

## Electronic Supplementary Information for

# Facile Quantification of Gold(III) Ions and Gold Nanoparticles

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### ***Experimental Section***

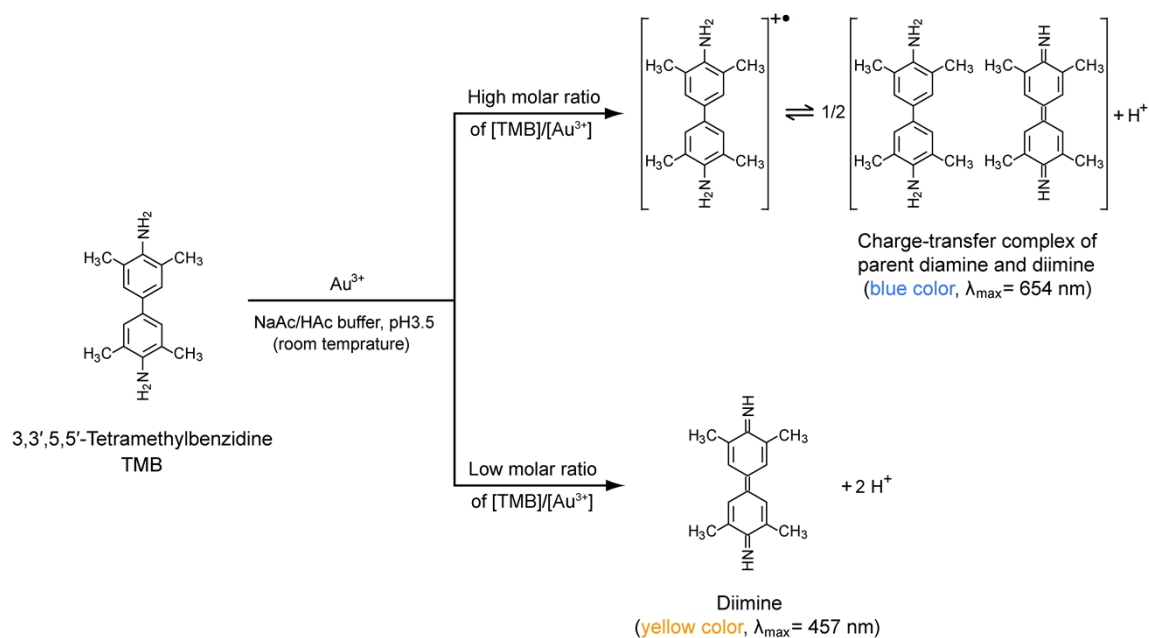
***Chemicals and Reagents.*** 3,3',5,5'-tetramethylbenzidine (TMB, >99%), gold(III) chloride hydrate ( $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ ,  $\geq 99.999\%$  trace metals basis), acetic acid (HAc,  $\geq 99.7\%$ ), sodium acetate (NaAc,  $\geq 99\%$ ), hydrochloric acid (HCl, 34-37%), nitric acid ( $\text{HNO}_3$ , 70%), palladium(II) chloride ( $\text{PdCl}_2$ ,  $\geq 99.9\%$ ), hexadecyltrimethylammonium bromide (CTAB,  $\geq 99\%$ ), L-ascorbic acid (AA,  $\geq 99\%$ ), sodium borohydride ( $\text{NaBH}_4$ ,  $\geq 99\%$ ), and silver nitrate ( $\text{AgNO}_3$ , >99%) were all obtained from Sigma-Aldrich. All aqueous solutions were prepared using deionized (DI) water with a resistivity of 18.0  $\text{M}\Omega \cdot \text{cm}$ . Tap water samples were collected from a household water pipe in our laboratory.

***Preparation of  $\text{Au}^{3+}$  standard solutions and the metal ion solutions in Fig. 3.*** The  $\text{Au}^{3+}$  standard solutions were prepared by dissolving  $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$  ( $\geq 99.999\%$  trace metals basis) in DI water. The 40  $\mu\text{M}$  of metal ion solutions labeled with #2-#23 in Fig. 3 were prepared by dissolving  $\text{Na}_2\text{PdCl}_4$ ,  $\text{Na}_2\text{PtCl}_4 \cdot x\text{H}_2\text{O}$ ,  $\text{AgNO}_3$ ,  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{CuCl}_2$ ,  $\text{CuCl}$ ,  $\text{CoCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{Cr}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{CaCl}_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , and  $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  respectively, in DI water. All the chemicals were analytical grade and were used as received without further purification. To improve the solubility, HCl (final concentration = 10 mM) was added to the solutions of  $\text{CuCl}$  and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , and the  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  solution was heated at 60  $^\circ\text{C}$  for 10 min prior to use.

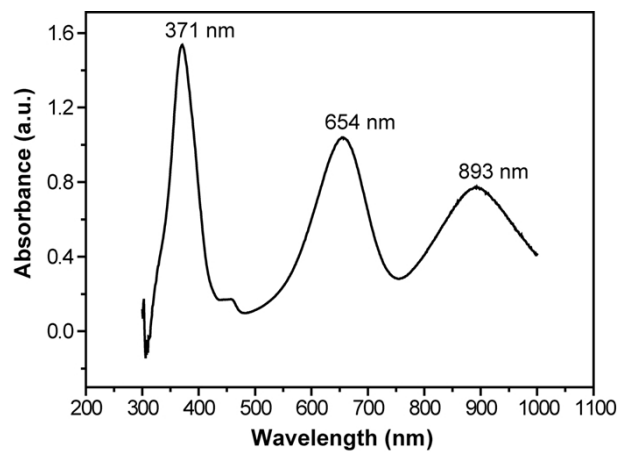
**Synthesis of Au nanorods (AuNRs).** The AuNRs shown in Fig. 5C were synthesized using a previously reported 2-step procedure with minor modifications.<sup>1</sup> The synthesis was conducted in aqueous system. In the first step, Au seeds were prepared using the following procedure: To a 20-mL glass vial, 5.0 mL of 0.5 mM HAuCl<sub>4</sub> solution and 5.0 mL of 200 mM CTAB solution were added. The solution was gently shaken, followed by the addition of 0.6 mL of freshly prepared 10 mM NaBH<sub>4</sub> solution. After a gentle shake, the mixture was incubated at a 30 °C water bath for 6 hours. In the second step, AuNRs were grown from the Au seeds prepared in the first step: To a 20-mL glass vial, 9.5 mL of 100 mM CTAB, 0.4 mL of 10 mM HAuCl<sub>4</sub> solution, 0.1 mL of 10 mM AgNO<sub>3</sub> solution, 0.1 mL of 1.0 M HCl, and 0.066 mL of 100 mM ascorbic acid were sequentially added. After a gentle shake, 0.04 mL of the Au seeds was added to the solution. The reaction solution was then incubated at a 30 °C water bath overnight. The final products (*i.e.*, AuNRs) were collected by centrifugation, washed twice with DI water, and finally redispersed in 2.0 mL of DI water.

**Synthesis of Au@Pd core-shell rods.** The Au@Pd rods were prepared according to a previously reported seeded growth method with minor modifications.<sup>2</sup> In a typical synthesis, 0.5 mL of AuNRs was added to 4.0 mL of 20 mM CTAB which was hosted in a 20-mL glass vial, followed by the addition of 0.05 mL of 40 mM ascorbic acid. After a gentle shake, 0.2 mL of 5.0 mM H<sub>2</sub>PdCl<sub>4</sub> (prepared by incubating a mixture of 0.1 mL of 10 mM PdCl<sub>2</sub> suspension and 0.1 mL of 20 mM HCl at 60 °C for 20 min) was added to the solution. The reaction solution was left undisturbed at room temperature overnight. The final products (*i.e.*, Au@Pd core-shell rods) were collected by centrifugation, washed twice with DI water, and finally redispersed in 0.5 mL of DI water.

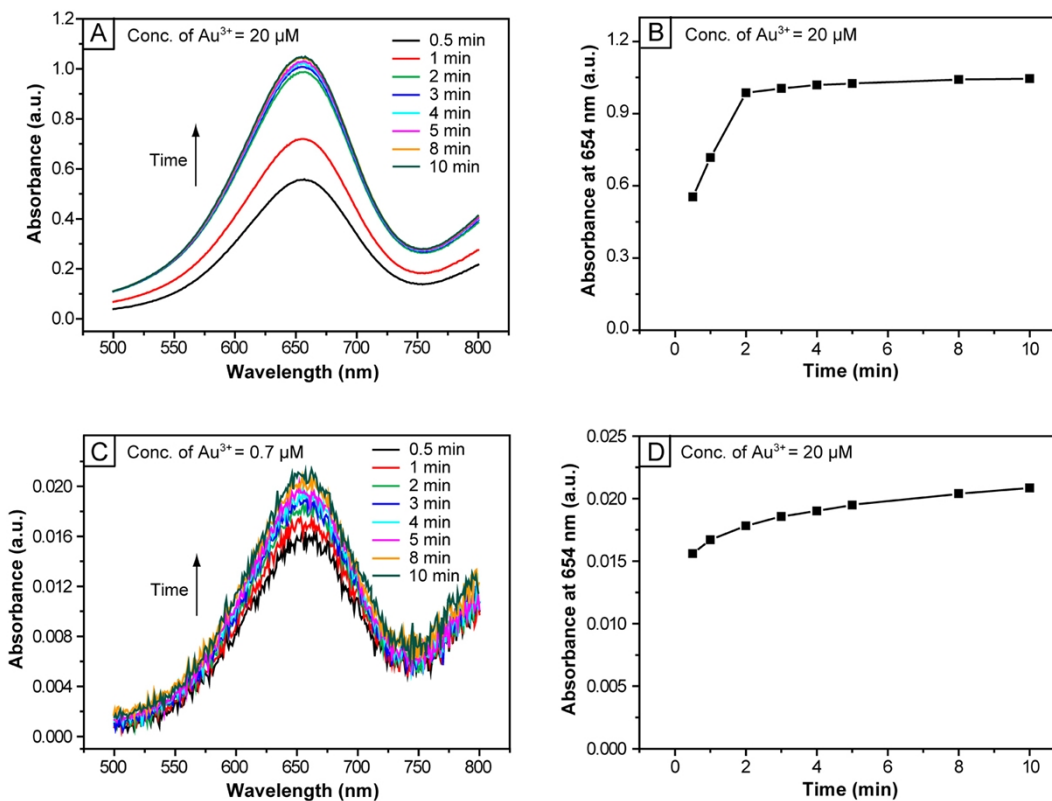
**Characterizations.** The absorption spectra were recorded using an Agilent Cary 60 UV-vis spectrophotometer. The transmission electron microscope (TEM) images were taken using a JEOL JEM-2010 microscope operated at 200 kV. Inductively coupled plasma-mass spectrometry (ICP-MS) analysis of Au was conducted using a NexION 300Q, Perkin Elmer. pH values of buffer solutions were measured using an Oakton pH 700 Benchtop Meter. Photographs of samples in cuvettes and glass vials were taken using a Canon EOS Rebel T5 digital camera.



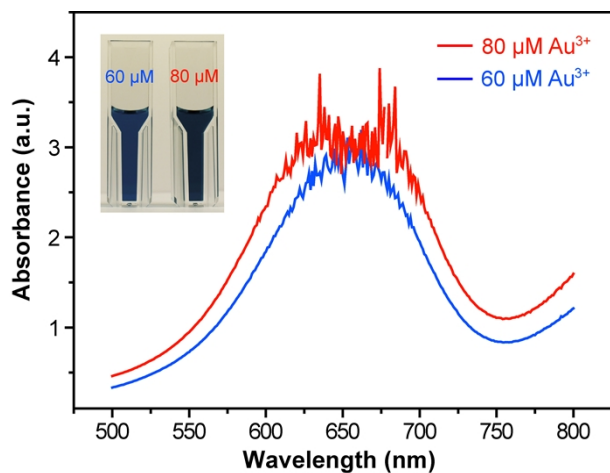
**Fig. S1** A plausible mechanism involved in the reaction between Au<sup>3+</sup> and 3,3',5,5'-tetramethylbenzidine (TMB). At a high molar ratio of [TMB] to [Au<sup>3+</sup>], a blue charge-transfer complex of the parent diamine and diimine (which exists in rapid equilibrium with the radical cation) is formed as the final product. At a low molar ratio of [TMB]/[Au<sup>3+</sup>], the final product is the yellow colored diimine.



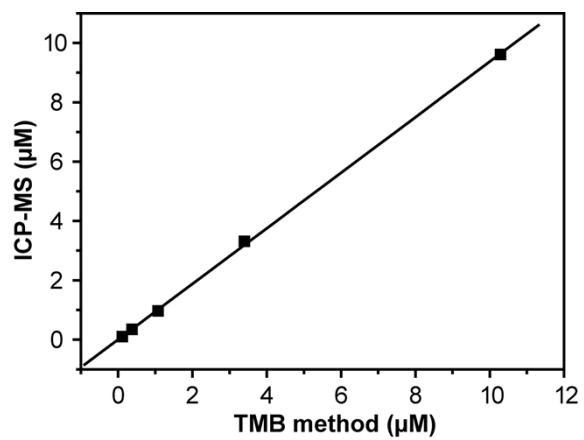
**Fig. S2** Representative absorption spectrum for the quantification of a 20 μM Au<sup>3+</sup> standard solution with TMB indicator using the standard procedure. Peak positions are labeled above the spectrum.



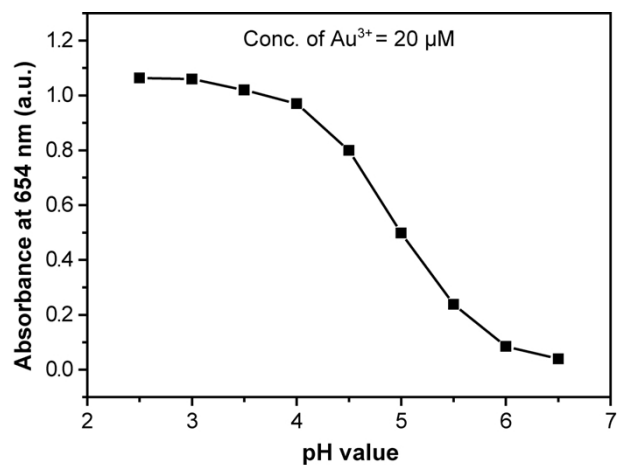
**Fig. S3** (A, B) Time-dependent absorption spectra and the corresponding plot for the quantification of  $20 \mu\text{M}$   $\text{Au}^{3+}$  standard solution with TMB indicator using the standard procedure. (C, D) Time-dependent absorption spectra and the corresponding plot for the quantification of  $0.7 \mu\text{M}$   $\text{Au}^{3+}$  standard solution with TMB indicator using the standard procedure. In (A) and (C), the reaction time are labeled with colored lines that correspond to the spectra highlighted with the same color.



**Fig. S4** Absorption spectra for the quantification of  $60 \mu\text{M}$  (red curve) and  $80 \mu\text{M}$  (blue curve)  $\text{Au}^{3+}$  standard solutions using the standard procedure. Inset shows a photograph of the corresponding reaction solutions in cuvettes.

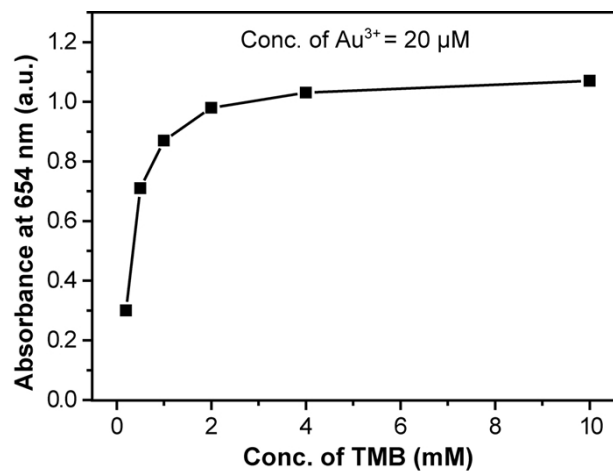


**Fig. S5** Correlation analysis between ICP-MS and the TMB method in quantifying 0.12, 0.37, 1.1, 3.3, and 10  $\mu\text{M}$   $\text{Au}^{3+}$  standard solutions ( $r = 0.9997$ ,  $n = 5$ ).

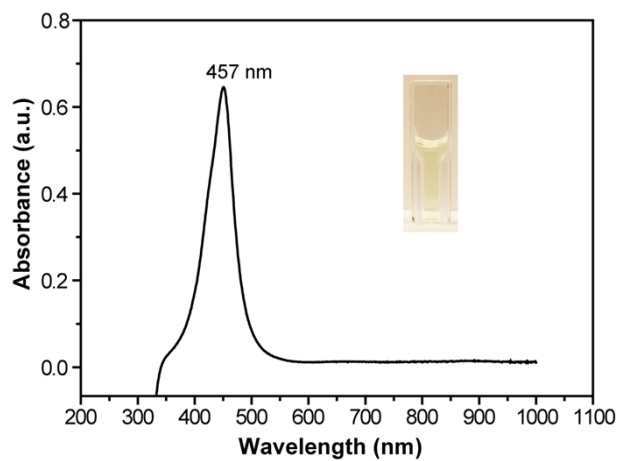


**Fig. S6** Calibration curve generated by plotting the pH value of NaAC/HAc buffer in the TMB indicator against the absorbance at 654 nm of the reaction solutions containing 1.0 mL of 20  $\mu\text{M}$   $\text{Au}^{3+}$  standard solutions and 0.2 mL of TMB indicators ( $t = 3$  min).

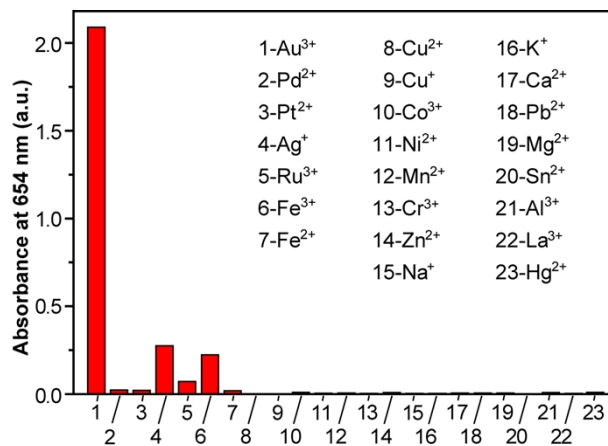




**Fig. S7** Calibration curve generated by plotting the concentration of TMB in the TMB indicator against the absorbance at 654 nm of the reaction solutions containing 1.0 mL of 20 μM Au<sup>3+</sup> standard solutions and 0.2 mL of TMB indicators ( $t = 3$  min).

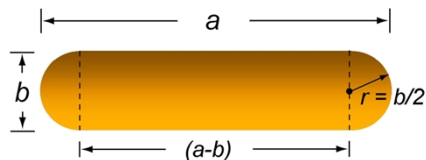


**Fig. S8** Absorption spectrum taken from 1.0 mL of 20  $\mu\text{M}$   $\text{Au}^{3+}$  standard solution after they had been incubated with 0.2 mL of TMB indicator at room temperature for 3 min. Note that, in this case, the concentration of TMB in the indicator was reduced from 2.0 mM (standard procedure) to 0.05 mM. Inset shows the photograph of the corresponding reaction solution in a cuvette.



**Fig. S9** Intensities of the absorbance at 654 nm recorded from various 40  $\mu$ M of aqueous metal ion solutions after they had been incubated with TMB indicator at room temperature for 20 min. Height of each bar represent the average value of absorbance from three independent measurements. The numbers under each bar correspond to the ions marked with the same numbers.

**$a \times b$  nm (length  $\times$  diameter) Au nanorod**

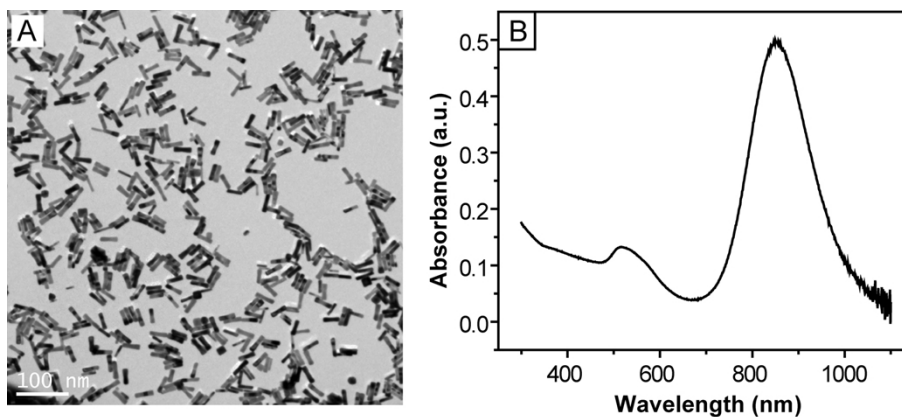


$$\begin{aligned}
 V_{\text{rod}} &= \frac{4}{3} \pi r^3 + (a-b) \pi r^2 \\
 &= \frac{3ab^2\pi - b^3\pi}{12} \text{ (nm}^3\text{)} \\
 \rho_{\text{Au}} &= 19.3 \text{ g/cm}^3 \\
 &= 1.93 \times 10^{-20} \text{ g/nm}^3
 \end{aligned}
 \Rightarrow m_{\text{rod}} = \rho_{\text{Au}} \cdot V_{\text{rod}} \approx (15ab^2 - 5b^3) \times 10^{-21} \text{ g}$$

$$\Rightarrow N_{\text{Au per AuNR}} = \frac{m_{\text{rod}}}{m_{\text{Au}}} \cdot 6.02 \times 10^{23} \approx 45.84ab^2 - 15.28b^3$$

Where,  
 $V_{\text{rod}}$  : volume of a single Au nanorod       $m_{\text{rod}}$  : weight of a single Au nanorod  
 $\rho_{\text{Au}}$  : density of gold       $N_{\text{Au per AuNR}}$  : number of Au atoms per Au nanorod

**Fig. S10** Schematic illustration showing the estimation of  $N_{\text{Au per AuNR}}$  for an ideal Au nanorod (AuNR) with size of  $a \times b$  nm (length  $\times$  diameter).



**Fig. S11** (A) Additional TEM image of the AuNRs at a lower magnification relative to the image shown in Fig. 5C. (B) Absorption spectrum taken from an aqueous suspension of the AuNRs shown in (A).

**References:**

1. B. Nikoobakht and M. A. El-Sayed, *Chem. Mater.*, 2003, **15**, 1957–1962.
2. H. Jing and H. Wang, *CrystEngComm*, 2014, **16**, 9469–9477.