Surpporting Information

AuNCs-Catalyzed Hydrogen Selenide Oxidation: Mechanism and Application for Headspace Fluorescent Detection of Se(IV)

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Experimental Section

Instrumentation. Fluorescence spectra were recorded on an F-7000 spectrofluorometer (Hitachi, Japan) equipped with a solid sensing cell. Scanning electron microscopy (SEM) was performed with a JSM-7500F scanning electron microscope (JEOL, Tokyo, Japan). X-ray photoelectron spectroscopy (XPS, PHI-5000 Versa Probe, ULVAC-PHI) was used to determine the valent state of the AuNCs before and after reaction with H_2Se. Fluorescence imaging was carried out with a gel image analysis system (JK02S, Beijing Junyi Electrophoresis Instrument Factory, F-2) equipped with a 365 nm reflected UV source. A commercial two-channel hydride generation nondispersive atomic fluorescence spectrometer (AFS-9600, Beijing Haiguang instrumental Co., Beijing, China) was used for the detection of the intensity of the selenium atomic fluorescence. A microwave synthesizer (UWave-1000, Shanghai sineo Microwave Chemistry Technology Co., China) was used to synthesize AuNCs.

Synthesis of GSH-AuNCs and 5-nm AuNPs. The water-soluble GSH-AuNCs were synthesized following the method as described in the literature.[1] GSH aqueous solution (0.30 mL, 100 mM) and $HAuCl_4$ aqueous solution (1.00 mL, 20 mM) mixed with 8.70 mL of ultrapure water at room temperature, and the mixture was under gentle stirring at 70 °C for 24 h followed by cooling to room temperature naturally. Then the final pale-yellow GSH-AuNCs solution was kept at 4 °C prior to use.

AuNPs were synthesized according to reference.[2] A 20 mL aqueous solution containing 2.5×10^{-4} M $HAuCl_4$ was prepared in an around bottomed flask at room temperature, then 0.6 ml of ice cold 0.1 M $NaBH_4$ was added to the above solution under stirring. The solution turned to orange-red color immediately after adding $NaBH_4$, indicating particle formation.

Sample preparation. A microwave digestion method was used to digest DOLT-5, DORM-4, selenium-enriched rice and selenium-enriched egg. Rice sample was washed three times with ultra-pure water and dried in an oven at 60 °C for 30 min. Then rice was grounded into powder. Subsequently, 0.125 g DOLT-5, 0.5 g DORM-4, 2 g selenium-enriched rice and 2 g selenium-enriched egg were accurately weighed into precleaned Teflon vessels and then 8 mL of HNO_3 and 2 mL of H_2O_2 were added. The sample blanks were processed along with the samples. The sealed vessels were heated in a microwave oven (Multiwave PRO, Shanghai Sineo Microwave Chemistry Technology Co., China) operated under the following conditions: 10 min at 700 W and 100 °C, 15 min at 1000 W and 150 °C, and 25 min at 1400 W and 200 °C. After cooling, the digested products were transferred into Teflon crucibles and continued to heat the remaining volume to 2 mL or so, must not be steamed to dryness. After cooling, added 5 mL HCl (6 mol/L) to the digested products and heated to almost dry. Se(VI) was then reduced to Se(IV). The residues were transferred to precleaned 10 mL volumetric flasks with 5% (v/v) HCl and added to the mark. Tap water and seawater sample added in hydrochloric acid were directly reacted with KBH_4 without microwave digestion.

Computational details. All of the calculations were carried out by employing DFT methods in the Dmol[3] software of the Materials studio package.[3,4] The generalized gradient approximation (GGA) with the PW91 function was used.[5-7] Localized double numerical plus polarization (DNP) basis sets were applied to expand the Kohn–Sham orbitals. These numerical basis sets are similar to 6-31G (d, p) in size, but tend to be more accurate than the latter and have little basis set superposition error (BSSE). The core electrons of the metal atoms were treated using density functional semicore pseudopotentials (DSPP), which include scalar (mass-velocity and Darwin) relativistic corrections for the core electrons. A real-space cutoff of 4.5 Å was used, which is

sufficient for accurate evaluation of the energies. The selfconsistent field (SCF) calculations have been done with a convergence criterion of 10^{-6} Ha on the total energy. All the SCF calculations were carried out with spin unrestricted and symmetry not enforced to allow for full geometry relaxation. The value of smearing is 0.005 Hartree.
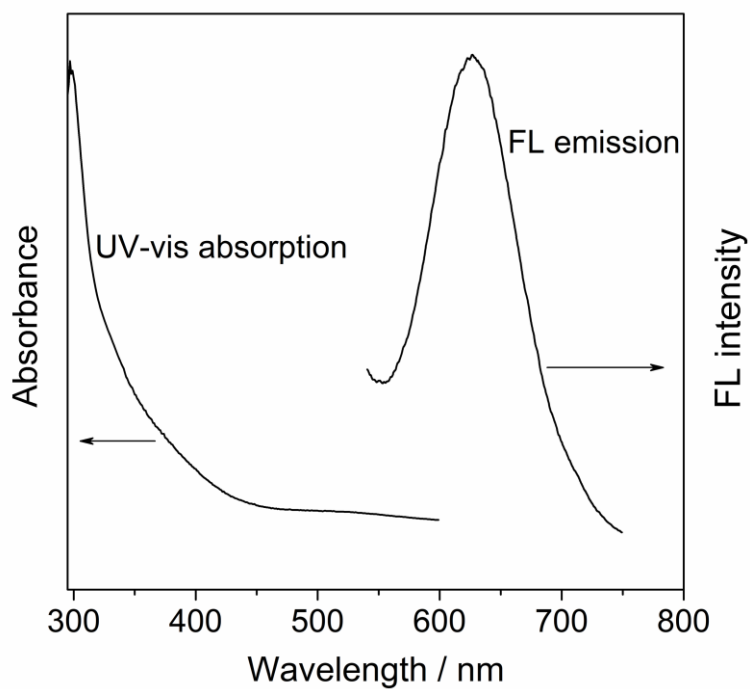

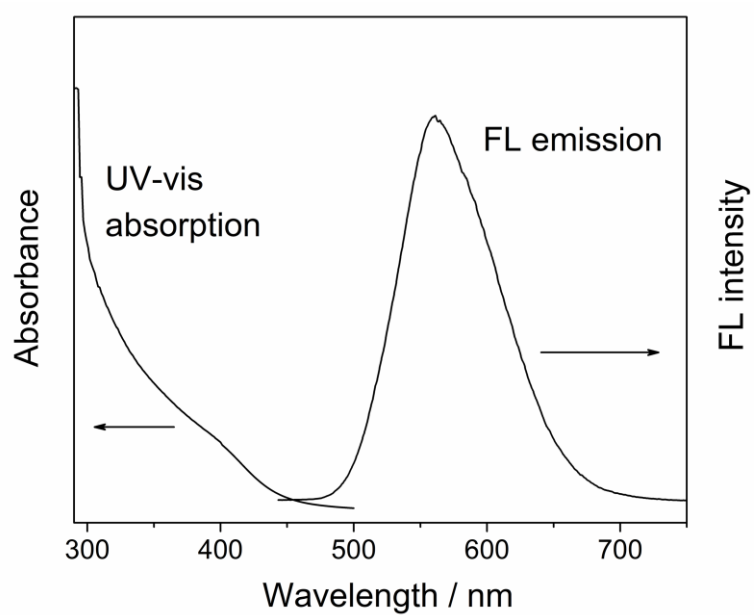**Figure S1.** UV-vis absorption and fluorescence emission spectra of BSA-AuNCs.

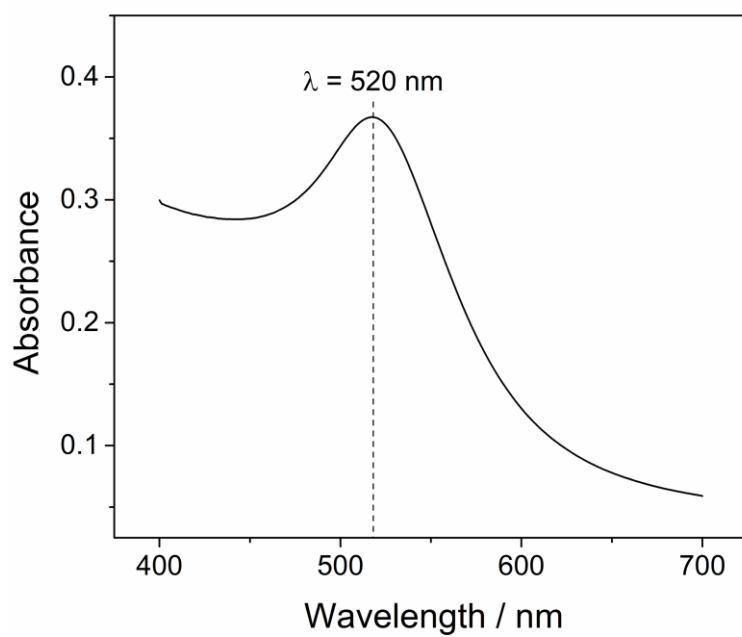**Figure S2.** UV-vis absorption and fluorescence emission spectra of GSH-AuNCs.

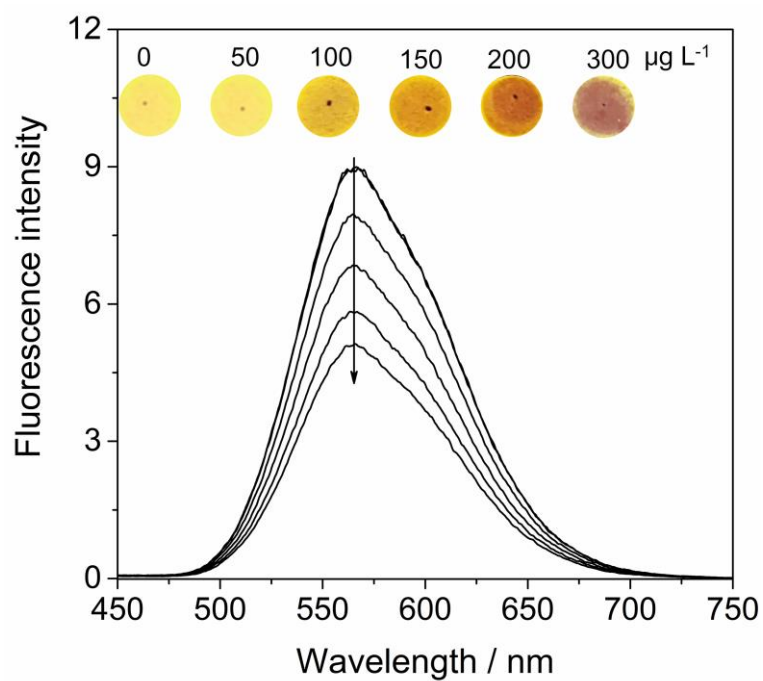**Figure S3.** UV-vis absorption spectrum of uncapped AuNPs.

Figure S4. Fluorescence spectra of GSH-AuNCs in the presence of increasing amounts of H_2Se. The inset shows the corresponding fluorescent images.
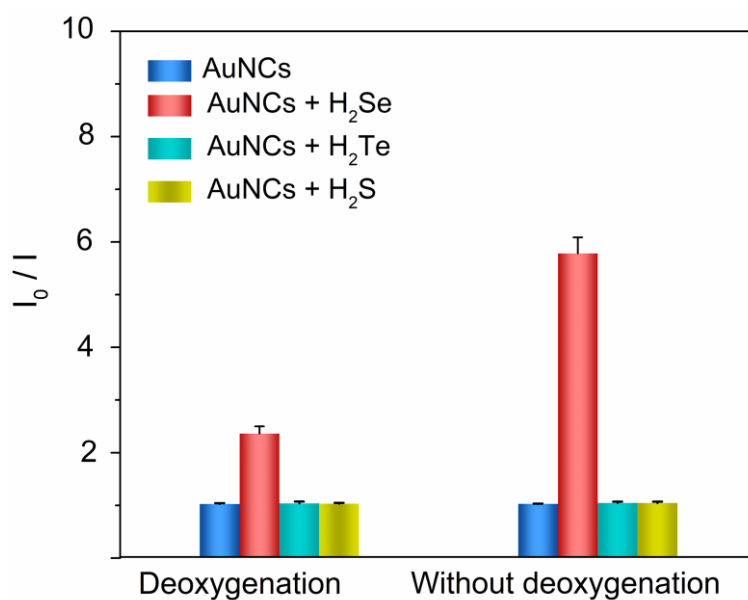

Figure S5. Effect of deoxygenation on the fluorescence response of S, Se and Te.
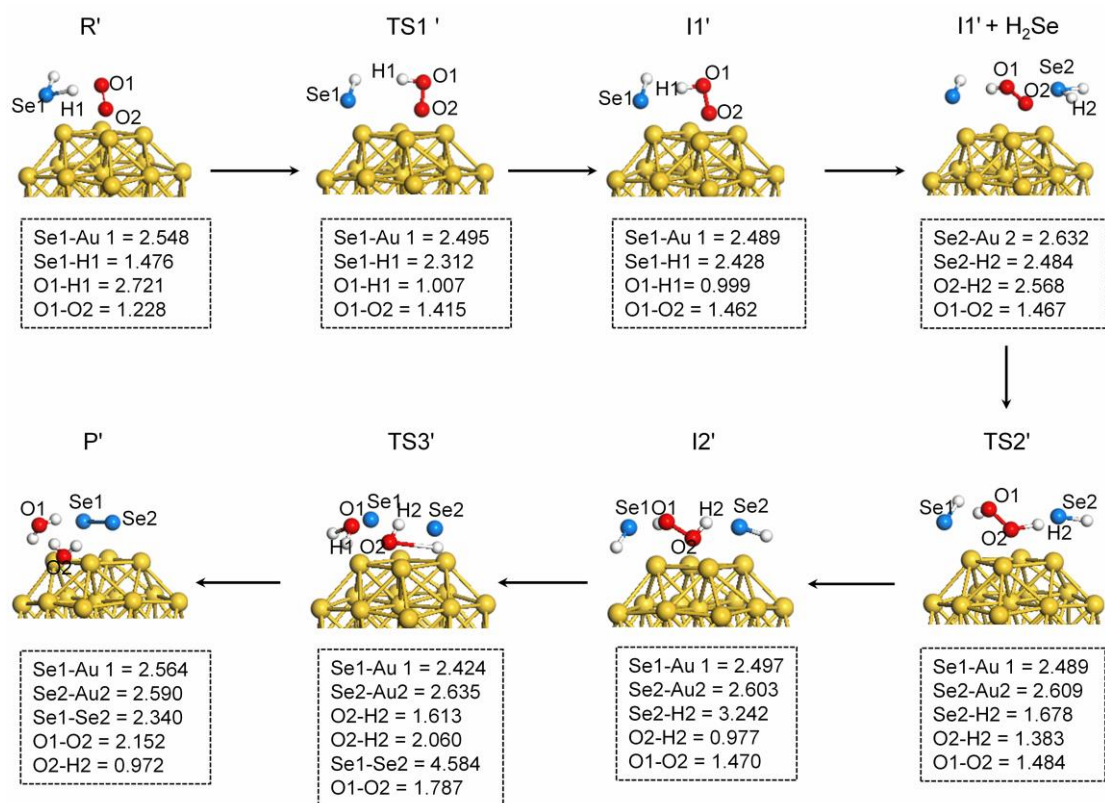
Figure S6. Geometric parameters (bond lengths in Å) of species in the reaction of H_2Se and O_2 on the Au_{38} cluster.
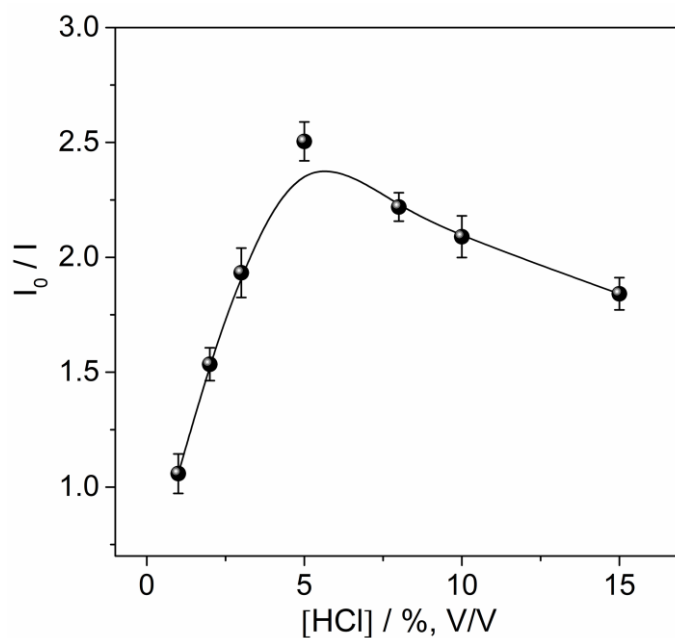

Figure S7. Effect of the concentration of HCl on the fluorescence response. Experimental conditions: concentration of Se(IV), 100 μg L^{-1}; concentration of AuNCs, 2.5 mM; concentration of KBH_4, 3 % (m/v); sample volume: 10 mL; reaction time: 20 min.
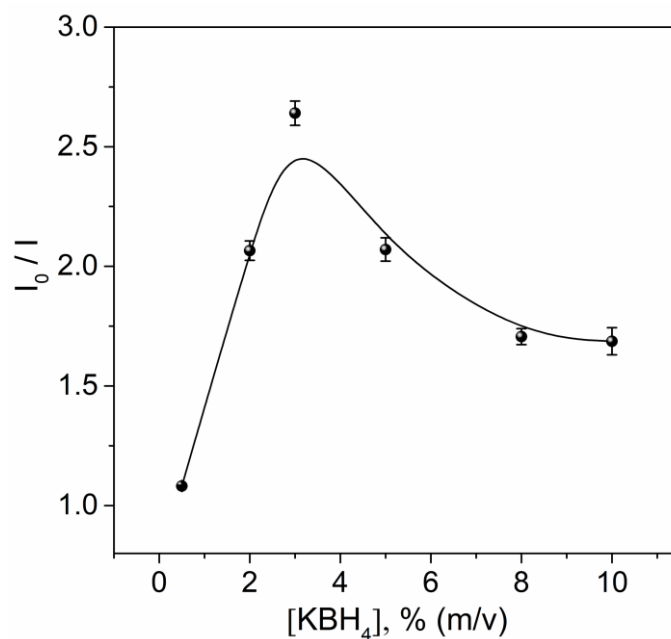
Figure S8. Effect of the concentration of KBH$_4$ on the fluorescence response. Experimental conditions: concentration of Se(IV), 100 μ g L^{-1}; concentration of AuNCs, 2.5 mM; concentration of HCl, 5 % (v/v); sample volume: 10 mL; reaction time: 20 min.
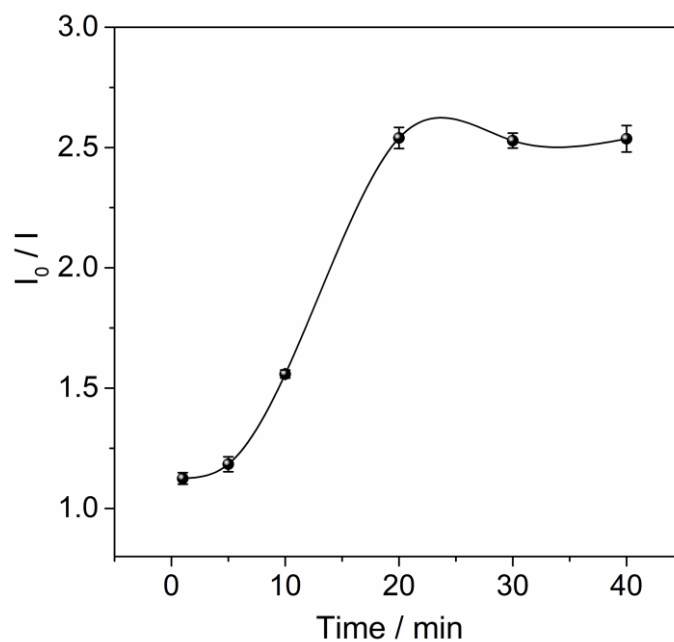

Figure S9. Effect of the reaction time on the fluorescence response. Experimental conditions: concentration of Se(IV), 100 μ g L^{-1}; concentration of AuNCs, 2.5 mM; concentration of HCl, 5 % (v/v); concentration of KBH$_4$, 3 % (m/v); sample volume: 10 mL.
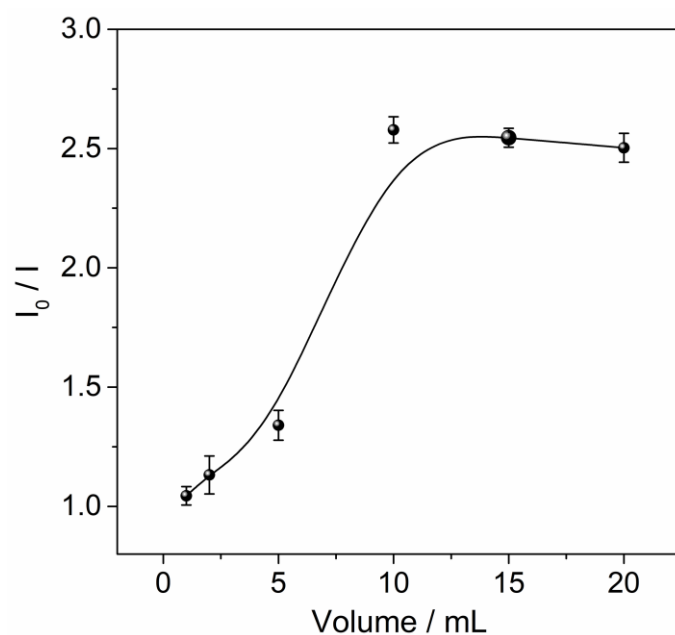
Figure S10. Effect of the sample volume on the fluorescence response. Experimental conditions: concentration of Se(IV), 100 μg L^{-1}; concentration of AuNCs, 2.5 mM; concentration of HCl, 5 % (v/v); concentration of KBH$_4$, 3 % (m/v); reaction time: 20 min.
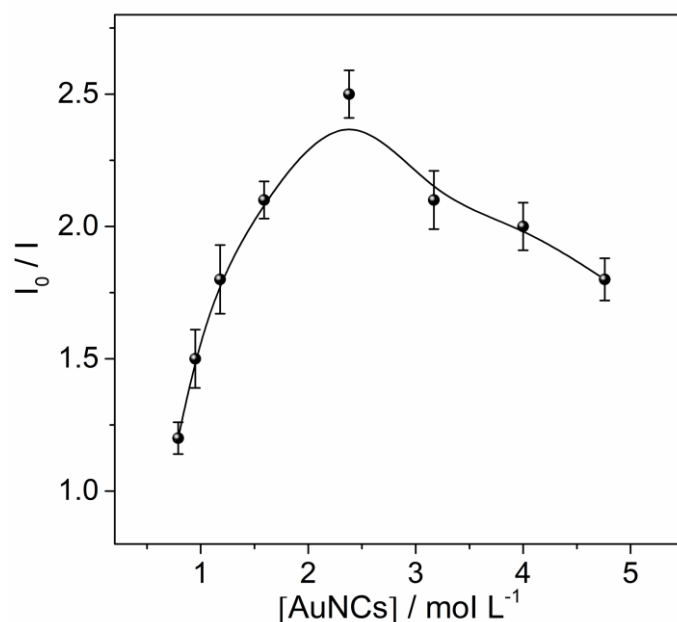
Figure S11. Effect of the concentration of AuNCs on the fluorescence response. Experimental conditions: concentration of Se(IV), 100 μg L^{-1}; concentration of HCl, 5 % (v/v); concentration of KBH$_4$, 3 % (m/v); sample volume: 10 mL; reaction time: 20 min.
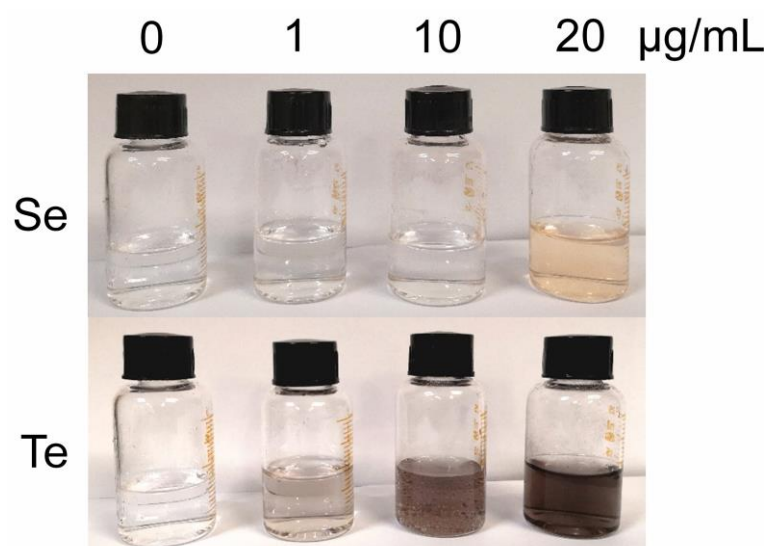
Figure S12. Photographs of the bottles containing different amounts of Se(IV) and Te(IV) after headspace hydride generation.
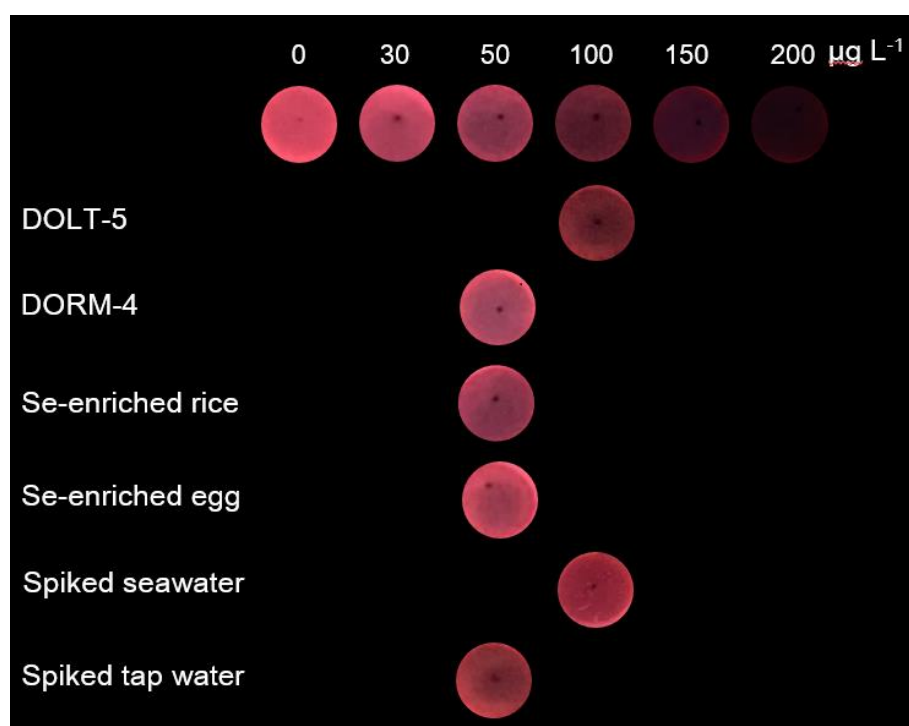

Figure S13. Fluorescent images for the sample analysis.

Table S1. Comparison of performance of the proposed assay with other similar ones

method	linear upper limit ($\mu g\ L^{-1}$)	limits of detection ($\mu g\ L^{-1}$)	RSD (%)	sample	ref.
AuNPs-FI-HG-Uv-vis	31.6−316	3.95	−	Se-rich egg	[8]
OQDs-HG-SPE- FS	5−100	0.1	2.4	human urine	[9]
QD-HS-SDME	50−750	12.6	5.0	tap water	[10]
QDs-HS-SDME-μFS	5.0−65.0	0.08	4.6	Lake water seawater	[11]
HS-SDME-ETAAS	−	0.15	2.5	seawater	[12]
HS-ETV–ICP-MS	0.05–20.00	0.008	7.0	Human hair	[13]
FI-HG-AAS	2.5−10.0	0.2	6.3	river sediment	[14]
AuNCs–HG–SPE–FS	30−200	4.0	2.8	Se-rich rice Se-rich egg	This work

FI, flow injection; SD, single drop; HG, hydride generation; SPE, Solid-Phase Extraction; FS, fluorospectrometry; HS-SDME, headspace single-drop microextraction; μFS, microfluorospectrometry; ETAAS, electrothermal atomization-atomic absorption spectrometry; ETV-ICP-MS, electrothermal vaporization inductively coupled plasma-mass spectrometry; AAS, atomic absorption spectrometry.

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