Electronic Supplementary Material (ESI) for Analytical Methods
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A novel hydride generation spectral method for trace Se based on resonance Rayleigh scattering of Cu_2O-Se nanoparticles

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Experimental

Apparatus and reagents

A model of F-7000 fluorescence spectrophotometer (Japan) , a model of F95S fluorescence spectrophotometer (Lengguang Technology Ltd, Shanghai, China), a model of TU-1901 double beam UV-Vis spectrophotometer(Purkinje General Instruments Ltd, Beijing, China), a model of JSM-6380 LV scanning electron microscopy (Japan), a model of SK8200LH ultrasonic reactor (Kedao Ultrasonic Instruments Ltd, Shanghai, China), a model of DTD-40 Constant temperature digestion apparatus (Posen electronic instrument factory, Changzhou, China), and a homemade HG-absorption device were used.

A 1.000 g/L selenium standard stock solution was prepared as following: a 0.1005 g of selenium powder was weighed (purity> 99.95%), and 1mL HNO_3 and a drop of HCl were added to in a 100 mL beaker, and heated to dissolve, and transferred to a 100 mL volumetric flask, and diluted to the mark with water. Selenium standard stock was stored in the refrigerator, and selenium working solution was obtained by diluting the stock solution with water. A 36 mg/mL $NaBH_4$ solution should be prepared before it is used. A 9.2 mol/L H_2SO_4, 1.23 mol/L potassium sodium tartrate ($KNaC_4H_4O_6$) including 6.25 mol/L NaOH, 6 mol/L HCl, mixed acid of HNO_3 + $HClO_4$ (1+3), and 1.0 % potassium ferricyanide ($K_3Fe(CN)_6$) were used. $CuSO_4$ absorption solution ($CuSO_4$-$KNaC_4H_4O_6$, Fehling reagent): 1.0 mL 0.02 mol/L $CuSO_4$, 2.0 mL 1.23 mol/L $KNaC_4H_4O_6$ are mixed in the reagent bottle, and diluted to 50 mL with water. All reagents were of analytical grade and the water was doubly distilled.

Sample preparation

The tea samples were purchased from market, and placed in a vacuum drying oven drying (70 ℃). A 1.00 g tea was weighed into a digestion tube, then added 10 mL mixed acid, and covered the funnel (refluxing), used ultrasonic treatment for 30 min [25], then put them in constant temperature digestion apparatus (170 ℃), added mixed acid in time during digestion, when the solution became clear and colorless, and accompanied by white smoke, continued to heat until residual volume about 2 mL, then

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quick get off after cooling added 5 mL HCl (1:1), placed in a boiling water bath and heated 10 min, removed the tube digestions, cooled to room temperature, and filtered. The residue was washed with water doubly, the washed solution was merged into the volumetric flask, and added 1.0 mL 1% $K_3Fe(CN)_6$ and diluted to 10 mL with water for use.

Procedure

A 0.100 g/L Se standard solution was added into a reactor bottle, then added 1.0 mL 9.2 mol/L H_2SO_4, and diluted to 10 mL. 10 mL of 36 mg/mL $NaBH_4$ were added into the separating funnel, and 5.0 mL $CuSO_4$ absorption solution were added into the gas absorption bottle (Figure 1S). Opened the ultrasonic reactor, and set time for 5 min, then slowly opened the piston of the separating funnel, the $NaBH_4$ would added in the reaction bottle, with flow rate of 5 mL/min. The reaction product of SeH_2 exported to the absorption bottle. After the reaction was complete, the solution was transferred into a test tube and placed for 15 min, then the RRS spectrum was recorded on a fluorescence spectrophotometer, using a synchronous scanning technique (λ_{ex}-λ_{em}=$\Delta\lambda$ = 0), voltage of 450 V, both excited slit and emission slit of 5 nm, and emission filter of 1% T attenuator. The RRS value at 374 nm (I_{374nm}) and a blank value without Se (IV) (I_0) were recorded. The value of ΔI_{374nm} = I_{374nm}-$(I_{374nm})_0$ was calculated.

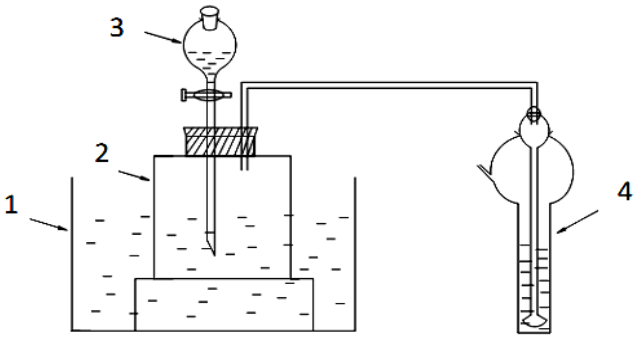

Figure 1S A scheme of the HQ equipment

1. Ultrasonic reactor; 2. Reaction bottle; 3. Separating funnel; 4. Gas absorption bottle

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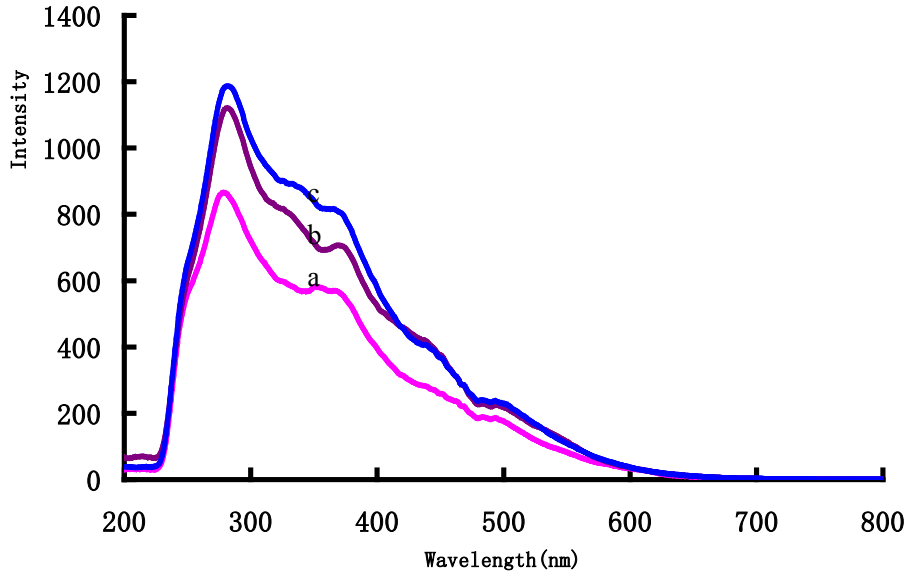

Figure 2S Resonance Rayleigh scattering spectra of the SeH_2-tartrate system
a: 49.2 mmol/L tartrate-0.46 mol/L H_2SO_4-36 mg/mL $NaBH_4$; b: a+0.5 mg/L Se; c: a+1.5 mg/L Se.

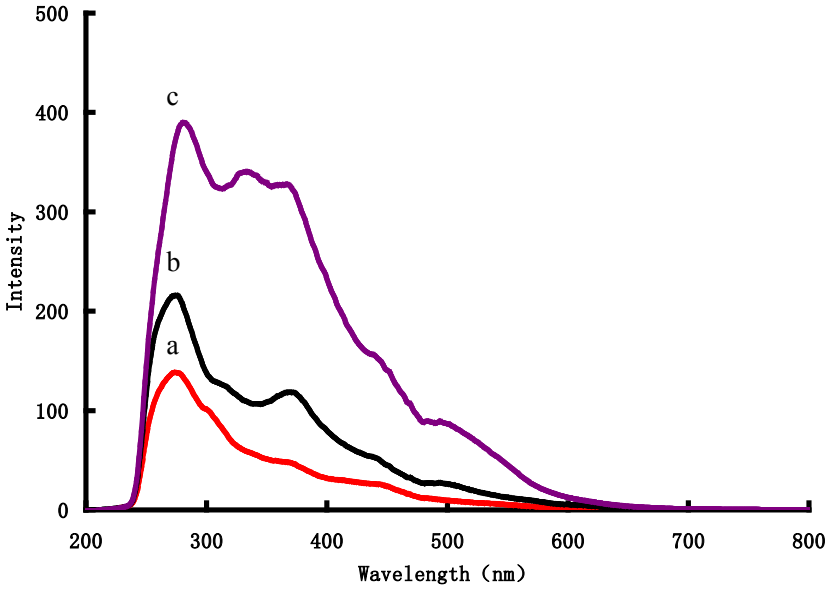

Figure 3S Resonance Rayleigh scattering spectra of the SeH_2-Se(IV) system
a: 0.0 mg/L Se-0.46 mol/L H_2SO_4-36 mg/mL $NaBH_4$ + absorption solution containing 0.06 g/L Se(IV); b: a+0.75 mg/L Se; c: a+4.5 mg/L Se.

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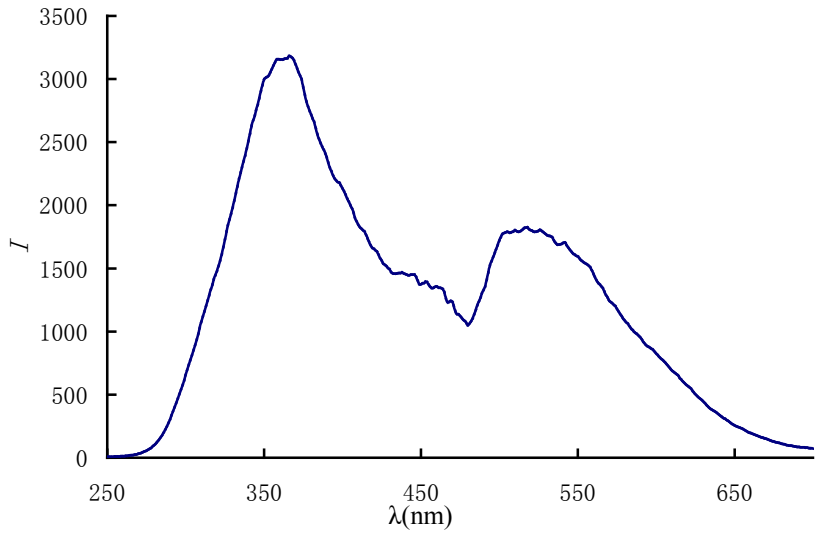

Figure 4S The Cu_2O particle RRS spectra in the glucose-Fehling reagent-Au nanoparticle catalytic system

2mmol/L $CuSO_4$+61.5mmol/L $KNaC_4H_4O_6$+0.37mmol/L glucose-16.2 ng/mL AuNP-70 ^oC 7 min.

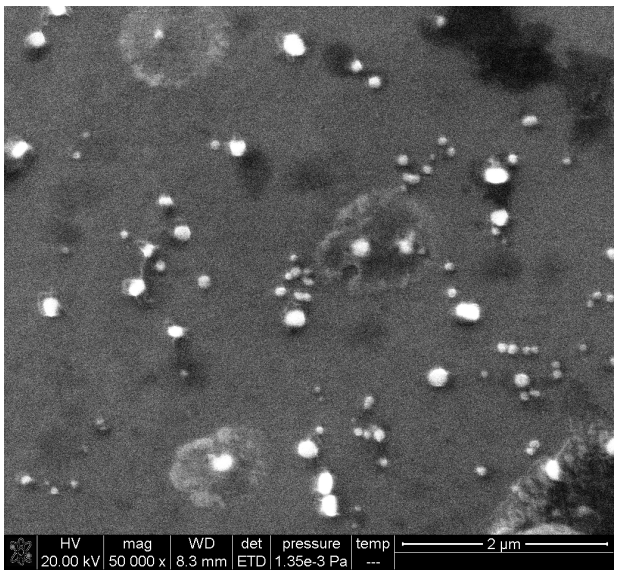

Figure 5S Scanning electron microscopy

1.5 mg/L Se-0.4 mmol/L $CuSO_4$-0.0492 mol/L $KNaC_4H_4O_6$-0.46 mol/L H_2SO_4-36 mg/mL $NaBH_4$.

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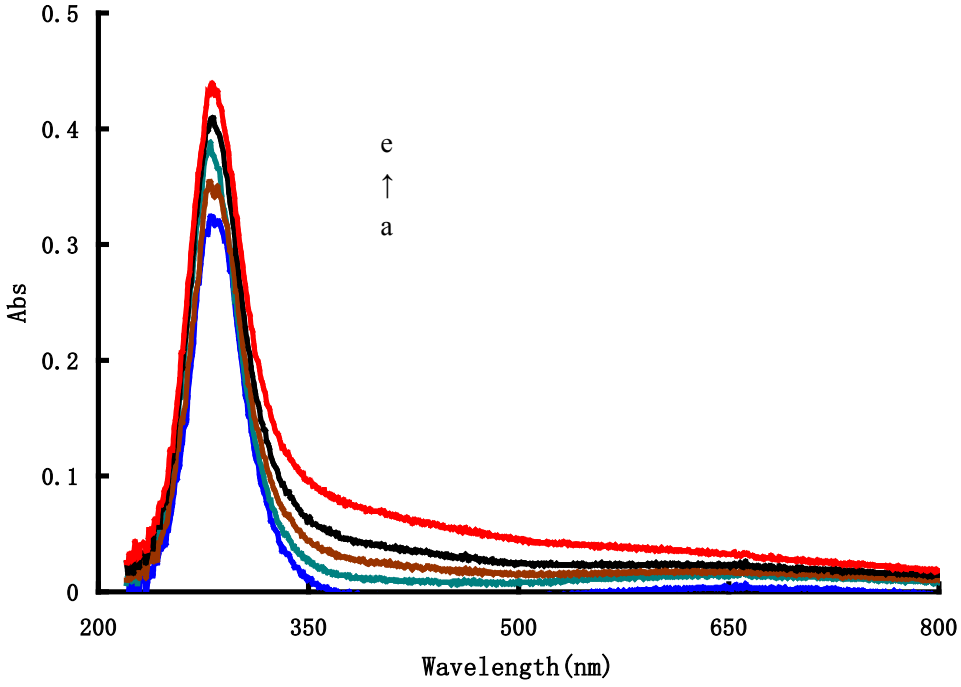

Figure 6S Absorption spectra of Cu_2O-Se particles system
a: 0.4 mmol/L $CuSO_4$ -0.0492 mol/L $KNaC_4H_4O_6$-0.46 mol/L H_2SO_4-36 mg/mL $NaBH_4$;
b: a+0.10 mg/L Se; c: a+0.50 mg/L Se;d: a+0.75 mg/L Se;e:a+1.50 mg/L Se

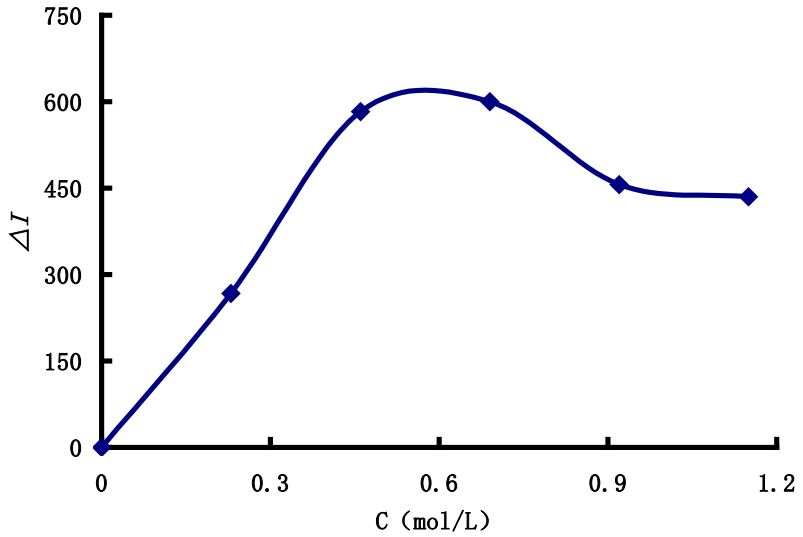

Figure 7S Effect of H_2SO_4 concentration on ΔI_{374nm}
0.5 mg/L Se-30 mg/mL $NaBH_4$-0.4 mmol/L $CuSO_4$ -0.0492 mol/L $KNaC_4H_4O_6$

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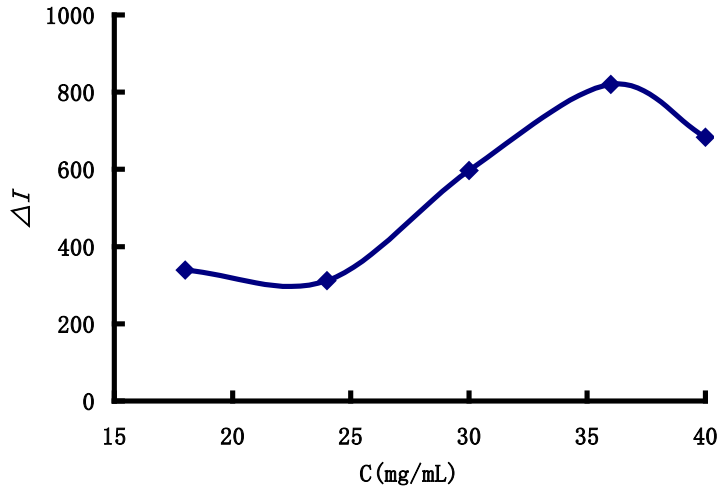

Figure 8S Effect of $NaBH_4$ concentration on ΔI_{374nm}
0.5mg/L Se-0.46 mol/L H_2SO_4-0.4 mmol/L $CuSO_4$-0.0492 mol/L $KNaC_4H_4O_6$

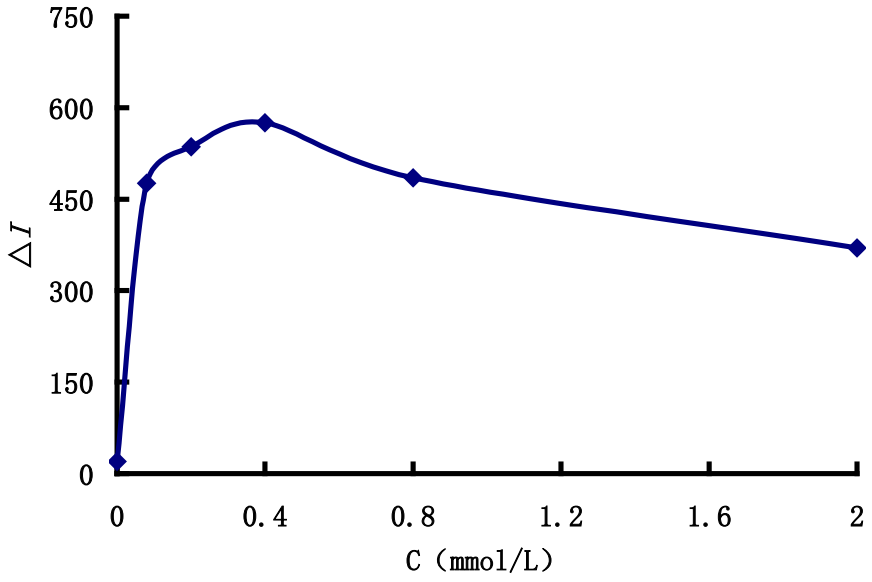

Figure 9S Effect of $CuSO_4$ concentration on ΔI_{374nm}
0.5 mg/L Se-0.46 mol/L H_2SO_4-36 mg/mL $NaBH_4$-0.0738 mol/L $KNaC_4H_4O_6$

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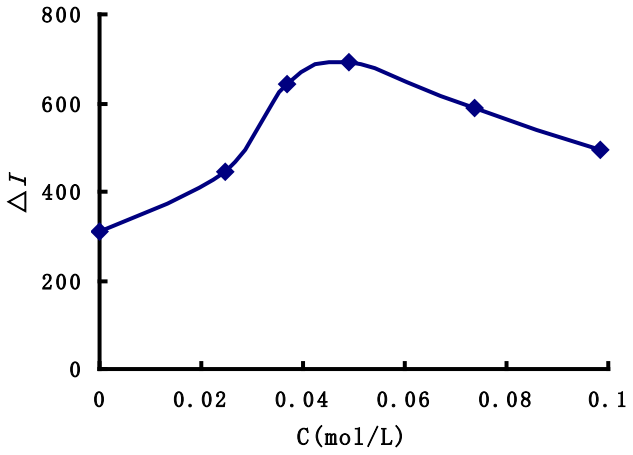

Figure 10S Effect of $KNaC_4H_4O_6$ concentration on ΔI_{374nm}
0.5 mg/L Se-0.46 mol/L H_2SO_4-36 mg/mL $NaBH_4$-0.4 mmol/L $CuSO_4$

Table 1S Effect of CES [a]

Coexistent substance	Tolerance (μmol/L)	Relative error (%)	Coexistent substance	Tolerance (μmol /L)	Relative error(%)
Fe^{3+}	174	9.4	Mg^{2+}	500	-3.2
Ca^{2+}	600	-7.4	Hg^{2+} [b]	100	2.4
As^{3+}	46	-3.8	Cu^{2+} [b]	150	-4.3
Te^{6+}	150	5.8	Pb^{2+}	150	-8.5
Sb^{3+}	200	-4.1	Bi^{3+}	20	-1.8
Ge^{4+}	50	4.9	Tl^{3+}	45	2.8
Sn^{4+}	45	3.2	Zn^{2+} [b]	100	-4.0
In^{3+}	80	4.1	Cd^{2+}	80	4.7
Ni^{2+} [b]	65	-3.7	Co^{2+} [b]	65	-4.1

[a] 6.33μmol /L Se , [b] addition of 100μL 1% $K_3Fe(CN)_6$.

Table 2S Analytical results of selenium in tea (n=3)

Sample	Content (ug/g)	Added Se (mg/L)	Found Se (mg/L)	RSD（%）	Recovery（%）
1	No detected	0.50	0.5080	6.2	101.6
2	No detected	0.50	0.5485	6.1	109.7
3	No detected	0.50	0.4967	3.5	99.4
4	0.805±0.055	-	-	6.8	-
5	0.750±0.064	-	-	7.2	-
6	0.450±0.035	-	-	7.8	-