

Electronic supplementary information for Communication Ref.: B403129F, Online Pre-reduction of Selenium (VI) with a Novel Designed UV/TiO₂ Photocatalysis Reduction Device

Preparation of nano TiO₂ multilayer film on the surface of the glass fibre

Nano TiO₂ multilayer film on the surface of the glass fibre was prepared as follows: solution A was obtained by dissolving 20 mL Ti(OBu)₄ in 50 mL EtOH with stirring for 30 minutes; solution B was prepared by dissolving approximately 4 mL 1:1 (V/V) HCl in 40 mL EtOH. Then solution B was added into solution A drop by drop with drastically stirring. The mixture obtained was kept stirring for 2 hours at 25 °C to get a uniform yellow sol. Finally the glass fibre was dipped into the sol for 30 seconds. After pulled out at the rate of 3 cm min⁻¹, the glass fibre was dried at 80 °C for 30 minutes, and then the temperature was ramped by the rate of 1.5 °C min⁻¹ to 450 °C and kept standing at 450 °C for 1 hour in an electric stove to get the anatase TiO₂ film on its surface. After cooled to 25 °C it was washed with water and dried again for 10 minutes at 80 °C, one layer of transparent nano TiO₂ film on the surface of the glass fibre was obtained. This procedure was repeated for 5 times to get 5 layers of nano TiO₂ film. The surface and cross-section of the nano TiO₂ film on the glass fibre were imaged by means of scanning electron microscope (SEM, Leo-1530, Germany) as shown in Fig. 1 in Body of text. The average diameter of TiO₂ particle is about 8 nm; the thickness of 5-layer nano TiO₂ film is about 600 nm. Stability of the TiO₂ film was evaluated by immersing the film in *aqua regia* for 24 hours, no obvious loss of the TiO₂ film was observed.

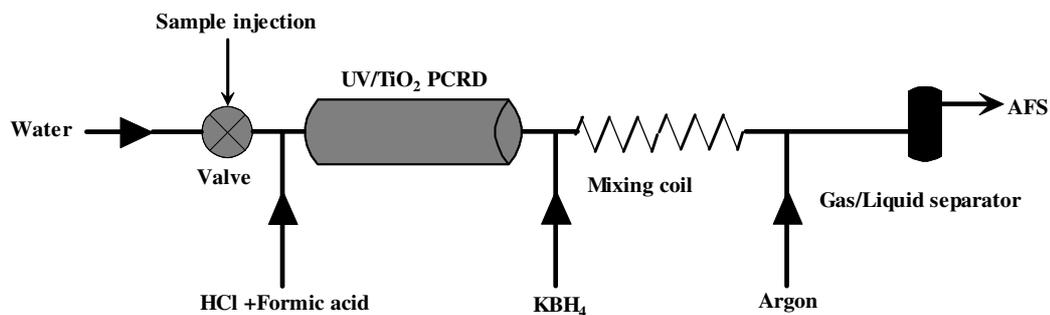


Fig. S1 Schematic diagram of UV/ TiO₂-PCRD-VG-AFS (the mixing coil is 30 cm in length and 0.8 mm I.D.)

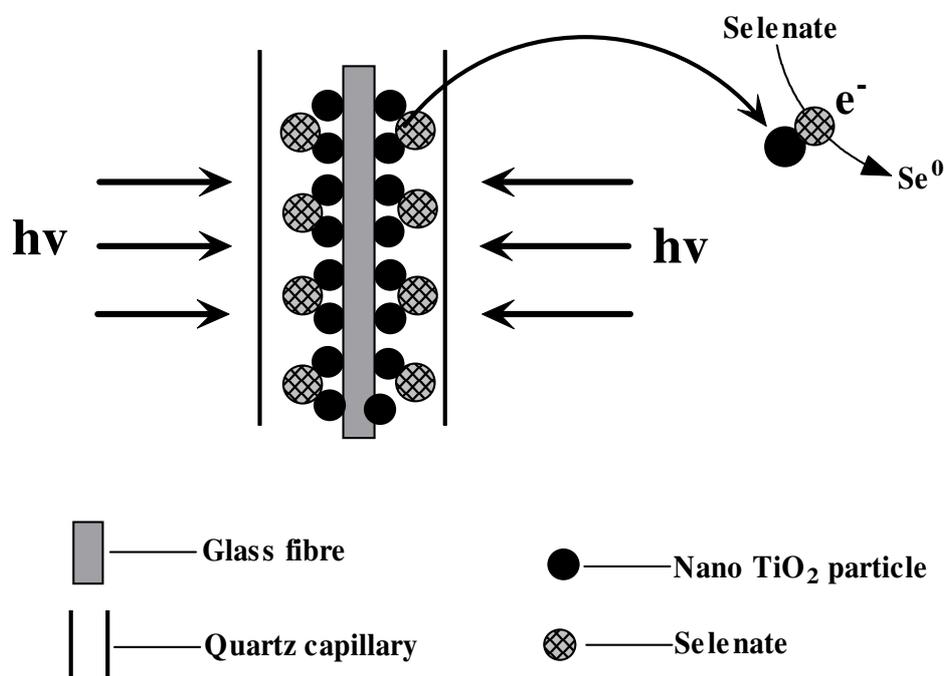


Fig. S2 Process of Se^{VI} reduction with UV/TiO₂-PCRD

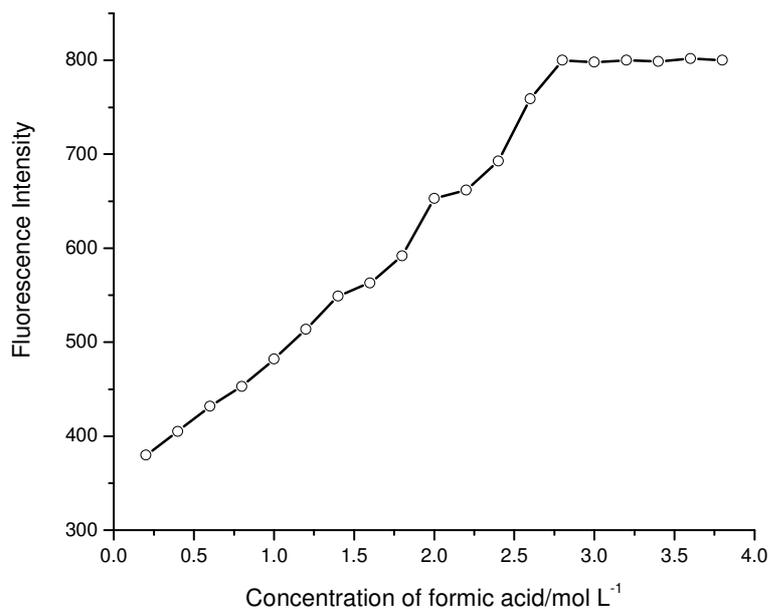


Fig. S3 Optimization of formic acid concentration.

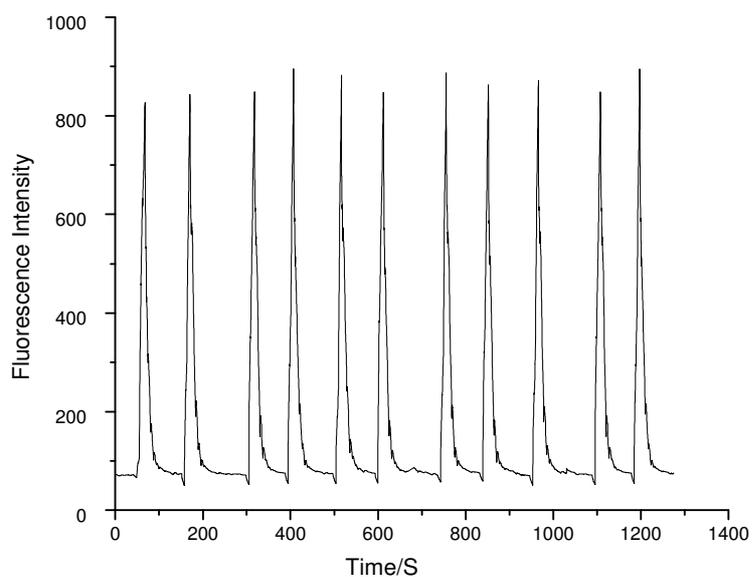


Fig. S4 Reproducibility for Se^{VI} in UV/TiO₂-PCRD-VG-AFS system (n=11)

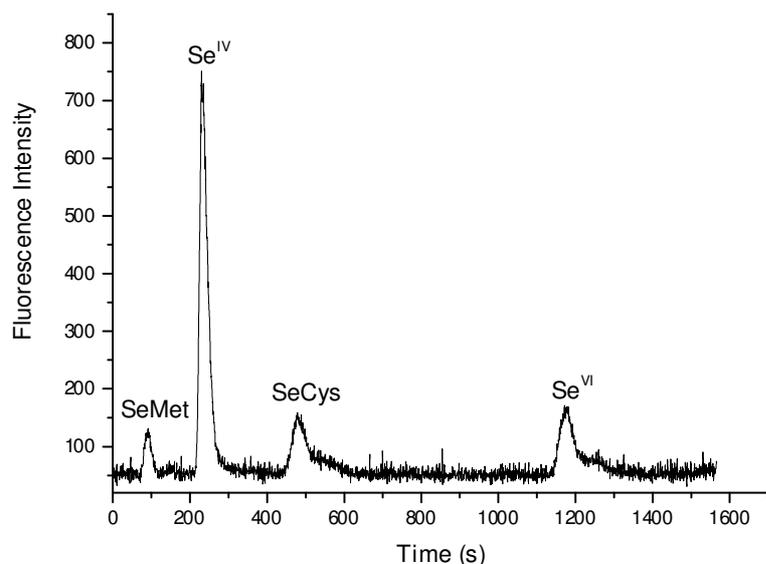


Fig. S5 Speciation of four selenium species by HPLC-UV/TiO₂-PCRD-VG-AFS Column: Shimadzu VP-ODS (4.6 μm) 4.6 I.D. × 150 mm in length; mobile phase: 5 mmol L⁻¹ tetrabutylammonium hydroxide (TBAH) + 4 mmol L⁻¹ oxalic acid + 5% (V/V) methanol (pH=6.0); flow rate: 1 mL min⁻¹; column temperature: 25 °C; sample size: 100 μL containing 1 μg mL⁻¹ each of selenium species.

Table 1 The optimized experimental conditions of FI- UV/TiO₂-PCRD-VG-AFS

Resonance wavelength/nm	196
Current of hollow cathode lamp (HCL)/mA	80
Photomultiplier Tube (PMT) voltage/V	- 320
Carrier gas (Argon) flow rate/mL min ⁻¹	400
Height of atomizer/mm	8
Read out mode	Peak height
HCl /mol L ⁻¹	2.3
Formic acid/mol L ⁻¹	2.8
KBH ₄ (W/V, %) containing 0.2% NaOH	2

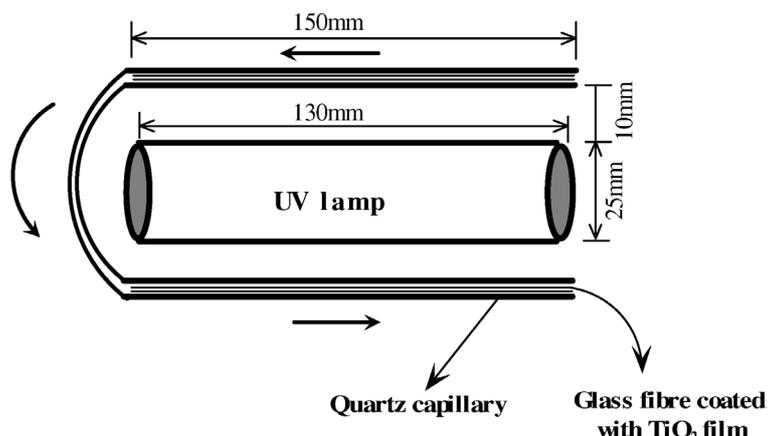


Fig. S6 Schematic diagram of UV/TiO₂ photocatalysis reduction device (UV/TiO₂-PCRD).

Details of the lamps and chromatographic equipment

A 40 W low pressure mercury lamp (Xinyuan Appliance Lighting Co. Ltd., China) was specially designed with 130 mm in length and 25 mm in diameter. The glass fibre was home made, 130 mm in length and 0.30 mm in diameter; the quartz capillary, 150 mm in length, 0.8 mm inner diameter and 1.6 mm outer diameter was purchased from Reafine Chromatography Ltd., China. A VG atomic fluorescence spectrometer (Beijing Raileigh Analytical Instrument Corporation) was used to monitor the concentration of selenium, in which a selenium coded hollow cathode lamp (196 nm, Beijing Institute of Vacuum Electronics Research, China) was used as an excitation-light source, and signal acquisition and processing were done by HWH software Version 1.0.¹ A Shimadzu HPLC 2010 was used for the separation of selenium species. All reagents were purchased from Sigma and Shanghai Chemicals, and were at least of analytical grade unless otherwise stated. Milli-Q water of 18 MΩ cm was purged with high purity nitrogen ($\geq 99.99\%$) for 30 min to remove dissolved oxygen and was used throughout this study.

Reference

1 Y. Hong, Q. Wang, H. Yan, J. Liang, X. Guo and B. Huang, *Spectrosc. Spectr. Anal.*, 2003, **23**, 354.