared in the laboratory. The starch used in the synthesis of GQDs was bought from Aladdin Reagent Co.,Ltd, Shanghai, China, and its information and physical properties are listed in **Table S1**.

Table S1 The information and physical properties of the starch

Material	Starch from potato (amylose)
CAS No.	9005-25-8
EC No.	232-679-6
Appearance	White powder
Molecular formula	$(C_6H_{10}O_5)_n$
Degree of polymerization	1100
Density	1.5
Melting point	256-258°C
PH value (20g/L, 25°C)	6.0-7.5
Burning residue	≤0.5%
Weight loss on drying	≤13.0%

UV-vis. absorption spectra were measured with a Perkin-Elmer Lambda 19 UV-vis. spectrometer.

Transmission Electron Microscopy (TEM) images of nanoparticles were obtained on a Tecnai G2 F20 (120 kV) microscope. The TEM samples were prepared by deposition of the nanoparticle suspension (10 μ L) onto a carbon-coated microscopy copper grid. Samples were left to dry in vacuum prior to insertion into the TEM microscope.

X-ray Photoelectron Spectroscopy (XPS)

Surface analysis by XPS was performed in a Thermo SCIENTIFIC ESCALAB 250Xi system spectrometer in an ultra-high vacuum (UHV) chamber. The X-ray sources employed for this analysis were an non monochromatic Mg K α (1253.6 eV) and 250

W or Al K α operated at 1.25 kV and 300W, calibrated using the 3d5/2 line of Ag with a full width at half maximum (FWHM) of 1.1 eV. The take-off angle was fixed at 90° and the analysis was conducted at a pressure of $\sim 10^{-6}$ Pa. Samples were dispersed onto glass, silicon or titanium surfaces, dry and inserted into the XPS. The selected resolution for the spectra was 30 eV of Pass Energy and 0.5 eV/step for the general survey spectra and 15 eV of Pass Energy and 0.15 eV/step for the detailed spectra of Cu 2p, Ag 3d and Au 4f photoelectron lines. Spectra were analyzed with the CasaXPS 2.3.15dev87 software. The analysis consisted of satellite removal, Shirley background subtraction, calibration of the binding energies related to the C 1s C-C peak at 285 eV, and peak fitting with Gaussian-Lorentzian line shapes where the FWHM of the peaks were constrained while the peak positions and areas were set free.

2. Preparation of the GQDs

GQDs was synthesized from only commercial natural polymer starch and water using the modified our previously reported method.^[7] The starch of 0.3g was firstly dispersed in 25mL deionized water and stirred at 60°C for 15 min. After it was dissolved, the solution was immediately poured into a 100 ml Teflon lined stainless autoclave, which was then heated in an oven at 180 °C for 8 h. Then, the autoclave was taken out to be cooled freely. The final brown product was transferred into centrifugal tubes, and centrifuged at 10000 r/min for 30 min to separate out the precipitate. The pale yellow liquid which was obtained finally was the solution of graphene quantum dots (GQDs): 0.31 g/L.

3. Preparation of the AuNPs

First, 1 mL(0.507 g/L) GQDs are dissolved in 3 mL of deionized water in a Schlenk flask, and the solution is stirred for 10 mins at 0 °C. Then a colorless solution of HAuCl₄.3H₂O (2.5×10^{-4} mmol in 1 mL water) is added dropwise, provoking the formation of claret (AuNPs) color (Figure S1) corresponding to the reduction of the cation to the zero-valent metal and AuNPs-1 formation. The AuNPs-1 were kept in aqueous solution for characterization and used as the catalysts. A plasmon band is

observed in the UV-vis. spectra for AuNPs (527 nm). Other AuNPs were synthesized using different amount of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ by the same method.

4. Catalysis of 4-nitrophenol reduction

An aqueous solution (2.5 mL) containing 4-nitrophenol (0.09 mmol) and NaBH_4 (9 mmol) is prepared in a standard quartz cuvette (3 mL, path length: 1 cm). The TMNPs catalyst (5 mol%) is injected into this solution, and the reaction progress is detected by UV-vis. spectroscopic analysis every min at 22°C. (Figure S19-S30)

5. Microscopy images of the AuNPs.

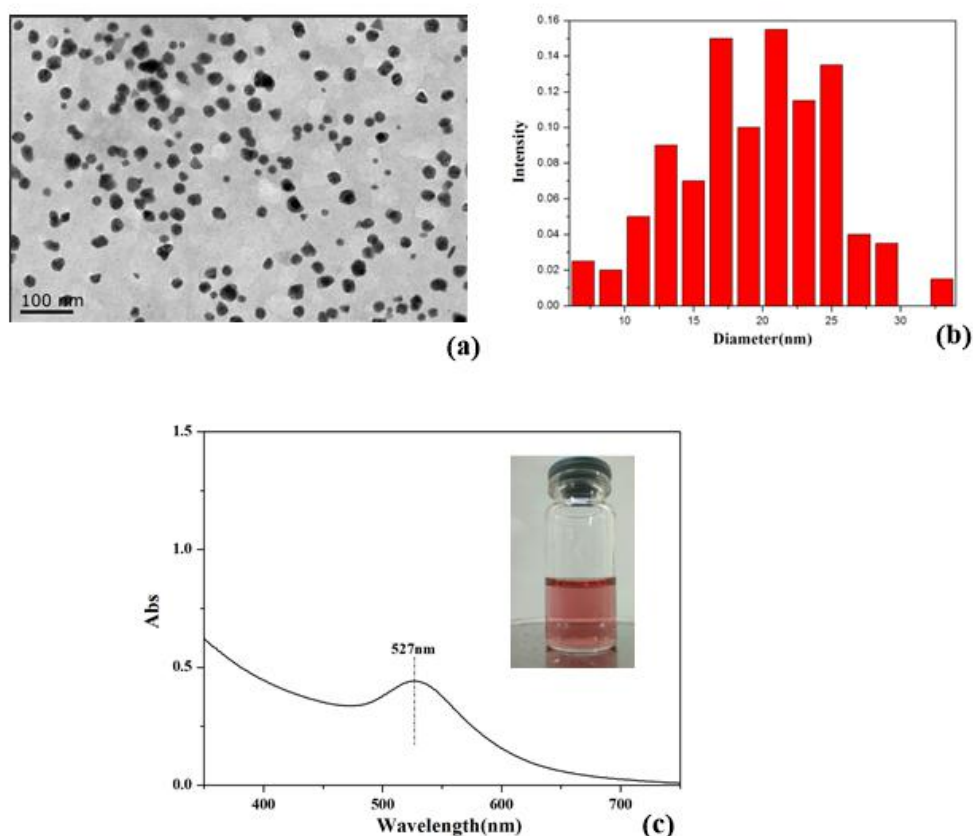


Figure S1. SEM image of **1**; (b) Diameter histogram distribution of **1**; (c) UV-vis. spectrum of **1**.

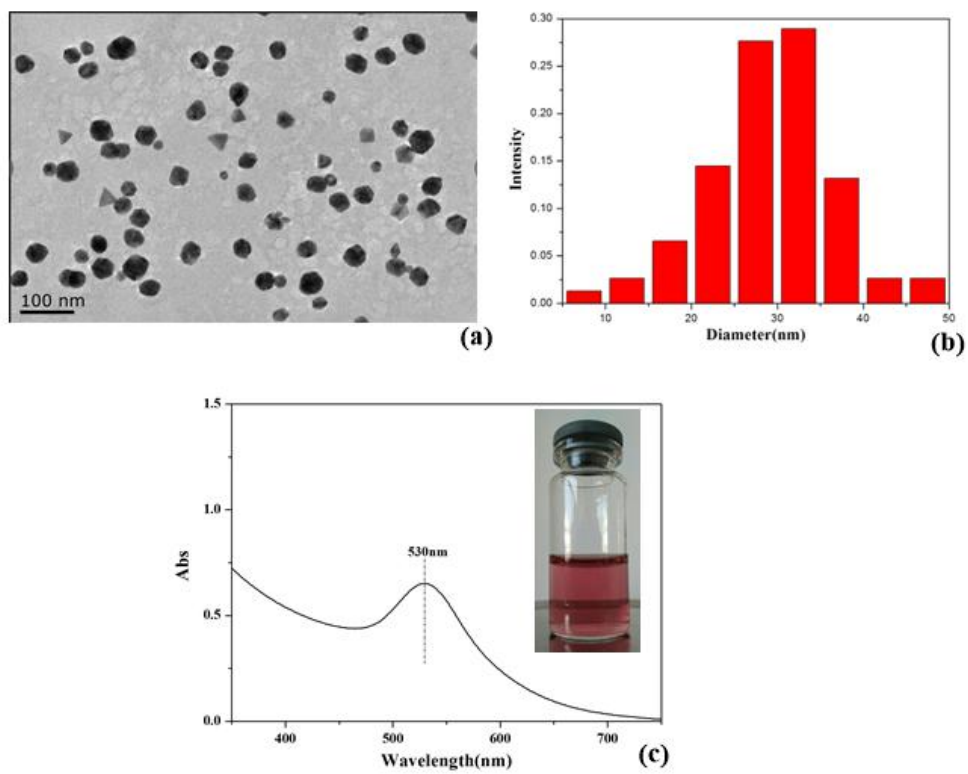


Figure S2. SEM image of **2**; (b) Diameter histogram distribution of **2**; (c)UV-vis. spectrum of **2**.

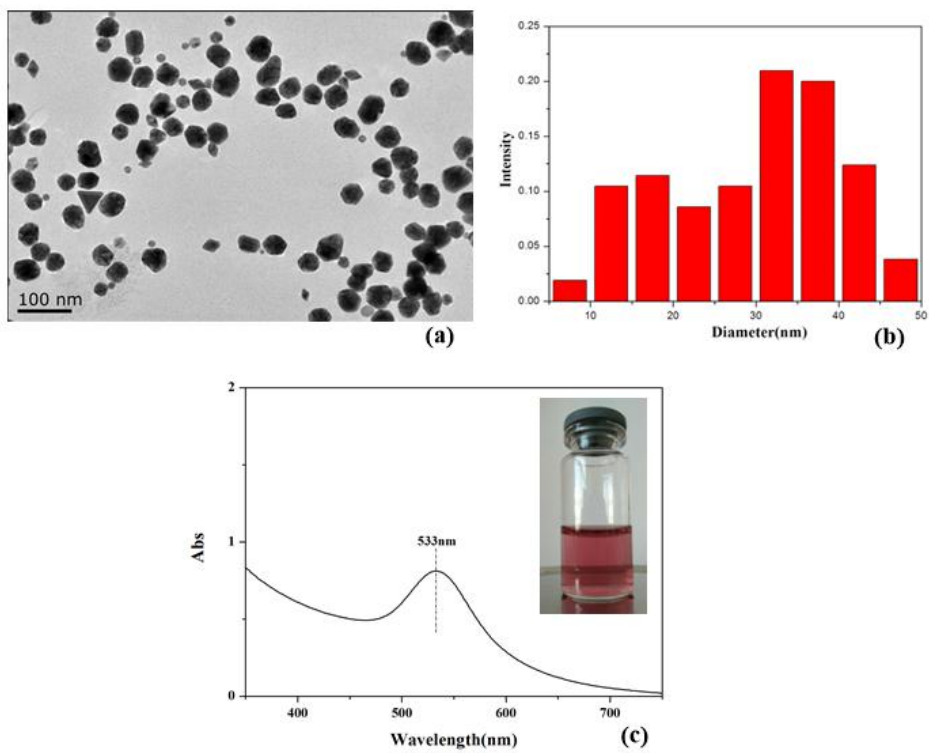


Figure S3. SEM image of **3**; (b) Diameter histogram distribution of **3**; (c)UV-vis. spectrum of **3**.

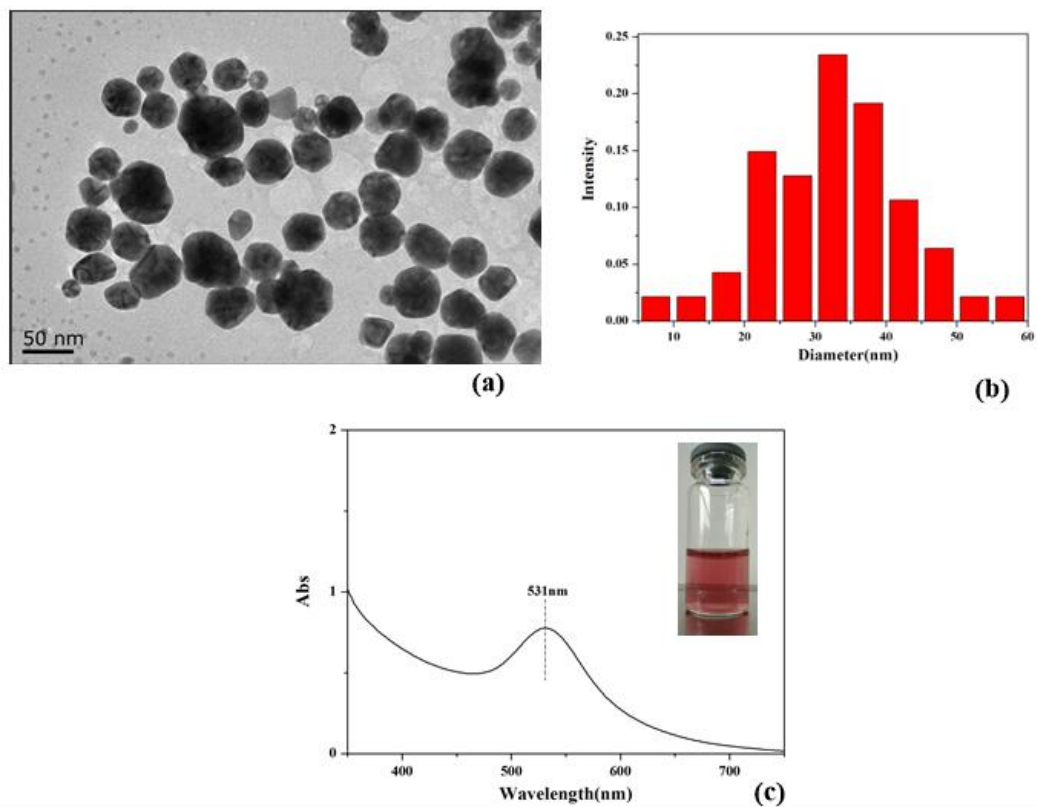


Figure S4. SEM image of 4; (b) Diameter histogram distribution of 4; (c)UV-vis. spectrum of 4.

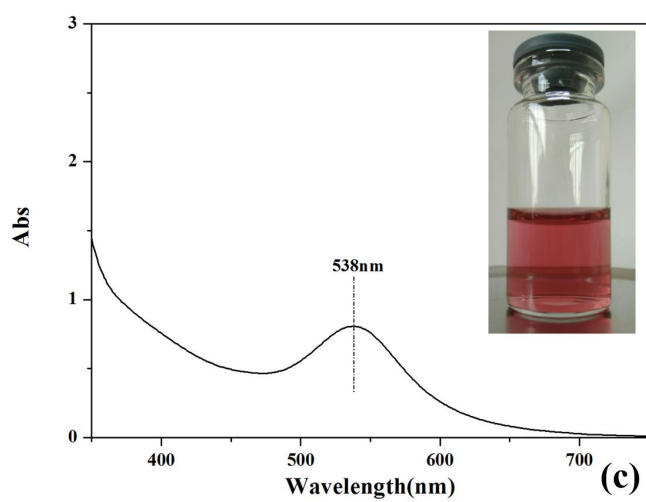
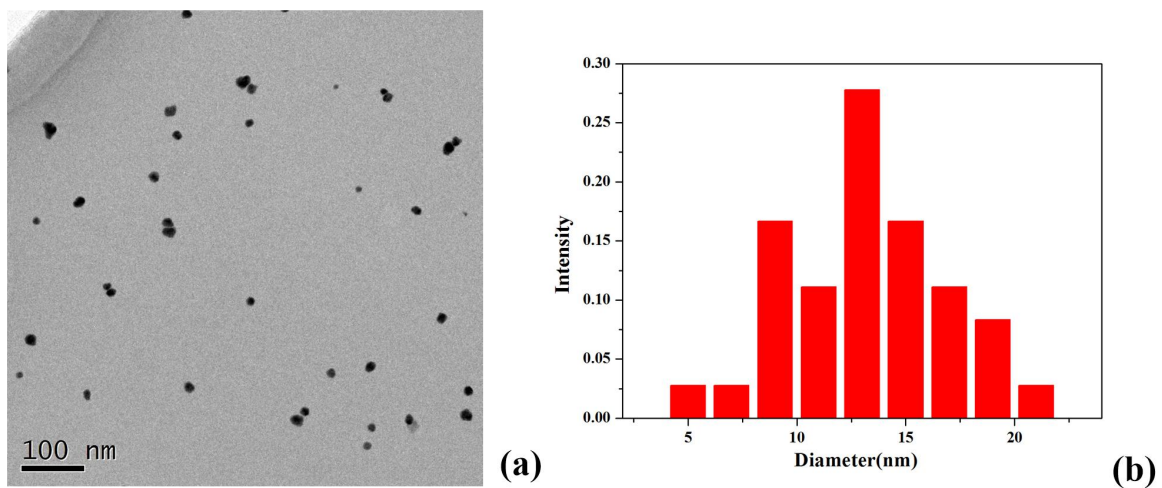


Figure S5. SEM image of **5**; (b) Diameter histogram distribution of **5**; (c)UV-vis. spectrum of **5**.

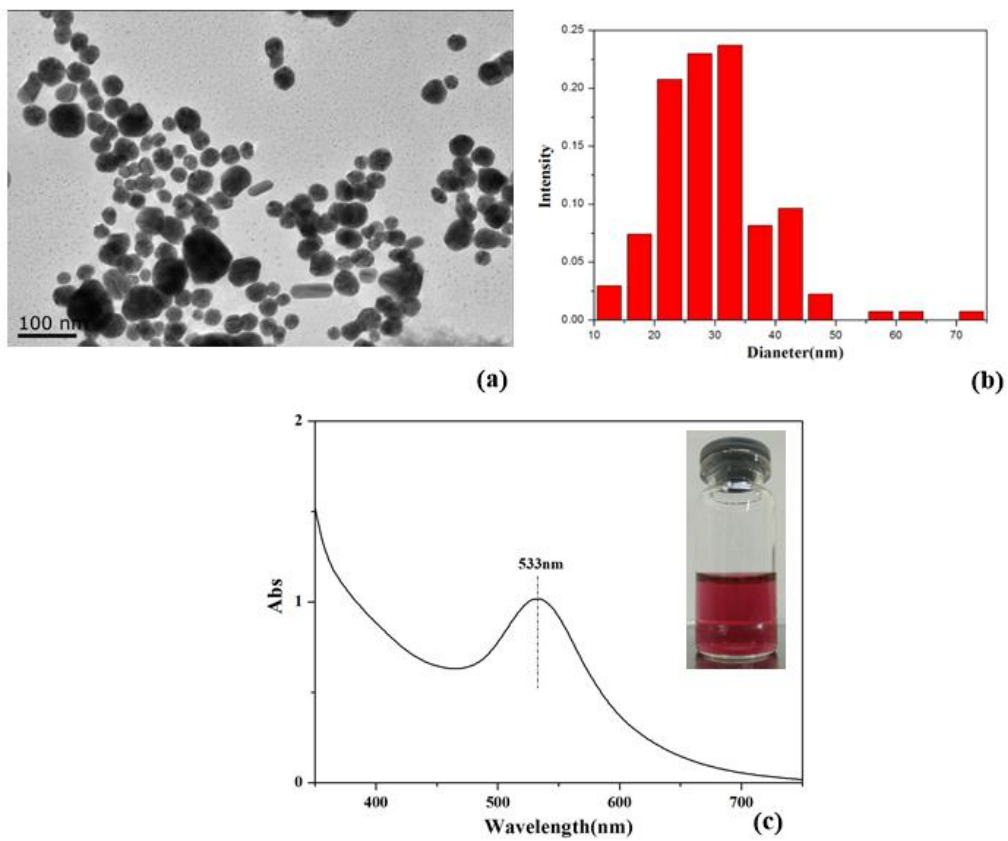


Figure S6. SEM image of **6**; (b) Diameter histogram distribution of **6**; (c)UV-vis. spectrum of **6**.

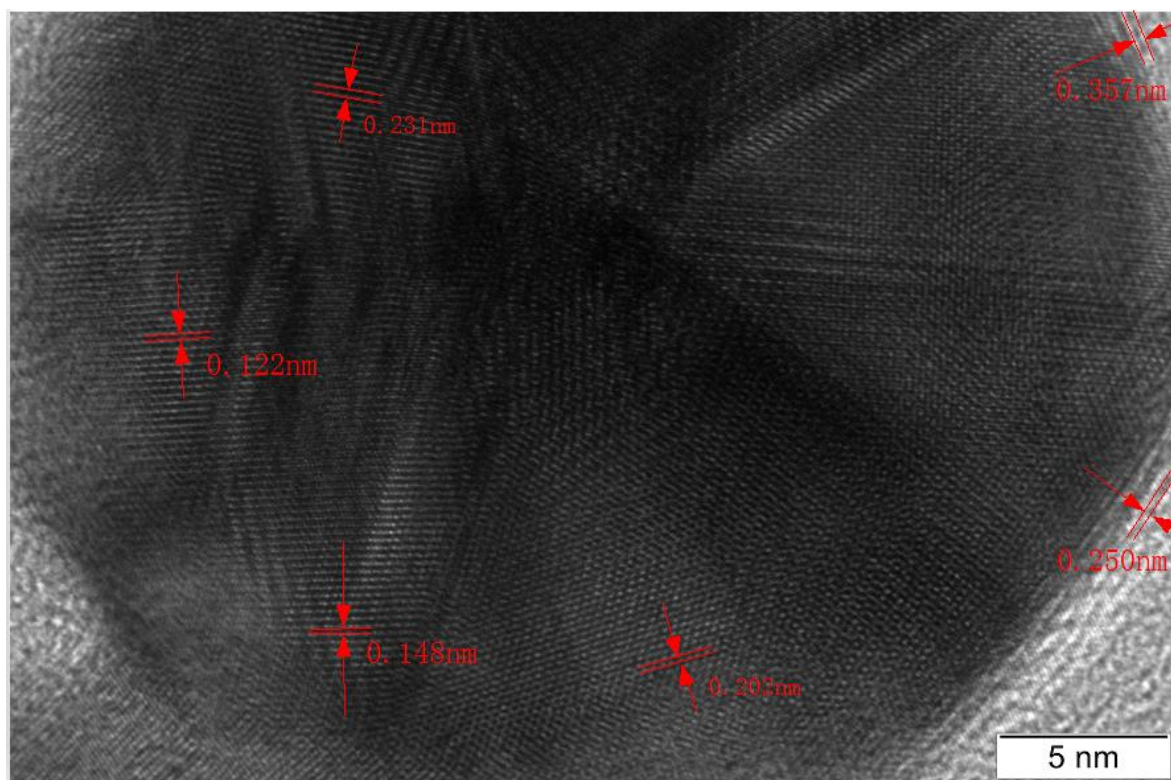


Figure S7. HRTEM of AuNPs-5

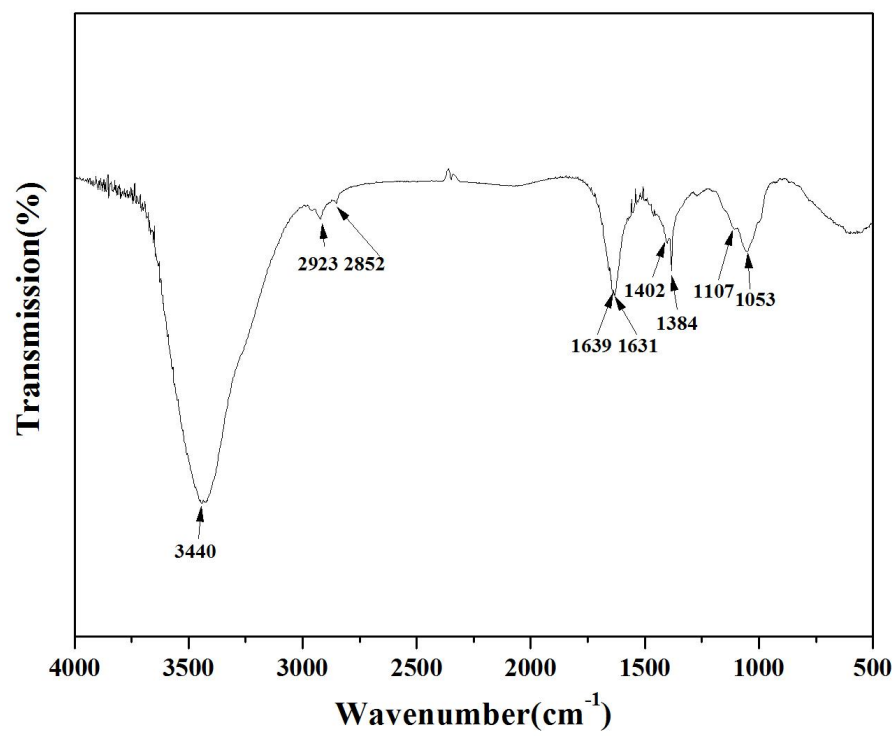


Figure S8. FTIR spectra of AuNPs-5.

6. UV-Vis spectra of AuNPs with the change of reaction time

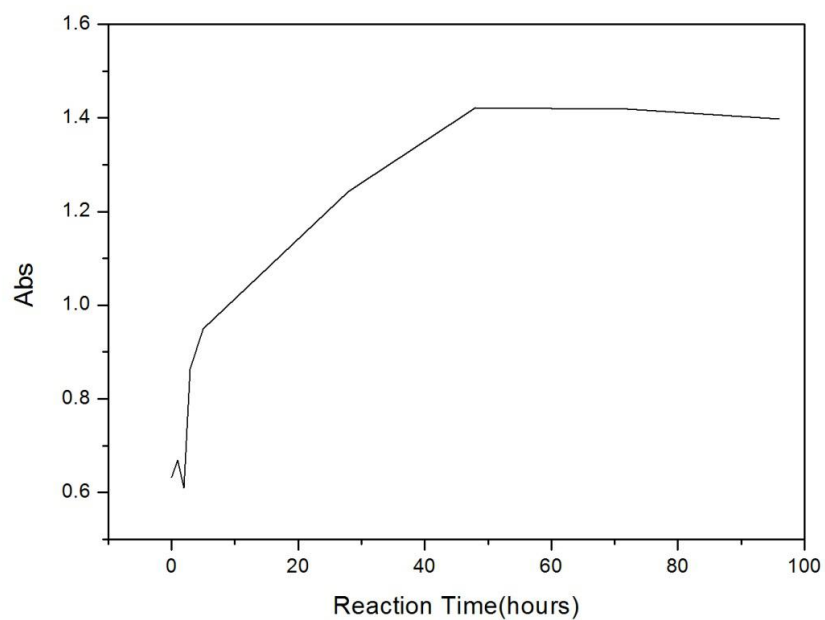


Figure S9. The absorption of AuNPs (527 nm) versus reaction time for AuNP-1.

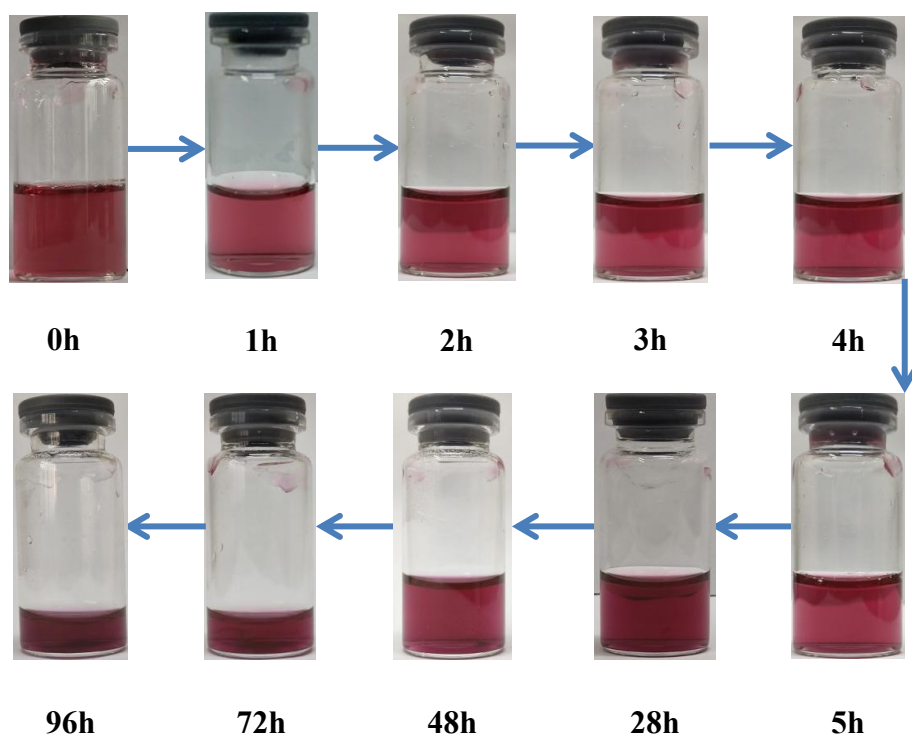


Figure S10. Photographs of AuNP-1 with the change of reaction time.

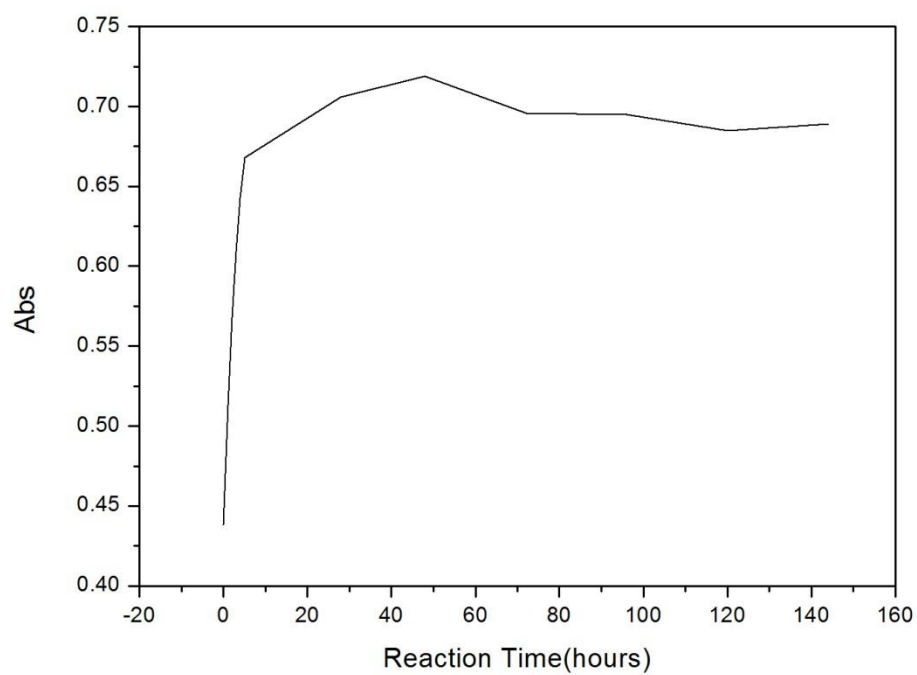


Figure S11. The absorption of AuNPs (530 nm) versus reaction time for AuNP-2.

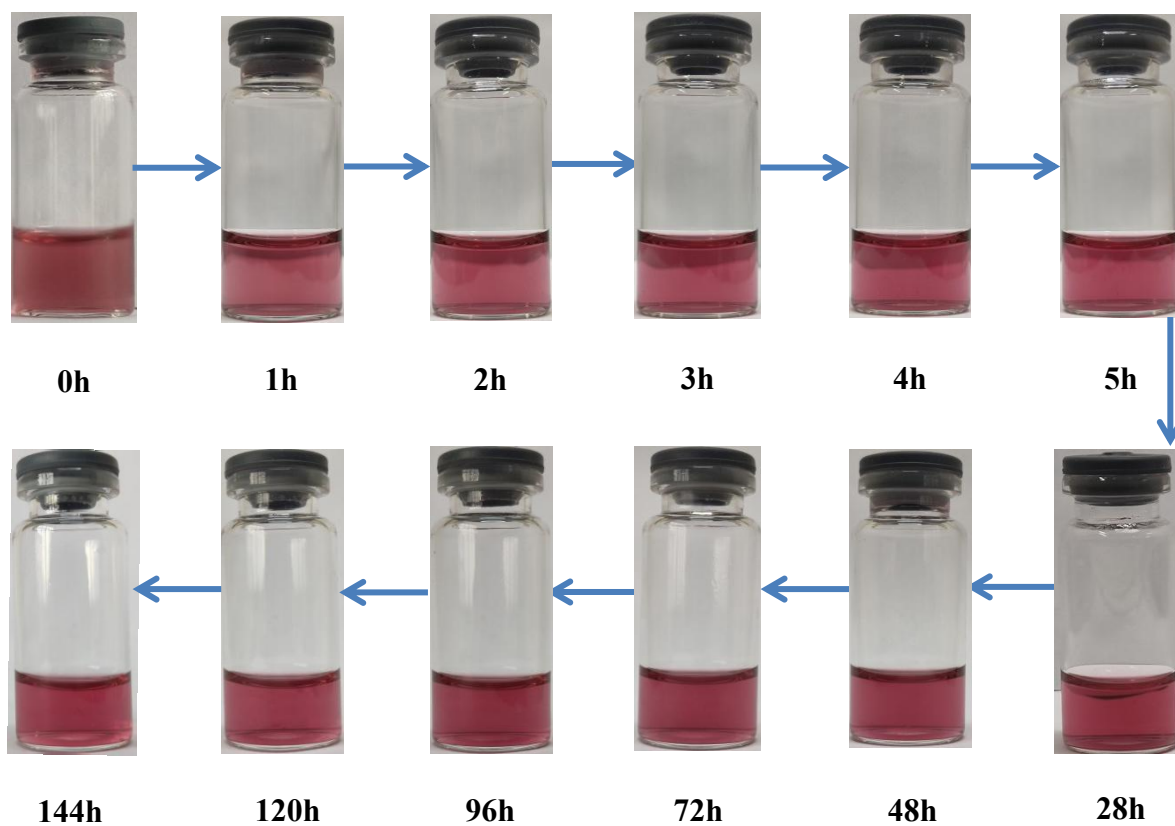


Figure S12. Photographs of AuNPs-2 with the change of reaction time.

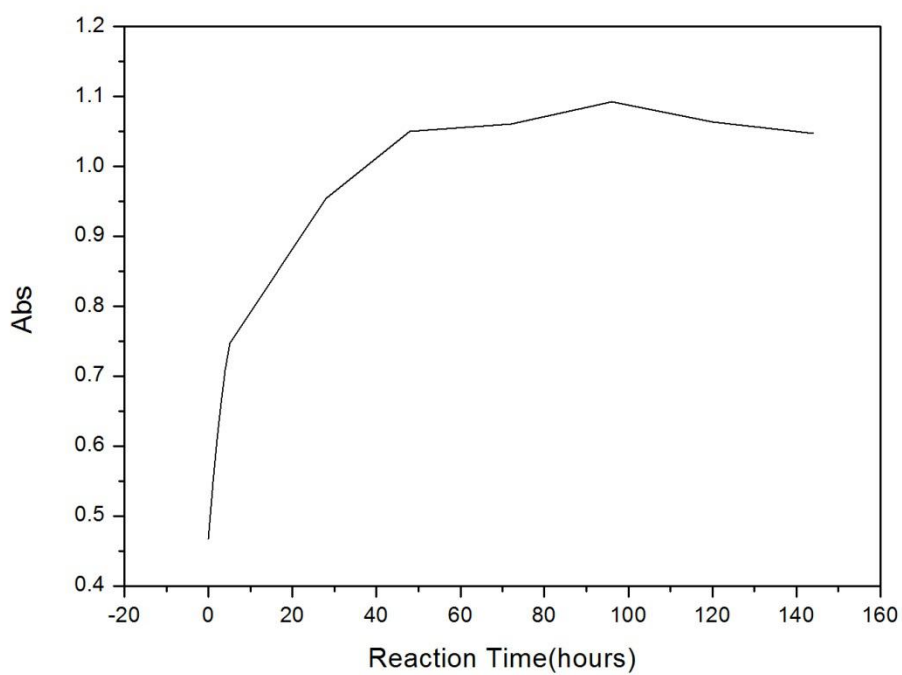


Figure S13. The absorption of AuNPs (533 nm) versus reaction time for AuNPs-3.

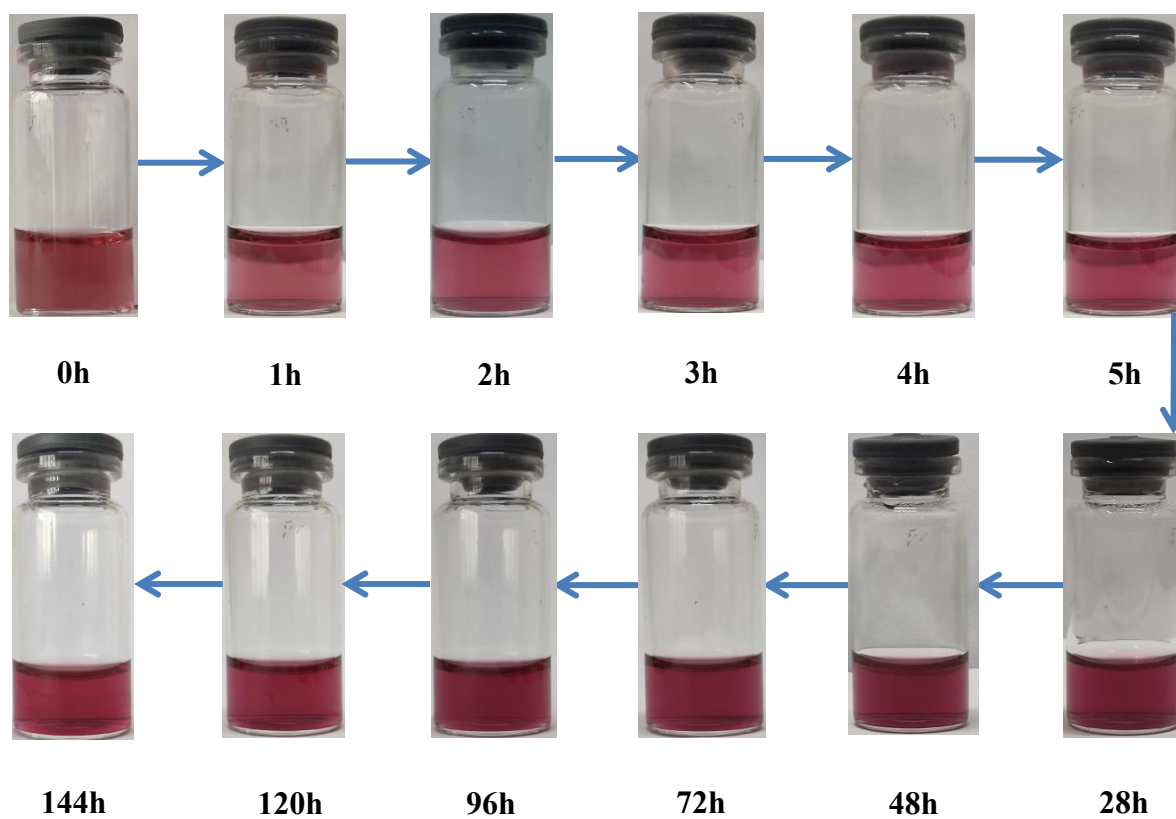


Figure S14. Photographs of AuNPs-3 with the change of reaction time.

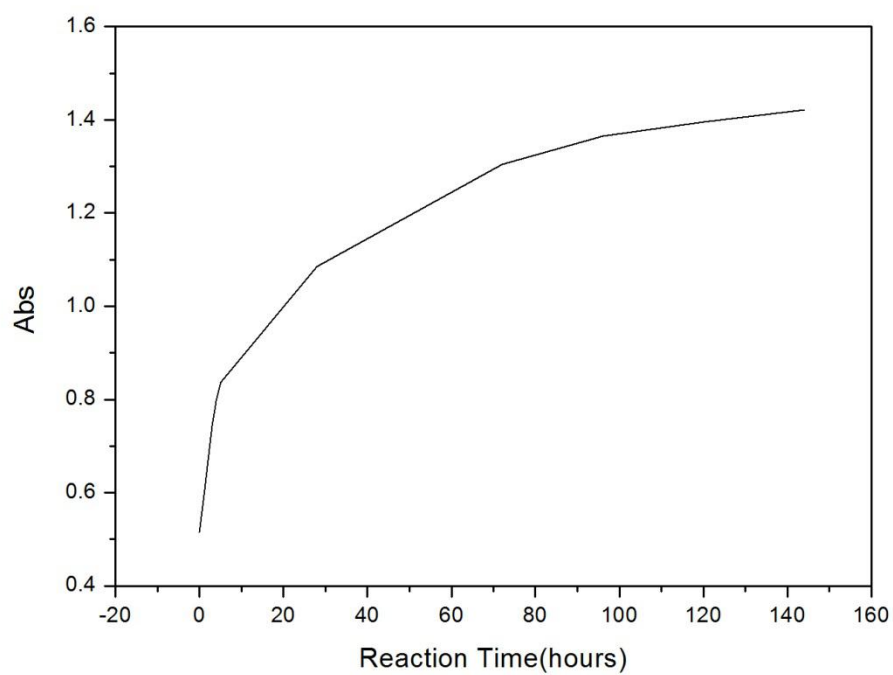


Figure S15. The absorption of AuNPs (531 nm) versus reaction time for AuNPs-4.

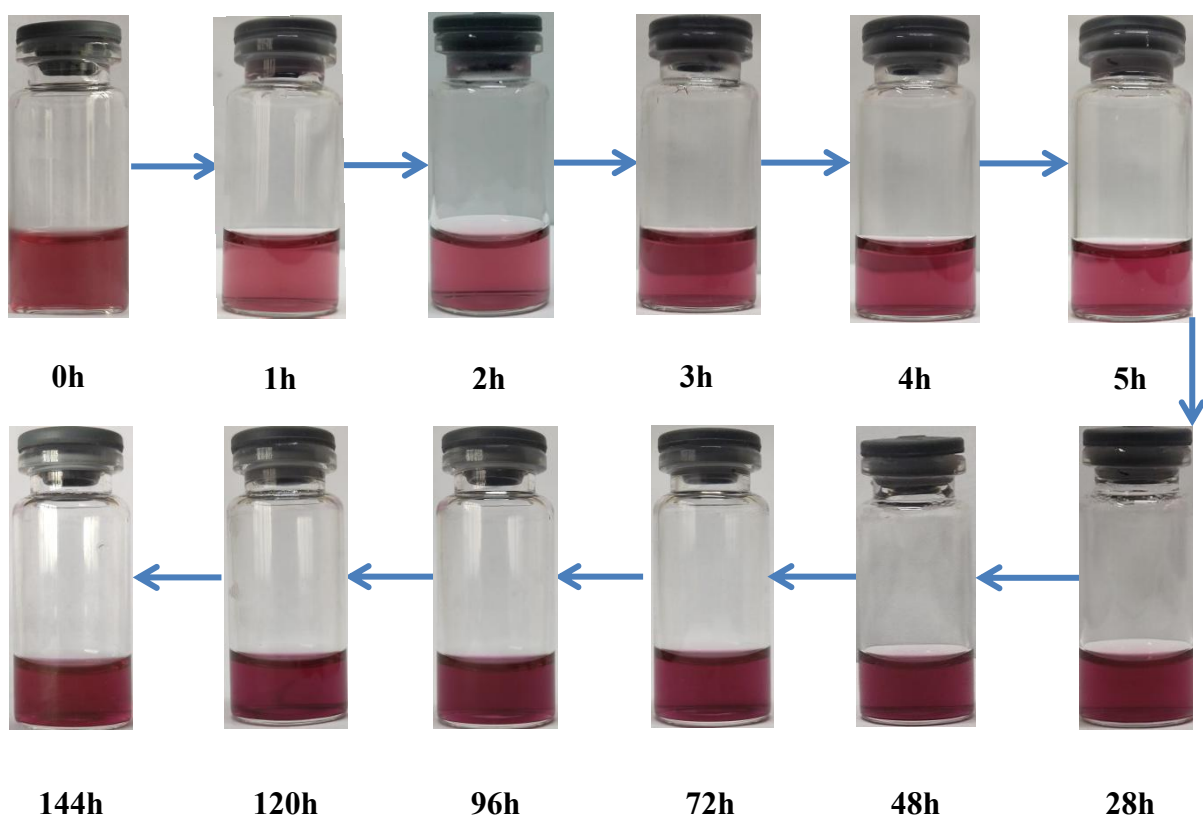


Figure S16. Photographs of AuNPs-4 with the change of reaction time.

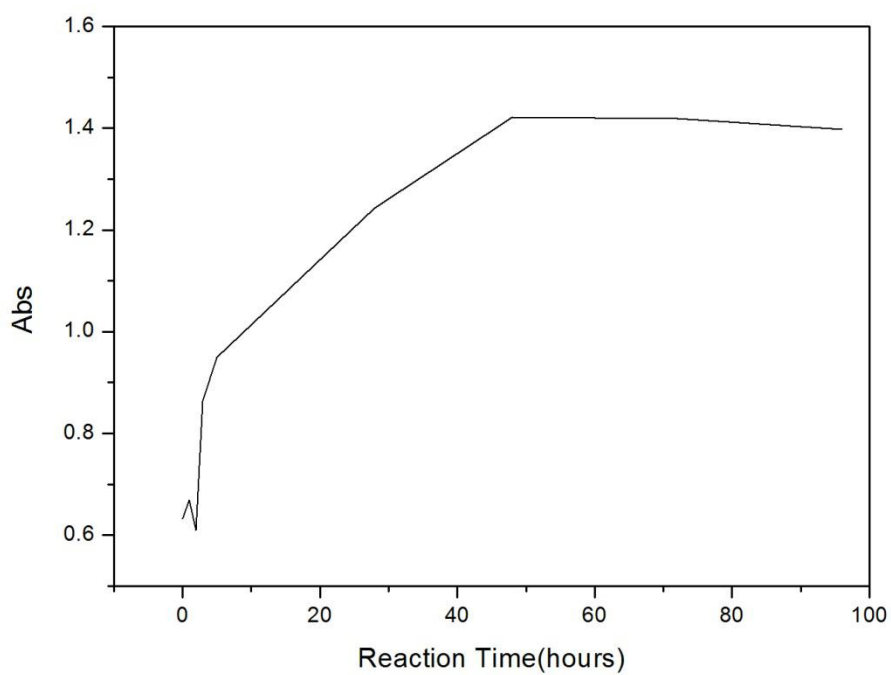


Figure S17. The absorption of AuNPs (538 nm) versus reaction time for AuNPs-5.

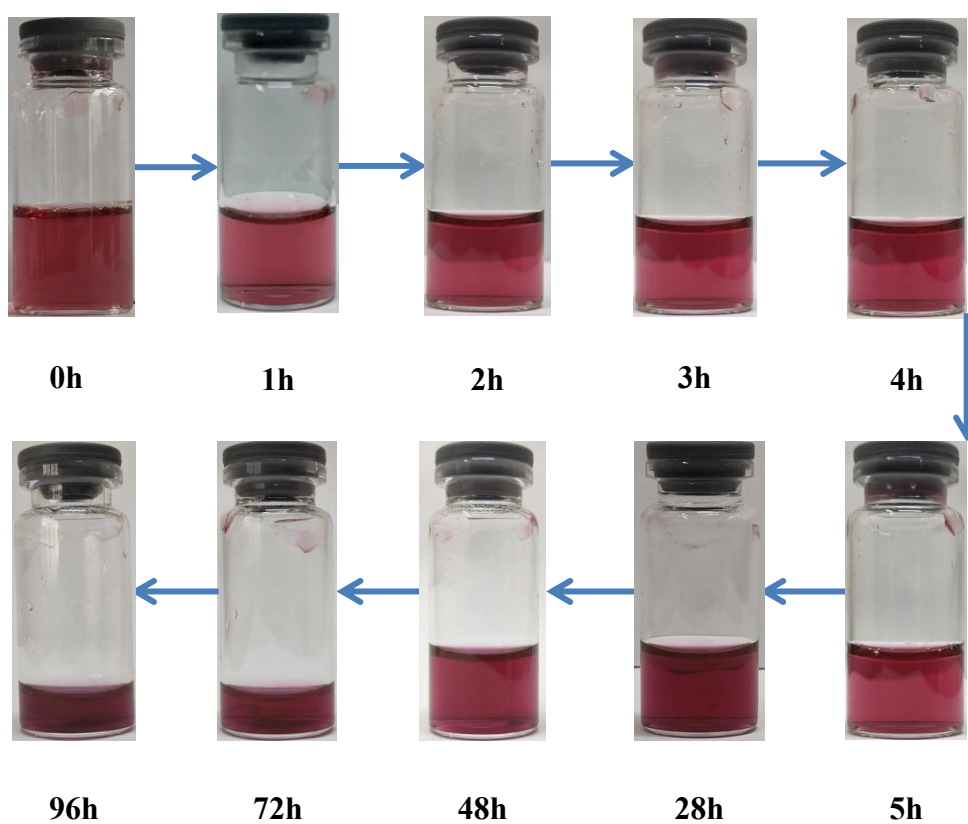


Figure S18. Photographs of AuNPs-5 with the change of reaction time.

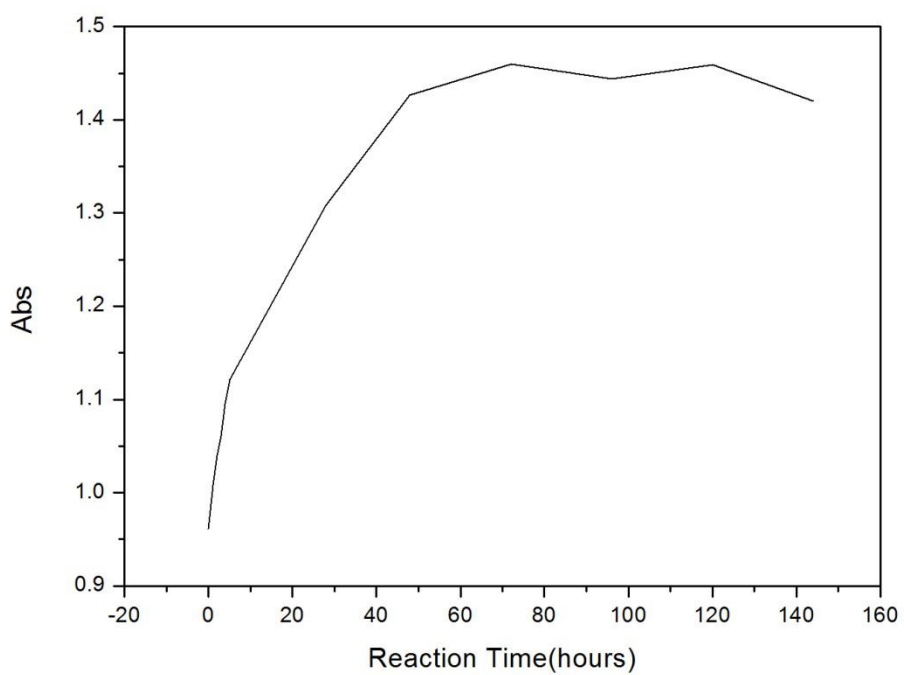


Figure S19. The absorption of AuNPs (533 nm) versus reaction time for AuNPs-6.

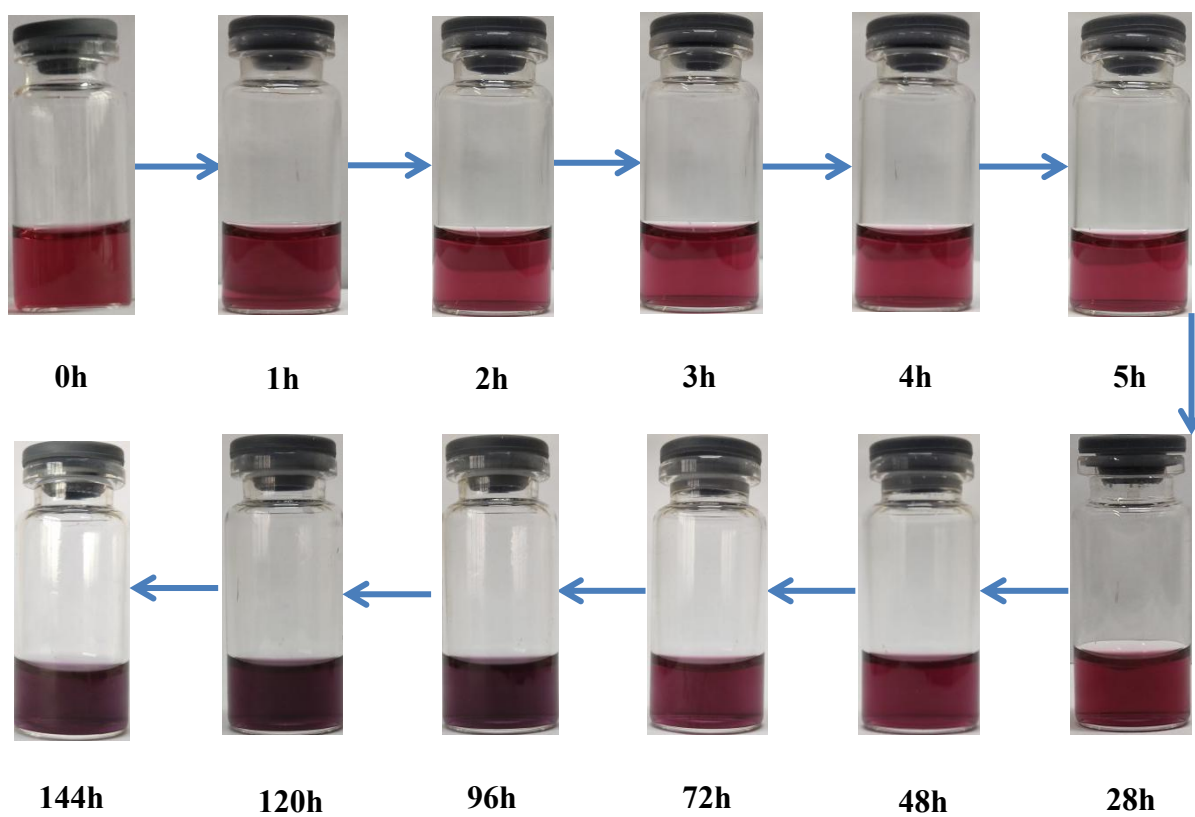


Figure S20. Photographs of AuNPs-6 with the change of reaction time.

7. UV-vis. spectra of 4-nitrophenol reduction

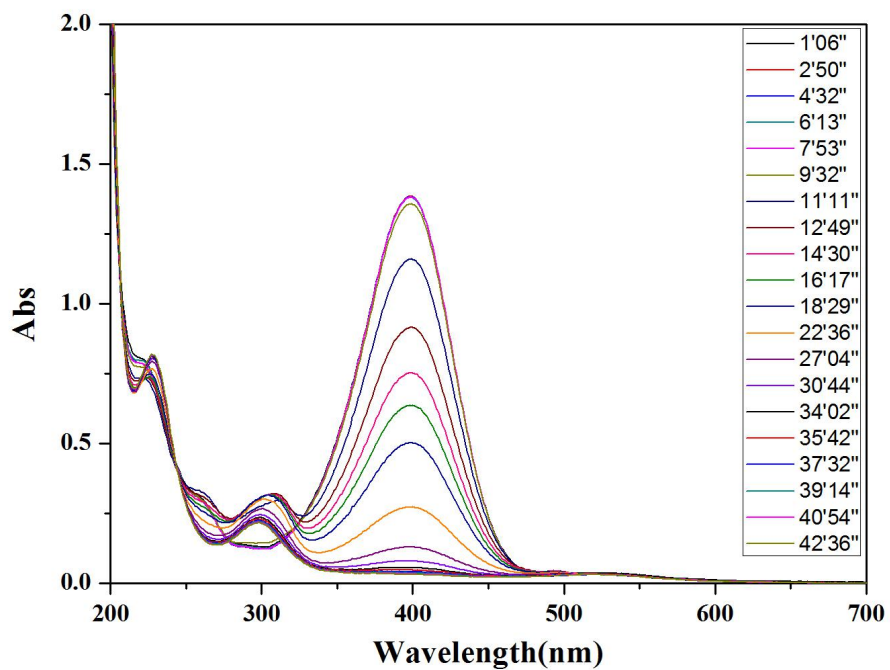


Figure S21. UV/Vis spectra in which the reaction is monitored 22 °C for AuNPs-1.

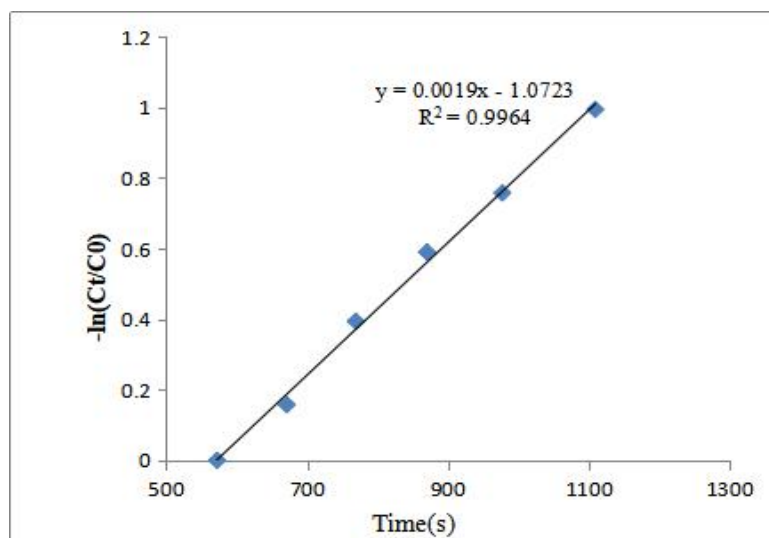


Figure S22. Consumption rate of 4-nitrophenol $-\ln(C_t/C_0)$ versus reaction time for AuNPs-1.

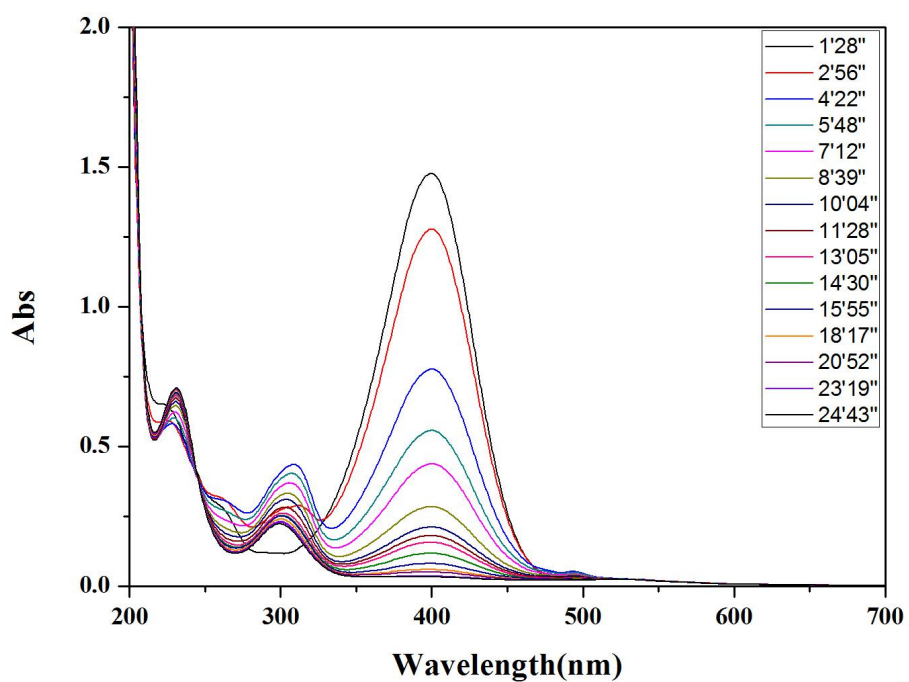


Figure S23. UV/Vis spectra in which the reaction is monitored 22 °C for AuNPs-2.

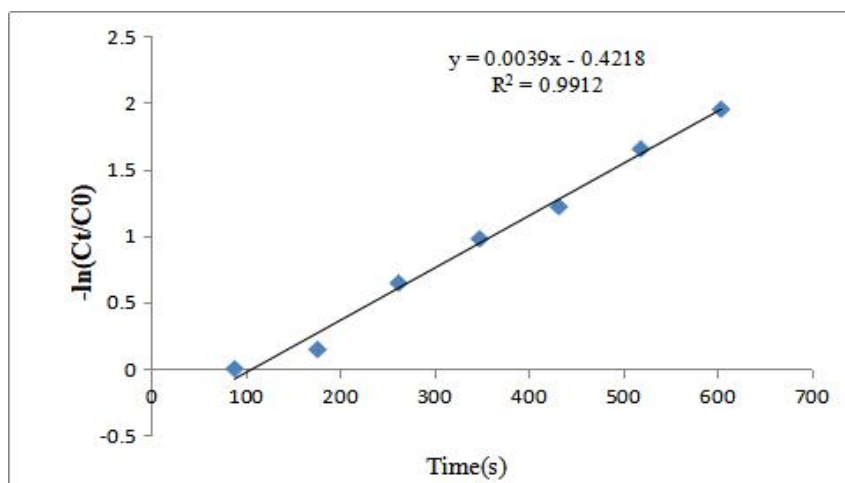


Figure S24. Consumption rate of 4-nitrophenol $-\ln(C/C_0)$ versus reaction time for AuNPs-2.

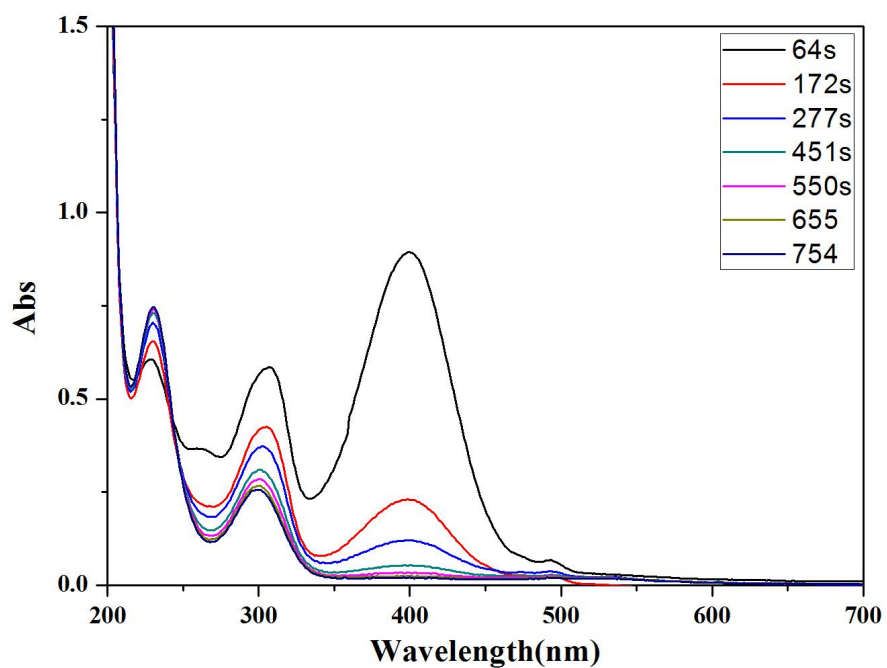


Figure S25. UV/Vis spectra in which the reaction is monitored 22 °C for AuNPs-3.

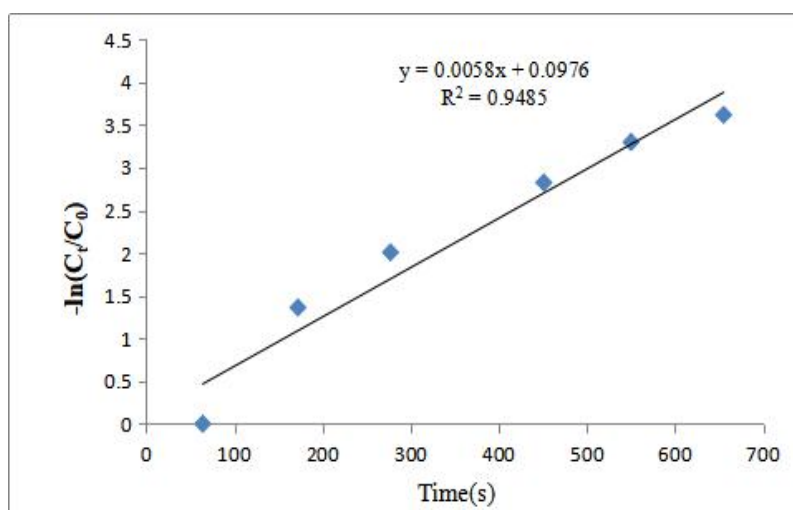


Figure S26. Consumption rate of 4-nitrophenol $-\ln(C/C_0)$ versus reaction time for AuNPs-3.

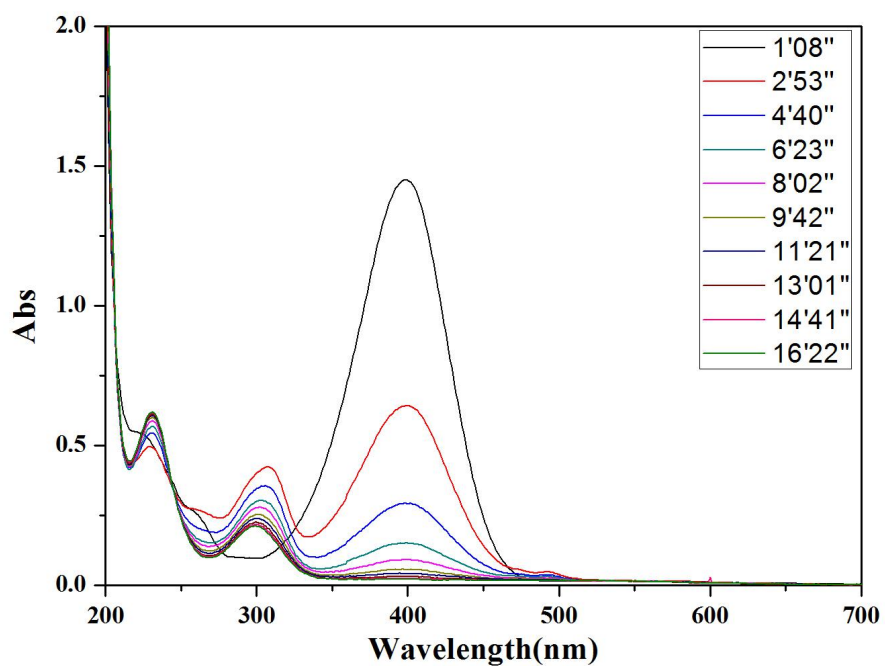


Figure S27. UV/Vis spectra in which the reaction is monitored 22 °C for AuNPs-4.

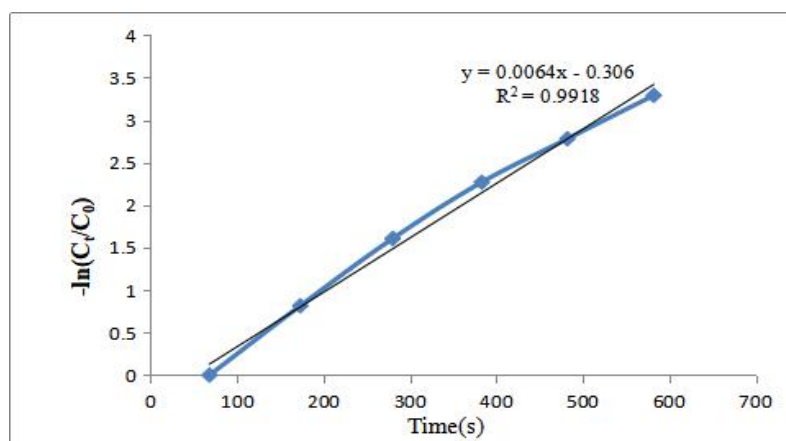


Figure S28. Consumption rate of 4-nitrophenol $-\ln(C/C_0)$ versus reaction time for AuNPs-4.

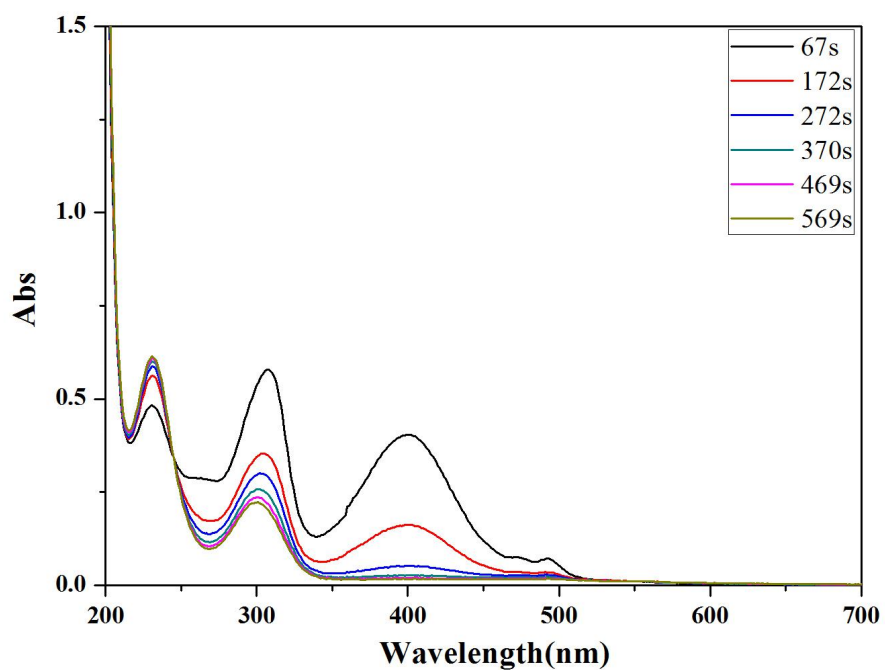


Figure S29. UV/Vis spectra in which the reaction is monitored 22 °C for AuNPs-5.

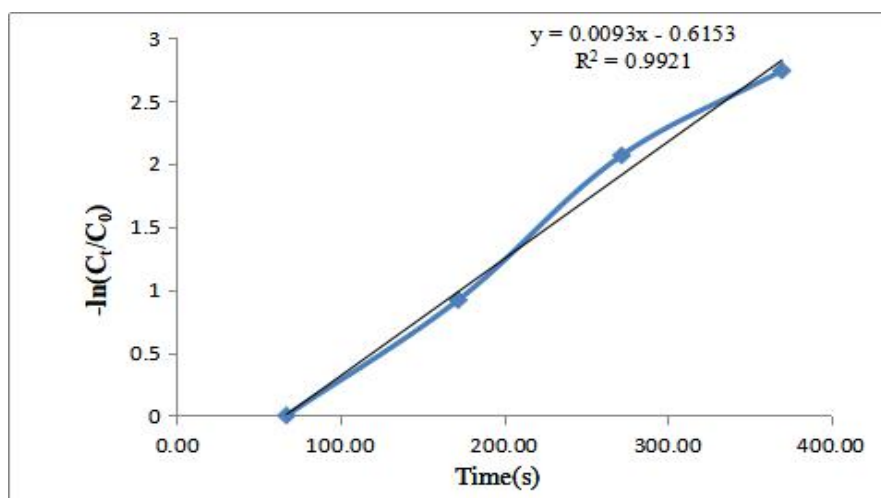


Figure S30. Consumption rate of 4-nitrophenol $-\ln(C/C_0)$ versus reaction time for AuNP@GQDs-5.

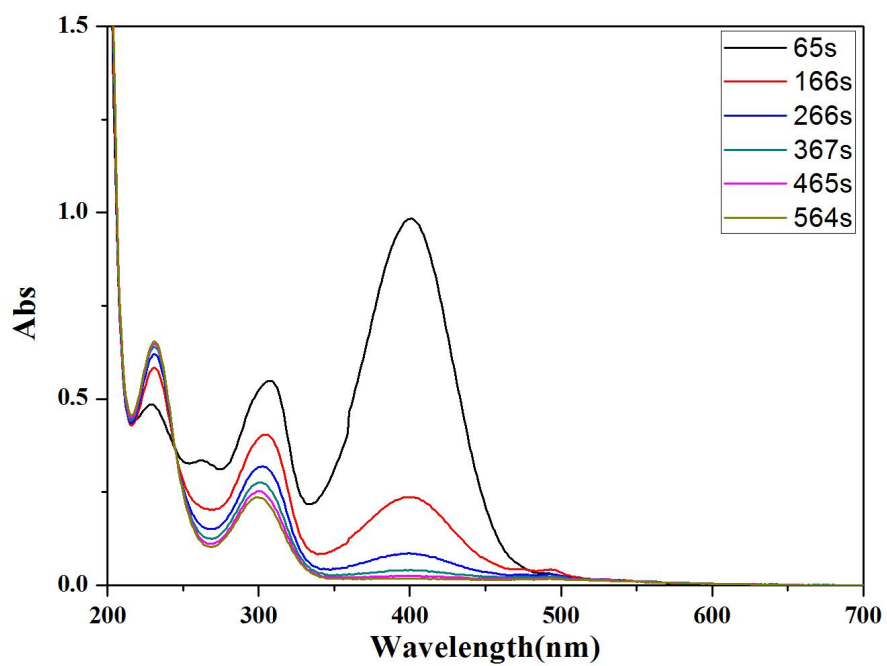


Figure S31. UV/Vis spectra in which the reaction is monitored 22 °C for AuNPs-6.

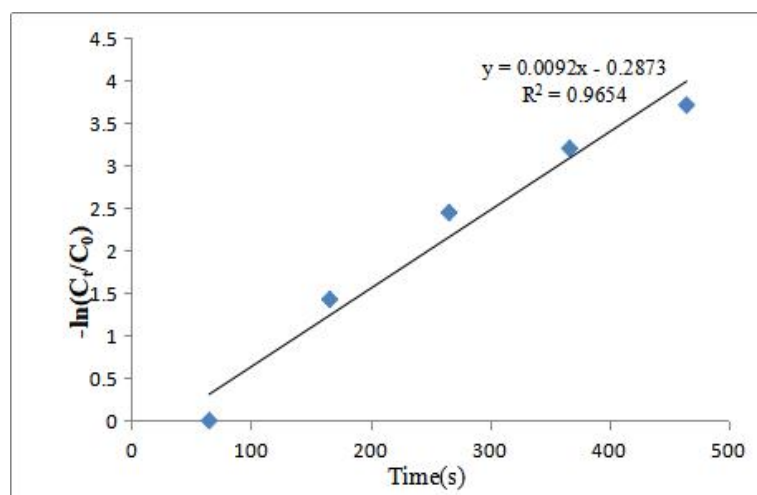


Figure S32. Consumption rate of 4-nitrophenol $-\ln(C/C_0)$ versus reaction time for AuNP@GQDs-6.

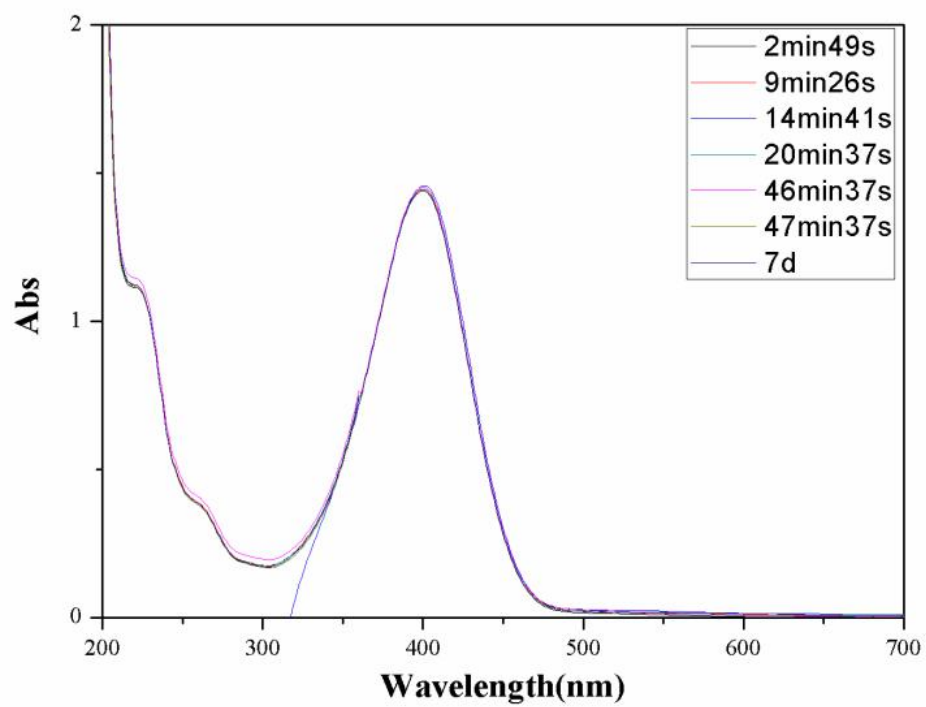


Figure S33. UV/Vis spectra in which the reaction is monitored 22 °C for only GQDs.

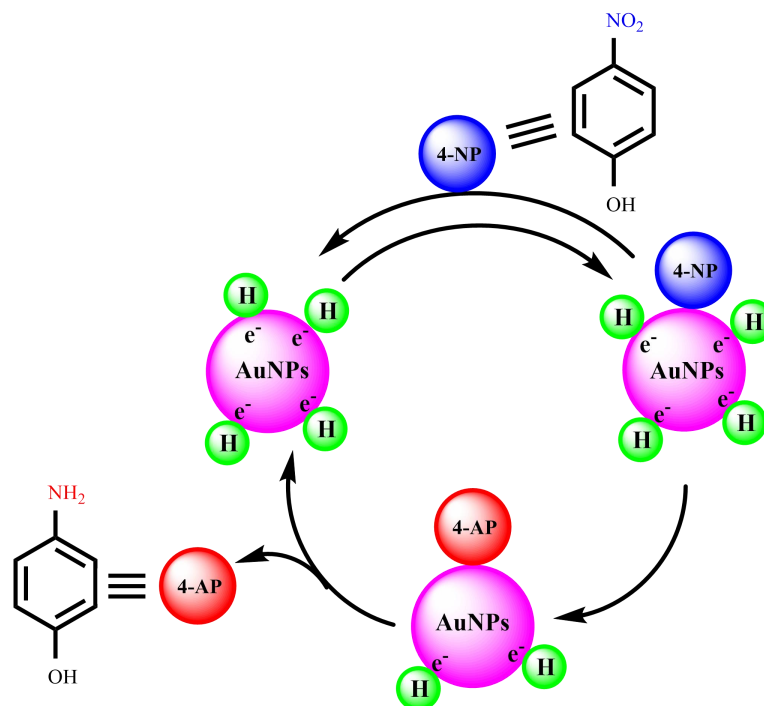


Figure S34. Mechanistic model of the reaction mechanism of 4-nitrophenol reduction

The mechanism of AuNPs catalyzed 4-nitrophenol to 4-aminophenol in the presence of NaBH_4 proceeded according to the LH mechanism^[1], and AuNP catalyzed reduction of 4-nitrophenol to 4-aminophenol was illustrated in Figure S32. In the first step, the NaBH_4 is decomposed by hydrolysis, then the $\text{B}(\text{OH})_4^-$ and active hydrogen are formed; then, the active hydrogen is transferred to the AuNPs and adsorbed at the surface; finally, the H at the AuNPs' surface reacts with 4-nitrophenol to yield the product 4-aminophenol.

Reference

- [1] (a) S. Wunder, Y. Lu, M. Albrecht, M. Ballauff, *ACS Catal.* 2011, 1, 908–916; (b) W. Xu, J.S. Kong, Y.E. Yeh, P. Chen, *Nat. Mater.* 2008, 7, 992; (c) P. Hervés, M. Pérez-Lorenzo, L.M. Liz-Marzan, J. Dzubiella, Y. Lu, M. Ballauff, *Chem. Soc. Rev.* 2012, 41, 5577.