

Supplementary Data

1. Infrared spectra

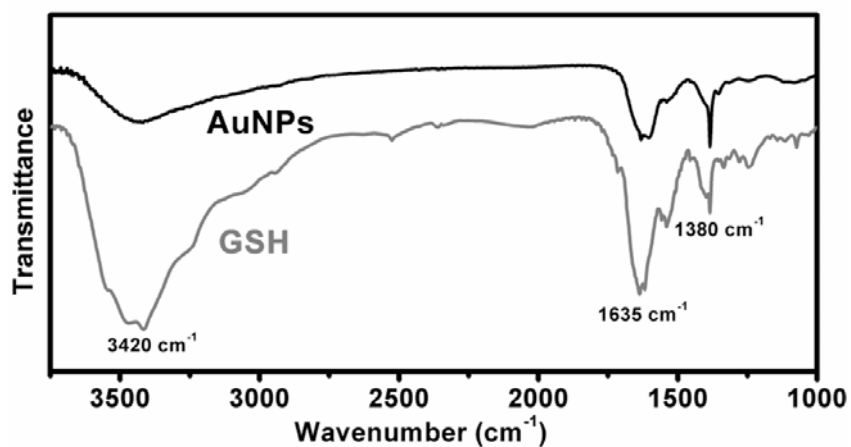


Fig. S1. Infrared spectra of GSH and a purified AuNPs sample.

2. XPS data

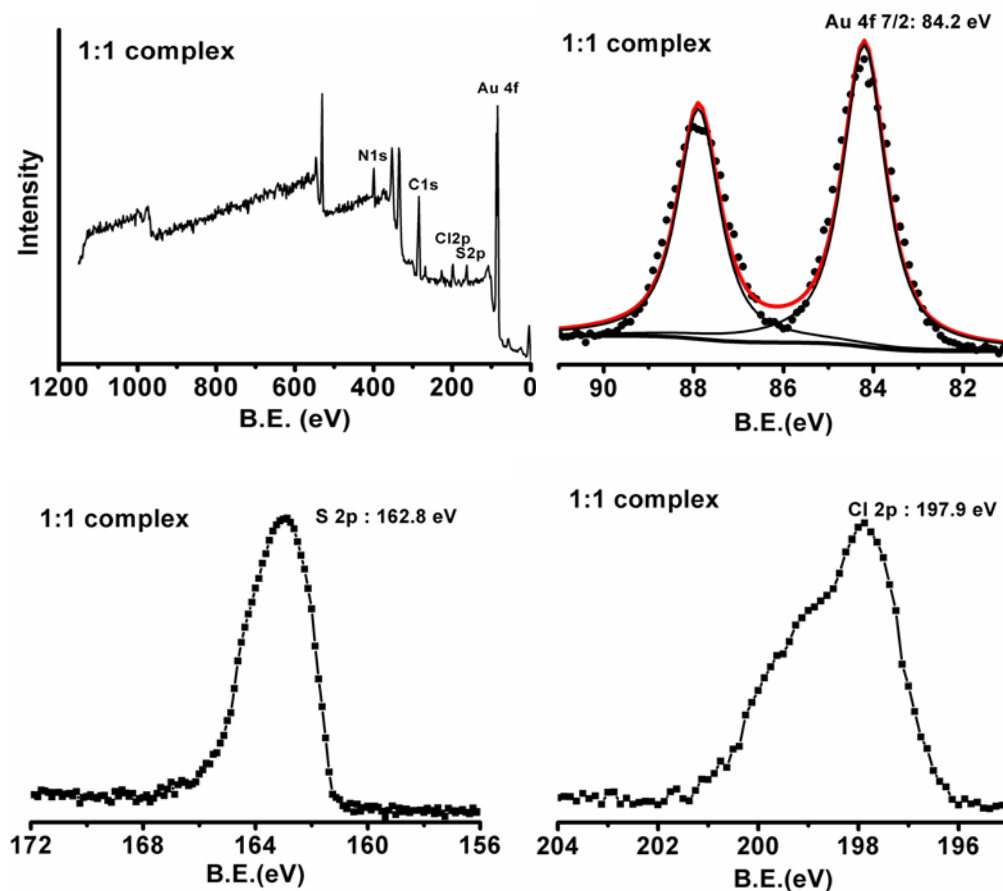


Fig. S2. XPS data of 1:1 complex.

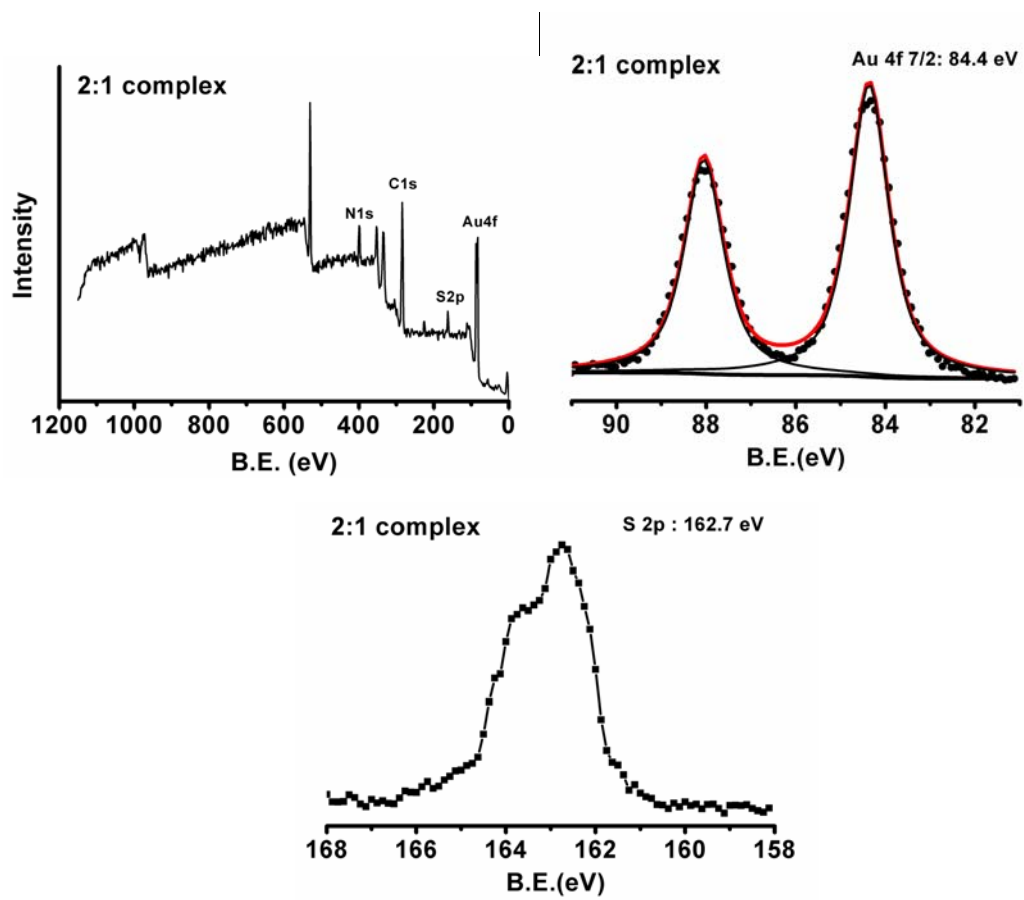
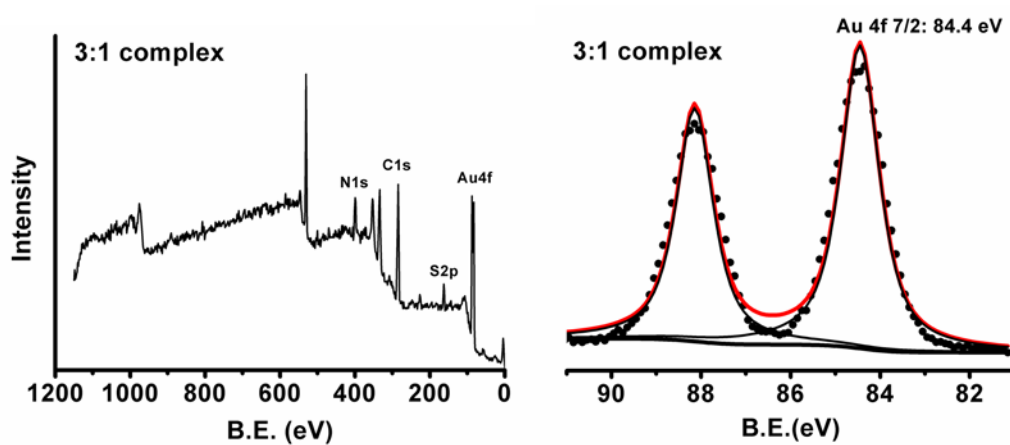


Fig. S3. XPS data of 2:1 complex.



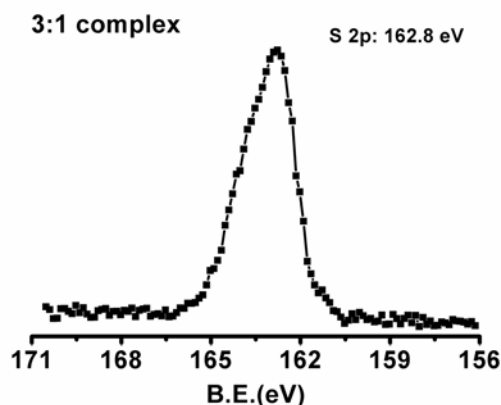


Fig. S4. XPS data of 3:1 complex.

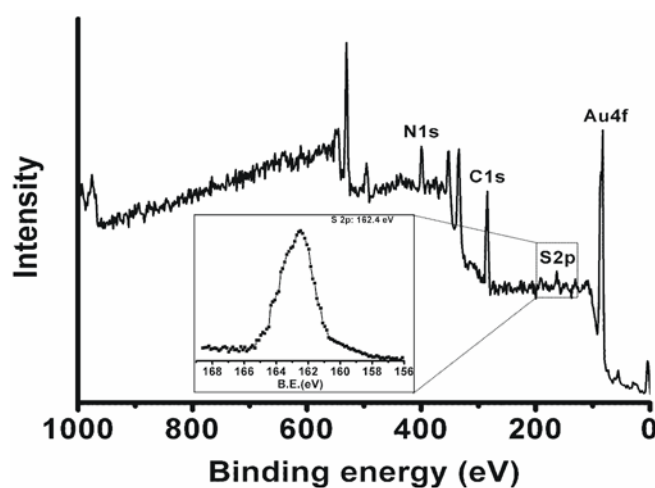


Fig. S5. XPS data of a AuNPs sample.

3. Evaluation of the reducibility of NADPH coupled with GR

As shown in equation 1, GSSG could be reduced into GSH by NADPH catalyzed by GR.



The reduced form NADPH has a specific absorption peak at 340 nm, while the oxidized form $NADP^+$ doesn't. This difference in UV-vis spectra between the oxidized and reduced forms at 340 nm makes it simple to measure the conversion of

one to another. When GSSG is reduced by NADPH, NADPH converts into NADP^+ and the absorbance at 340 nm decreases. Thus the magnitude of $\Delta A_{340\text{nm}}$ could reveal reducibility the NADPH/GR system. The conversion of NADPH to NADP^+ involves the removal a hydride ion, which needs another proton to participate in it. Therefore, pH value could have crucial impact on it.

The general procedure is presented in detail. 5 mg GSSG and 6.6 mg NADPH were dissolved in 1 mL ultrapure water respectively and stored at 4°C before use. A series Britton-Robinson buffer solutions with pH from 3-9 were also prepared. A typical procedure was followed: 2.3 mL buffer solution and 60 μL GSSG solution were mixed in a 4 mL cuvette. Subsequently 30 μL NADPH solution plus 1 unit GR (or not) were added to the solution and quickly measured the absorbance at 340 nm. The reaction was allowed to proceed for 2 minutes at 37°C. And then the absorbance at 340 nm was recorded again. The concentrations of GSSG and NADPH in the solution were 0.2 mM and 0.1 mM. Decreases of absorbance at 340 nm in two minutes versus pH values were plotted in the form of histogram (Fig. S6).

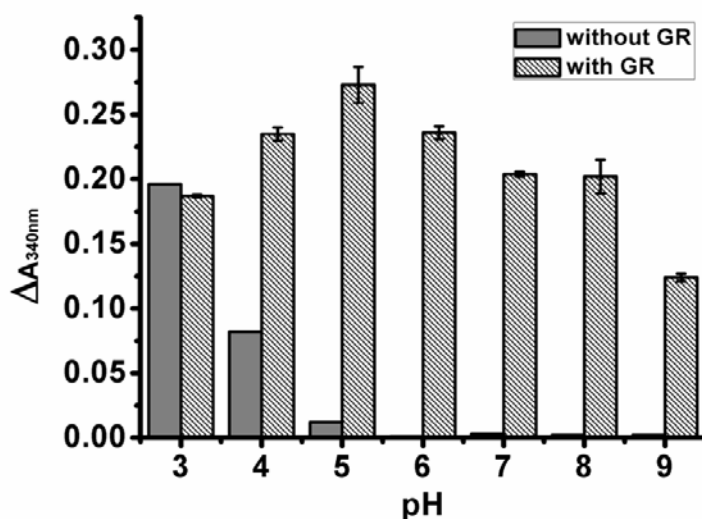


Fig. S6. The histogram of decreases of absorbance at 340 nm after two minutes of adding NADPH into GSSG solution versus pH values.