Electronic Supplementary Information

In Situ Formation of Nano-CdSe as a Photocatalyst: Cadmium Ion-Enhanced Photochemical Vapour Generation Directly from Se(VI)

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Experimental Section

1. Chemicals

All the reagents used were at least of analytical grade or better. Ultrapure water (18.2 M Ω cm) used throughout this study was produced with a water purification system (PCWJ-10, Pure Technology Co. Ltd, Chengdu, China). Sodium selenate (Se(VI)) and sodium selenite (Se(IV)) were purchased from the Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Other reagents used in this work were purchased from the Aladdin Reagents Co. Ltd. unless otherwise specified. The stock solutions (1 mg/mL) of Se(IV) and Se(VI) were prepared by dissolving an appropriate amount of the corresponding compound in ultrapure water. All standards and stock solutions were stored in a refrigerator until use.

2. Instrumentation

Chromatographic separation was carried out on a DIONEX Ultimate 3000 high-performance liquid chromatography (HPLC) (Idstein, Germany) using a Dionex IonPac AS22 (250 mm × 4 mm). The atomic fluorescence spectrometric data were obtained by using an AFS-9600 (Beijing Haiguang Instrument Co., Beijing, China) equipped with a high-intensity Se hollow cathode lamp (196.0 nm, Research Institute of Non-Ferrous Metals, Beijing, China). Hydrogen was generated using a hydrogen generator (SPGH-300, Zhongya Gas & Instrument Research Institute, Beijing, China). An ICAP-Q ICPMS (Thermo Fisher Scientific, Hemel Hempstead, UK) was also used for detection of selenium. Gas chromatography-mass spectrometry (GC-MS) spectra were recorded with a GCMS-QP2010 plus (Shimadzu, Japan). An Agilent (Santa Clara, USA) GC-78 90B system with a capillary control unit, a split injection port, and a flame ionization detector was used for all GC separations. Highly pure N_2 gas (99.999%) was used as the carrier gas. The instrument control and data acquisition were carried out with a ChemStation software (Agilent, USA). The X-ray photoelectron spectra (XPS) were collected with an AXIS Ultra DLD 800 X (Kratos, UK). TEM and EDX were performed with a Tecnai G2 F20 S-TWIN 20 transmission electron microscope at an accelerating voltage of 200 kV (FEI Co., USA).

The flow PVG reactor: It was obtained from Beijing Titan Instruments Co. (Beijing, China) and provided a source of 185 nm radiation. The sample solution was pumped through a narrow-bore synthetic quartz tube (800 μ L internal volume) internally positioned along the central axis of the low-pressure mercury discharge. This allowed efficient and uniform irradiation of a thin film of the sample from all directions and with deep-UV lines from the discharge. Argon carrier gas was introduced through a "Y" connection between the outlet of the photoreactor and a homemade gas–liquid separator (GLS). The generated analyte-containing vapour was directed from the GLS to the AFS or ICPMS for detection of selenium.

The batch PVG reactor: The radiation from the UV lamp (15 W, CnLight Co., Ltd., Foshan, China) irradiated onto the suspension in the quartz tube to effectively induce vapour generation from Se(VI) in the solution. A flow of carrier gas Ar (300 mL min⁻¹) passed through the catheter to the bottom of the solution and purged the gaseous Se-containing species to the AFS detection system.

Hydrogen generator was used to produce excessive hydrogen which together with argon was ignited to form an argon–hydrogen flame in the quartz atomizer of the AFS for the atomization of the gaseous Secontaining species when AFS was used as a detector.

3. Synthesis

Synthesis of ZnS: $3.5 \text{ mL } 0.1 \text{ M Zn}(\text{NO}_3)_2$ and 20 mL 0.07 M mercaptopropionic acid were combined with 45.0 mL water in a three-neck flask. After the pH of the solution was adjusted to ~11.5 using 2.0 M NaOH, 4.5 mL freshly prepared 0.1 M Na₂S was quickly injected with stirring. After 10 min, the mixture solution was refluxed at 100 °C for one hour. ¹

Synthesis of CdS: 10 mL 0.02 M CdCl₂ and 25 mL water were mixed in a 100 mL a three-necked flask. After that, 10 mL 0.1 M L-cysteine was pulled in quickly and the pH of the mixture solution was adjusted

to 8.0 with 1.0 M NaOH, then 20 mL 4 mM Na₂S was added drop by drop. Finally, the mixed solution was heated to 100 $^{\circ}$ C for 45 min in the N₂ atmosphere under stirring.²

Synthesis of CdSe and CdTe: $CdCl_2 \cdot 2.5H_2O$ (0.5 mmol), 3-mercaptopropionic acid (52 μ L) and 0.20 g trisodium citrate dihydrate were dissolved in 25 mL water in a three-necked flask. The pH of mixture was adjusted to 10.5 with 1 M NaOH, Na₂TeO₃/Na₂SeO₃ (0.1 mmol) and NaBH₄ (0.05 g) were added. The mixture was refluxed at 100 °C for 1h.³



Fig. S1 Effect of added Cd²⁺ on the AFS response of 0.1 μg mL⁻¹ Se(VI) with PVG in 20% CH₃COOH.



Fig. S2 Effect of added Cd²⁺ on the ICP-MS response of ⁷⁷Se(VI) and ¹¹²Cd with PVG in 20% CH₃COOH.



Fig. S3 Calibration curve. R²: 0.999, and LOD (3 σ): 0.01 ng mL⁻¹.



Fig. S4 The GC chromatogram of gaseous products generated from the PVG system in UV + CH₃COOH and UV + CH₃COOH + Cd²⁺. CH₃COOH concentration: 20% (V/V).



Fig. S5 (A) High-magnification TEM image and (B) the selected area electron diffraction of *in-situ* generated CdSe nanoparticles in the collected outflow solution after PVG in the Se(VI)-Cd²⁺-CH₃COOH system.



Fig. S6 XPS spectra of CdSe nanoparticles in the collected outflow solution after the PVG in the Se(VI)-Cd²⁺-CH₃COOH system: (A) XPS survey spectrum; and (B) XPS spectrum of Cd 3d, (C) XPS spectrum of Se 3d.



Fig. S7 Relative Te AFS intensity obtained from 1 μ g mL⁻¹Te(VI), 1 μ g mL⁻¹Te(VI) mixture with 1 μ g mL⁻¹ prepared nanomaterials (CdSe, CdS, CdTe, and ZnS) (in 20% CH₃COOH, V/V).

Table S1 Summary of recent	reported PVG methods for Se(VI) determination
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Catalyst	Detector	Linear range (ng mL ⁻¹)	LOD (ng mL ⁻¹)	Reference
g-C ₃ N ₄ /TiO ₂	AFS	0.25-20	0.08	4
UiO-66(Zr/Ti)	AFS	0.1-100	0.01	5
MIL-125-NH ₂	ICP-OES	-200	0.3	6
CAU-1	AFS	-200	0.04	7
TiO₂	AFS	2-30	0.05	8
Cd ²⁺	AFS	0.05-500	0.01	this work

Table S2 Chemical composition in terms of atomic percentage of nano-CdSe from EDX spectra.

Element	Atomic/%
Se (K)	63.12
Cd (K)	36.02

Table S3 The atomic compositional ratio of Cd, Se_{tot} (total Se), Se_{CdSe} (Se from CdSe compound) calculated from XPS and EDX spectra.

	Atomic compositional ratio
Cd:Se _{tot}	0.57
Secdse:Setot	0.59
Cd:SecdSe	0.97

Table S4 The portion of Se(VI) transformed to the nano-CdSe and the Se(CH₃)₂ calculated with analytical result data from HPLC-ICPMS

C _{Se(VI)} / µg mL ⁻¹	CdSe / %	Se(CH ₃) ₂ / %
0.01	10.1	74.4
0.10	9.3	75.0
1.00	8.1	77.2

Table S5 The working parameters for the HPLC-ICPMS System

	HPLC	
Mobile phase	13.5 mM Na ₂ CO ₃ , 4.2 mM NaHCO ₃	
Column	As 22	
Flow rate	1.5 mL min ⁻¹	
Sample volume	20 µL	
Column temperature	45 ℃	
	ICP-MS	
RF power	1500 W	
Plasma gas flow rate	14 L min ⁻¹	
Auxiliary gas flow rate	1 L min ⁻¹	
Nebulizer gas flow rate	1 L min ⁻¹	

Table S6 The working parameters of the AFS

	AFS	
PMT voltage	-300 V	
HCL current	90 mA	
Auxiliary current	45 mA	
Argon flow rate	400 mL min ⁻¹	
Hydrogen flow rate	200 mL min ⁻¹	

Table S7 The working	parameters of the	GC-MS
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	GC	
Column	Rtx-5 MS capillary column 30 m in length × 0.25 mm i.d. × 0.25 mm	
	coating	
Carrier gas (He) flow rate	5 mL min ⁻¹	
Sample volume	1 mL	
Column temperature	35 ℃	
MS		
Ion source temperature	155 ℃	
Electron impact ion source	70 eV	
Auxiliary gas flow rate	1 L min ⁻¹	
Interface temperature	155 °C	

Table S8 The working parameters of the GC-FID

	GC
Column	DB-1 capillary column 30 m in length × 0.15 mm
Carrier gas (N ₂) flow rate	1 mL min ⁻¹
Sample volume	1 mL
Temperature program	40 °C for 3 min, 20 °C min ⁻¹ from 40 °C to 180 °C and at 180 °C until
	the end

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