

**Electronic Supplementary Information (ESI) for
Gold nanoparticles for highly sensitive and selective copper
ions sensing - old materials with new tricks**

Yi-Min Fang, Jing Song, Jin-Shui Chen, Song-Bo Li, Le Zhang, Guo-Nan Chen,
Jian-Jun Sun*

*Ministry of Education Key Laboratory of Analysis and Determination for Food Safety, Fujian
Provincial Key Laboratory of Analysis and Detection for Food Safety, College of Chemistry &
Chemical Engineering, Department of Chemistry, Fuzhou University, Fuzhou, 350108, China*

Corresponding Author E-mail: jjsun@fzu.edu.cn.

Experimental details

Synthesis of Au nanoparticles. Au nanoparticles are synthesized with the traditional citrate reduction method. UV-vis absorption spectra were recorded by a spectrophotometer Lambda 750 PerkinElmer. TEM and HRTEM of Au nanoparticles are performed on a TECNAI F-20 high-resolution transmission electron microscope operating at 200 kV. All the other chemicals were of analytical grade. Deionized water (Millipore, Bedford, MA, USA) was used throughout.

Synthesis of Au nanoparticles. Au nanoparticles are synthesized with the traditional citrate reduction method. 1g HAuCl₄ • 4H₂O was dissolved in 100 mL second-distilled water. 1 mL of the resulted HAuCl₄ solution was diluted to 100 mL and heated up and in a flask with reflux while stirring. After the solution was boiling, 3 mL citrate solution (C₆H₅Na₃O₇ • 2H₂O, 1.14g/100mL) was quickly added into the solution, allowed to react for 40 mins, resulting in red wine color Au nanoparticles solution.

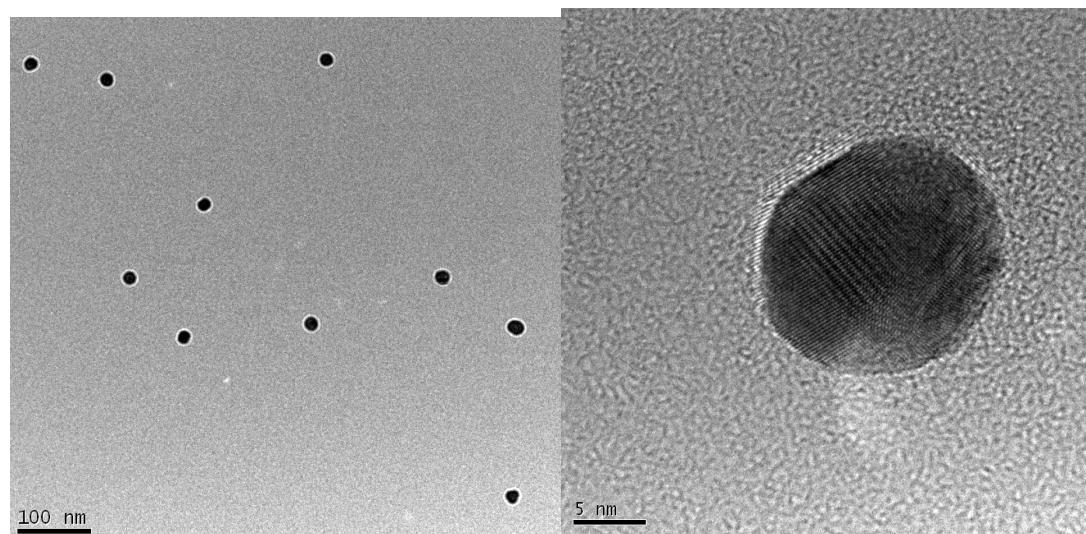


Fig. S1 TEM and HRTEM of Au nanoparticles.

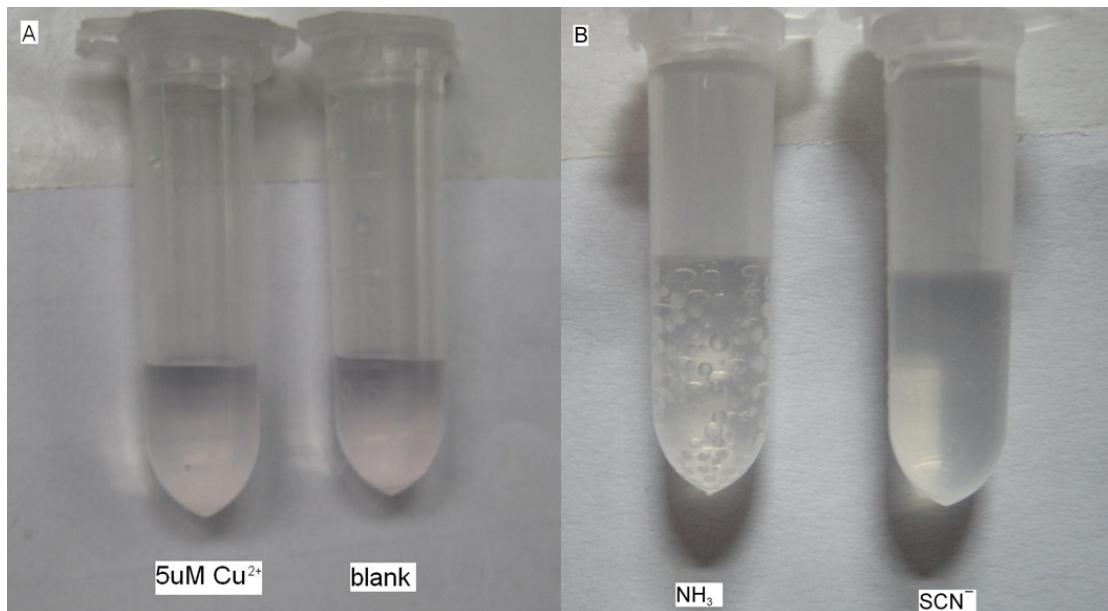


Fig. S2 (A) A photograph of solution (25 mg/L Au nanoparticles, 10 mM KSCN, 20 mM H₂O₂, buffer in 60°C bath for 8 min) in the absence and presence of 5 μM Cu²⁺. (B) A photograph of solution (5 μM Cu²⁺, 20 mM H₂O₂, in 60°C bath for 1 min) in the presence of 10 mM KSCN, or 10 mM NH₃/NH₄Cl buffer without shaking.

As can been seen in Fig. S2-A, without the NH₃, the catalytic effect from the bare Cu²⁺ is almost neglectable at low concentration. The catalytic effect of Cu(NH₃)₆²⁺, is very strong even at very low concentration, as a lot of bubbles (O₂) can be observed due to the decomposition of H₂O₂ as shown in Fig. S2-B.

Table S1 Solubility product (K_{sp}) and stability constant (lgβ) of heavy metal ions iodide

M	K _{sp} of iodide	lgβ of ML ₄
Ag(I)	8.3×10^{-17}	14.28
Cd(II)	-	6.15
Hg(II)	2.9×10^{-29}	29.8
Cu(II)	-	-
Pb(II)	7.1×10^{-9}	3.9

Although CuI₂ is known to be instable in water, and easily decompose to CuI, due to the strong binding of Cu(I)-I⁻ (K_{sp} = 1.27×10^{-12}). However, because of the existence of oxidant H₂O₂, which is likely to oxidize Cu(I) to Cu(II), as well as the other complexing agent, such as NH₃, which can complex with Cu²⁺ and stabilize it. Therefore, in our experiment, Cu(I) is unlikely to be produced, as the presence of I⁻ does not influence the color change of Au nanoparticles solution in the detection of Cu²⁺, either.

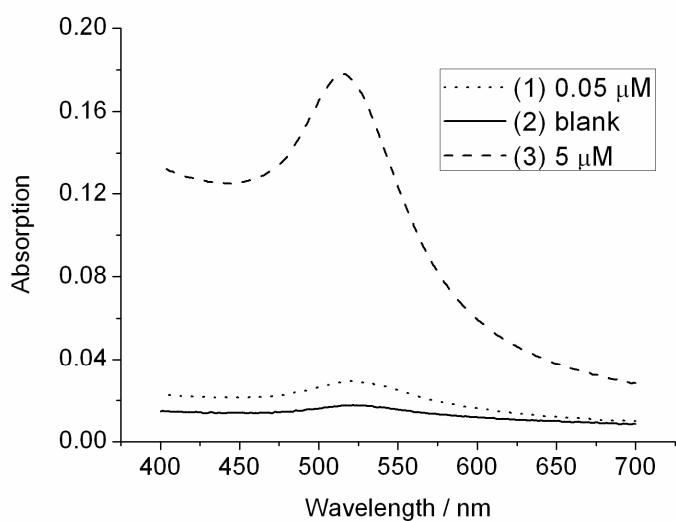


Fig. S3 UV-vis absorption spectra of solution (25 mg/L Au nanoparticles, 10 mM KSCN, 20 mM H_2O_2 , 10mM NaI, 10 mM $\text{NH}_3/\text{NH}_4\text{Cl}$ buffer in 60°C bath for 8 min) containing Cu^{2+} of different concentration.