Electronic Supplementary Information (ESI)

Tunneling Current Recognition through Core-Satellite Gold Nanoparticles for Ultrasensitive Detection of Copper Ions

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Experimental details

Reagents and Apparatus

Gold (III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.9+ % metals basis), sodium citrate tribasic dehydrate ($C_6H_5Na_3O_7 \cdot 2H_2O$, 99%), L-Cysteine ($C_3H_7NO_2S$, 98%), hydrogen peroxide solution (H_2O_2, 30%), Ethylenediaminetetraacetic acid (EDTA), copper (II) sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$ 99%) and sodium chloride (NaCl, 99%) and different metal salts were purchased from Sigma-Aldrich and used as received. Concentrated sulfuric acid (H_2SO_4, 98%) was purchased from Merck and used as received. Mounted AuMB8000 micro band addressable gold

microelectrode (GME) with a gap width of 10 μm was purchased from Windsor Scientific, UK. Ultraupre water of resistivity 18.2 MΩ cm (Millipore) was used to prepare all the solutions.

An ultrasonic waterbath (Grant Ultrasonic Bath XUBA3) was used to prepare L-Cysteine solution. The size distribution and the surface charge of GNPs were measured by Zetasizer Dynamic Light Scattering (Nano-ZS, Malvern Instrument). The pH of GNPs solutions was measured by Oakton® pH 2700 pH/mV/°C/°F Meter (Oakton Instruments, Illinois, USA). UV-visible spectroscopy was carried out using CARY 300 Bio UV–Vis spectrometer at room temperature. The morphology and size of the GNPs were characterized using scanning electron microscope (SEM) (ZEISS Supra 55VP, Oberkochen, Germany). The resistance was measured by using a potentiostat (BASi, USA).

Methods

Synthesis of Gold Nanoparticles

GNPs with diameters of 13 nm and 45 nm were synthesized with chemical reduction method as reported previously.[1, 2] Briefly, a solution of 5.0 mM HAuCl4 was made by adding 196.9 mg $HAuCl_4 \cdot 3H_2O$ in 100 mL deionized water. 1 mL of this solution was added to 18 mL deionized water under stirring and heating till boiling. Reducing agent (0.5% w/w^{-1} sodium citrate) was added to reduce the Au^{3+} to Au0 from chloroauric acid ($HAuCl_4$) in deionized water followed by heating and stirring. By varying the amount of sodium citrate (1 mL and 0.365 mL), GNPs with different sizes (13 and 45 nm) were synthesized, respectively. The final solution was topped up to 20 mL the final concentration of the prepared gold colloid was approximately 0.25 mM. The size was determined with Zetasizer (**Fig. S1**). The quality of the synthesized GNPs was examined under UV/Vis spectrophotometry (**Fig. S2**). The sizes of nanoparticles can be

controlled through the different ratio of $HAuCl_4$ and $Na_3C_6H_5O_7$. The GNPs with diameter of 13 nm were prepared with the addition of 1000 µL of sodium citrate into 19 mL chloroauric acid solution while it is 365 µL sodium citrate added for 45 nm GNPs preparation.

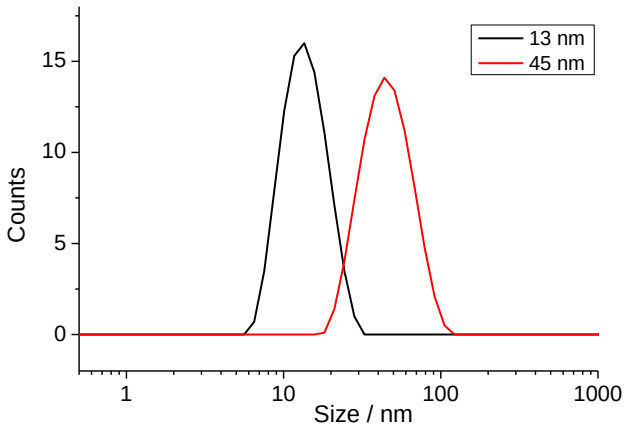

Fig. S1 The sizes of GNPs measured by DLS

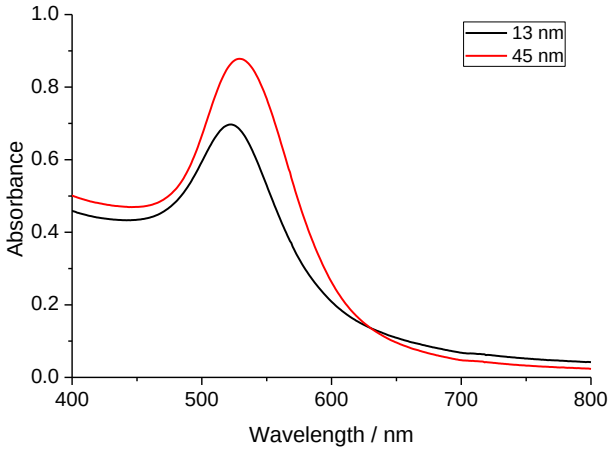

Fig. S2 UV spectroscopy for 13 and 45 nm GNPs

Synthesis of L-Cysteine functionalized core-satellite GNPs (FGNPs)

The core-satellite GNPs was prepared by mixing 13 nm and 45 nm GNPs in 1:1 ratio (v/v). 100 µL of 0.1 mM L-Cysteine was added to 5 mL 0.25 mM GNPs (2.5 mL, 13 nm & 2.5 mL, 45 nm) with pH at ~5.50 followed by 2 hours stirring and 24 hours incubation. The final concentration of L-Cysteine is about 2 µM. L-Cysteine coats GNPs via hydrogen bond formation and leads to

core-satellite GNPs structure which is a slow process and may take up to 24 hours. The L-cysteine surface coverage on GNPs with diameters of 13 nm to 45 nm can also be calculated to be 0.4/ nm^2. The whole surface area of GNPs equals to the product of the number of particles multiplying the single particle surface area shown in the following:

$A=S_B+S_S=4\pi（N_BR^2+S_Sr^2）$

While L-cysteine surface coverage equals the number of L-cysteine divided by surface area：

χ_{GNPs} = N/A=0.4/ nm^2

S_B and S_S refer to the surface area of GNPs, respectively. N_B and N_S refer to number of GNPs with diameters of 45 and 13 nm, respectively

Film preparation and conductance measurement

There are 8 microelectrodes on one chip and the gap distance between two neighboring microelectrode is 10 μm. The chips were cleaned using distilled water before the deposition of GNPs. 20 μL of as-synthesized L-Cysteine functionalized core-satellite GNPs (0.25 mM) was dropped on the gold microelectrode arrays and dried in vacuum oven at room temperature for 2 hours to form the biosensor film for detection of Cu^{2+}. The GNPs surface coverage in core satellite structures (13 nm: 45nm = 1:1) can be calculated to be 2.77×10^9 /mm^2 and 6.7×10^7/mm^2 for 13 and 45 nm GNPs respectively. The GNPs surface coverage on the electrode can be quantified through the equation:

χ_{GNPs} = N/A N: the number of 20ul GNPs A: the area of silicon wafer surface which will not change when the GNPs solution fully cover the GME which can be calculated to be about 8 mm2 from the length and width of silicon wafer where the GME deposited on.

10 µL of Cu^{2+} at different concentration was added to GME and dried in vacuum oven for 2 hours. To bind with core-satellite GNPs tightly, the GME surface was functionalized with (3-aminopropyl) triethoxysilane (APTES) layer by immersing in 2% (v/v) APTES toluene solution for 10 minutes and rinsed with toluene. 20 µL core-satellite FGNPs solution was then dropped on the GME and dried in vacuum oven at room temperature for 2 hours to work as core-satellite biosensor for the detection of Cu^{2+}. Electrical measurements were performed in the range of +10 to -10 mV. The resistance of the sample is calculated by dividing the potential by the current. The measurements were repeated 6 times to confirm the concordance of the system.

Modified electrodes used for Cu(II) analysis could be regenerated by elimination of Cu(II) by immersing the sensor into 100 mM Ethylenediaminetetraacetic acid (EDTA) solution (pH = 10.0) for 2 hours. Then the sensor was rinsed with water and dried in vacuum oven.

Optimization of nanoparticle numbers ratio of big and small GNPs in the core-satellite structures

To optimize nanoparticle numbers ratio of big and small GNPs in core-satellite, the effect of different ratio of 45 nm to 13 nm GNPs was tested. The self-assemblies of 3:1, 1:1 and 1:2 (v/v) of 45 nm to 13 nm GNPs solutions in the presence of Cu^{2+} were recorded. The corresponding particle number ratio of small to big GNPs is 1:14, 1:42 and 1:84, respectively. The optimum ratio of 45 nm GNPs to 13 nm GNPs was expected to be equal to the amount of 13 nm GNPs to fully cover the surface of 45 nm GNPs. From the resistance change with Cu^{2+} concentration (Figure S3), 1:1 (v/v) of 13 nm GNPs to 45 nm GNPs solution shows the most sensitivity to Cu^{2+}

concentration in both high and low concentration of Cu^{2+}. In another word, core-satellite with a particle number ratio of 1:42 of 45 nm to 13 nm GNPs is most sensitive.

On the other hand, we can calculate the nanoparticle number ratio of small to big GNPs which fully fill in a cubic (**Figure S4**). We suppose big GNPs (2R= 45 nm) completely filled a cubic with a length of 135 nm (6R) and the rest space of the cubic is filled with small GNPs (2 r= 13nm). Then there are 27 big GNPs in the cubic. The volume of cubic and the big GNPs are 2.46×10^6 and 1.28×10^6, respectively. According to the radius of small GNPs, we can calculate the number of small GNPs is 1026. Then the particle number ratio of big to small GNPs is ~27:1026 (~1:38), which is well agreement with 1:42, which we have optimized.

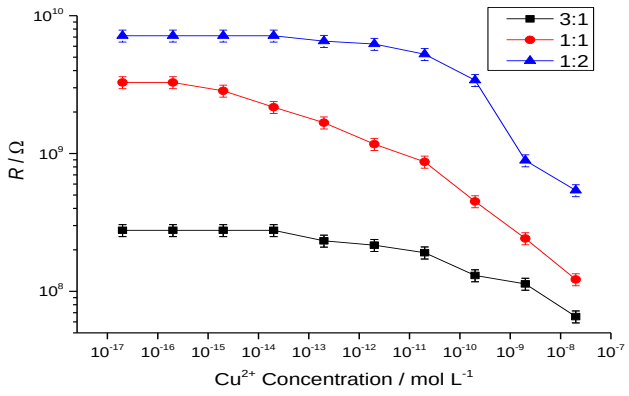

Fig. S3 The resistance of core-satellite GNPs with different volume ratio of 45 nm to 13 nm GNPs to different Cu^{2+} concentration.

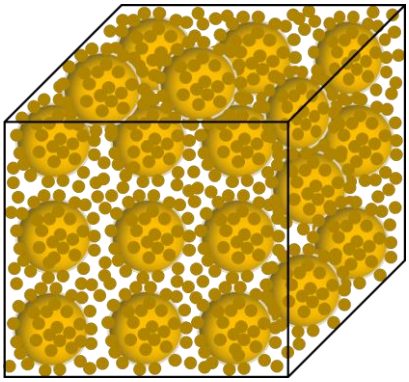

Fig. S4 The schematic of small and big GNPs of core-satellite fully filled a unit cubic used to calculate the pa number ratio. 13 nm GNPs, 45 nm GNPs.

Tab. S1 Number of particles of 20 μL of solution on the gold electrodes.

13 nm GNPs	45nm GNPs	13 and 45nm GNPs in core-satellite solution
~4.432×10^{10}	~1.072×10^{9}	N13= ~2.216×10^{10} (97.5%) N45= ~5.360×10^{8} (2.5%)

Tab. S2 Validation of core-satellite GNPs biosensor to detect lake water, tap water, and pure distilled water spiked with known concentration Cu^{2+}

Spiked concentration	Detected concentration Meana±SDb	Recovery (%)
Lake water	1. 2± 0.3 μM	
Tap water	0.7 2± 0.08 μM	0.78 μM (0.05 mg L^{-1}) [3]
20 fM	21.0 ± 3.0 fM	105
2.0 pM	1.8 ± 0.3 pM	90
2.0 nM	1.9 ± 0.2 nM	95

a The mean of three independent measurements. b SD = standard deviation.

References

1. I. I. S. Lim, D. Mott, M. H. Engelhard, Y. Pan, S. Kamodia, J. Luo, P. N. Njoki, S. Zhou, L. Wang and C. J. Zhong, *Anal Chem*, 2008, **81**, 689-698.
2. Z. Weng, H. Wang, J. Vongsvivut, R. Li, A. M. Glushenkov, J. He, Y. Chen, C. J. Barrow and W. Yang, *Anal Chim Acta*, 2013, **803**, 128-134.
3. Australian Drinking Water Guidelines, Version 2.0 updated July 2013,Page 520. https://www.nhmrc.gov.au/guidelines/publications