

Photo-induced Recovery, Optical Detection, and Separation of Noxious SeO_3^{2-} Using Mesoporous Nanotube Hybrid Membrane

Wojciech Warkocki,^[a] Sherif El-Safty,^{[a],[b]*} Mohamed A. Shenashen,^[a] Emad Elshehy,^[a] Hitoshi Yamaguchi,^[a] Naeem Akhtar^{a,b}

^aNational Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba-shi, Ibaraki-ken, 305-0047, Japan.

^bGraduate School for Advanced Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo, 169-8555, Japan.

E-mail: sherif.elsafty@nims.go.jp & sherif@aoni.waseda.jp

Supporting information S1:

Materials characterizations

Field-emission scanning electron microscopy (FE-SEM) images were obtained (Hitachi S-4300). Before insertion into the chamber, the samples were fixed onto the SEM stage using carbon tape. The Pt films were deposited on the membrane substrates at room temperature using an ion-sputter (Hitachi E-1030); the distance between the target and the membrane substrate was 5.0 cm. The membrane samples were also examined by high-resolution transmission electron microscopy (HR-TEM), bright-, and dark-field scanning transmission electron microscopy (BF- or DF-STEM), and dispersive X-ray analysis for elemental mapping (STEM-EDS) (JEOL, JEM model 2100F microscope). TEM instrument was operated at 200 kV acceleration voltage to obtain a lattice resolution of 0.1 nm and a spherical aberration of 1.0 mm. STEM and STEM-EDS instruments were operated at a camera length of 40 nm and a spot size of 1 nm. TEM and STEM images were recorded using a CCD camera. To obtain cross-sectional HRTEM image, the TSN-MS hybrid membrane was immersed in a 5 wt% phosphoric acid solution to etch the alumina matrix. The supernatant was collected through the centrifugation and the resultant solid was thoroughly washed several times. To record the plan-view TEM image, the TSN-MS hybrid membrane was prepared by dimple grinding followed by Ar ion polishing.

Small-angle X-ray scattering (SAXS) experiments were performed at room temperature. A two-dimensional (2D) confocal mirror (Rigaku Nanoviewer) and a pinhole collimator were used to obtain a focused high-flux/high-transmission and monochromatic X-ray beam of Mo-K α radiation ($\lambda = 0.07$ nm). SAXS profiles of the TSN-MS disc was subjected to absolute intensity scaling after normalizing the in-plane diffracted beams with substrate thickness.

Wide-angle powder X-ray diffraction (WA-XRD) patterns were measured by using a 18 kW diffractometer (Bruker D8 Advance) with monochromated CuK α radiation. The diffraction data were analyzed using the DIFRAC plus Evaluation Package (EVA) software with the PDF-2 Release 2009 databases provided by Bruker AXS. The standard diffraction data were identified according to the databases of the International Centre for Diffraction Data (ICDD). For poor quality diffraction data, the TOPAS package program provided by Bruker AXS 2009 for profile and structure analysis was applied to integrate various types of X-ray diffraction analyses by supporting all profile fit methods currently employed in powder diffractometry.

The textural surface properties of TSN-MS, including the specific surface area and the pore structure, were determined by N₂ adsorption–desorption isotherms obtained using a BELSORP MIN-II analyzer (BEL Inc., Japan) at 77 K. The pore size distribution was determined from the adsorption isotherms using the Barrett–Joyner–Halenda method. Specific surface area (S_{BET}) was calculated using multi-point adsorption data from a linear segment of the N₂ adsorption isotherms using the Brunauer–Emmett–Teller (BET) theory. Before N₂ isothermal analysis was performed, all of the samples were pre-treated at 300 °C for 8 h under vacuum until the pressure equilibrated to 10⁻³ Torr.

The SeO₃²⁻ anion concentration was determined using a Perkin Elmer Elan-6000 ICP-MS. The reflectance spectrum of the solid membrane sensor was recorded using UV-VIS-NIR spectrophotometer (Shimadzu, SolidSpec-3700). The SolidSpec-3700 enables measurements in the range from 175nm to 2600nm with an integrating sphere and three detectors: a photomultiplier tube (PMT) detector for the ultraviolet and visible region; InGaAs and PbS detectors for the near-infrared region. The use of the InGaAs and PbS detectors makes the sensitivity in the near-infrared region significantly high.

Buffer solutions were adjusted to ambient pH values using a Horiba F-24 (Kyoto, Japan) model micro-computerized pH/Ion meter.

Thermogravimetric and differential thermal analyses (TG and DTA, respectively) were measured using a simultaneous DTA-TG Apparatus TG-60 (Shimadzu, Japan).

Energy Dispersive X-ray microanalysis (EDX-130S) was used to determine the elemental compositions of the DPTC-immobilized TSN/PAA membrane.

The photo-induced recovery process of TSN-MS-selenite membrane disc was performed by using UV light and visible light sources (UV Lamp SLUV-6, T.HIROTA 100v, 50/60Hz, and λ of 254 and 365 nm) and (High pressure sodium (HPS) lamp, Philips Master SDW-T 100W, with wavelength range of 420-700 nm), respectively.

Photo-electrochemical measurements were recorded by a Zennium/ZAHNER-Elektrik instrument controlled by Thales Z 2.0 software. The cell device was designated with a conventional three-electrode systems under front side illumination of UV light (190 nm to 400 nm) containing, Ag/AgCl (3 M NaCl) as reference electrode, Pt (platinum) wire as counter electrode and a working electrode, respectively. The working electrode was prepared by dispersion of a minute amount of recovered TSN-MS amount in 100 μ L of water, and 10 μ L of the resulting colloidal dispersion was drop-cast onto a piece of ITO electrode with a fixed area of 1 cm² and dried in air at room temperature to form TSN-MS modified ITO working electrode. A constant potential of 0.5 V (vs. saturated Ag/ AgCl) was applied to measure transient photocurrent spectrum by using a mixture of 0.24 M Na₂S and 0.35 M Na₂SO₃ as an electrolyte.^[65] The cell device including the TSN-MS membrane was connected to an Avantes system of Ava-light-DHS deuterium-halogen light sources, which exhibit standard wide-range bands of deep UV deuterium (190 nm to 400 nm), deuterium lamp (215 nm to 400 nm), and halogen lamp (360 nm to 1500 nm). An Ava-Spec Avantes Fiber Optic spectrometer system (Avantes CIMPS-Abs-UV Ava-spec-2048x14) was used as a detector to determine the amplifying signal of the photocurrents.

Supporting Information S2

Immobilization of DPTC into NTs-PAA

The immobilization of DPTC into TSN-MS channels was evident by TG-DTA, element composition and EDX analyses (Fig. 2). A 10% wt.% weight loss was accompanied by two DTA endothermic and exothermic peaks from 25-550 °C. The weight loss of 1.7% of the adsorbed H₂O into membrane assigned the endothermic DTA peak around 50–150 °C. The exothermic DTA peak around 200–550 °C indicates the weight loss of 8.3% of immobilized organic moiety (DPTC). The EDS peaks of Si, Al, O, Ti, C, N, and S atoms indicated the embedding of DPTC into TSN-MS. The contributions of O, Si, and Al were mainly from the NTs/PAA membrane platforms. The C, N, and S peaks with 8 mass % were from the direct immobilization of DPTC (see *Fig.2D*), in agreement with the calculated amount of adsorption (q , mg/g) of the DPTC immobilized TSN-MS membrane.

Supporting Information S3

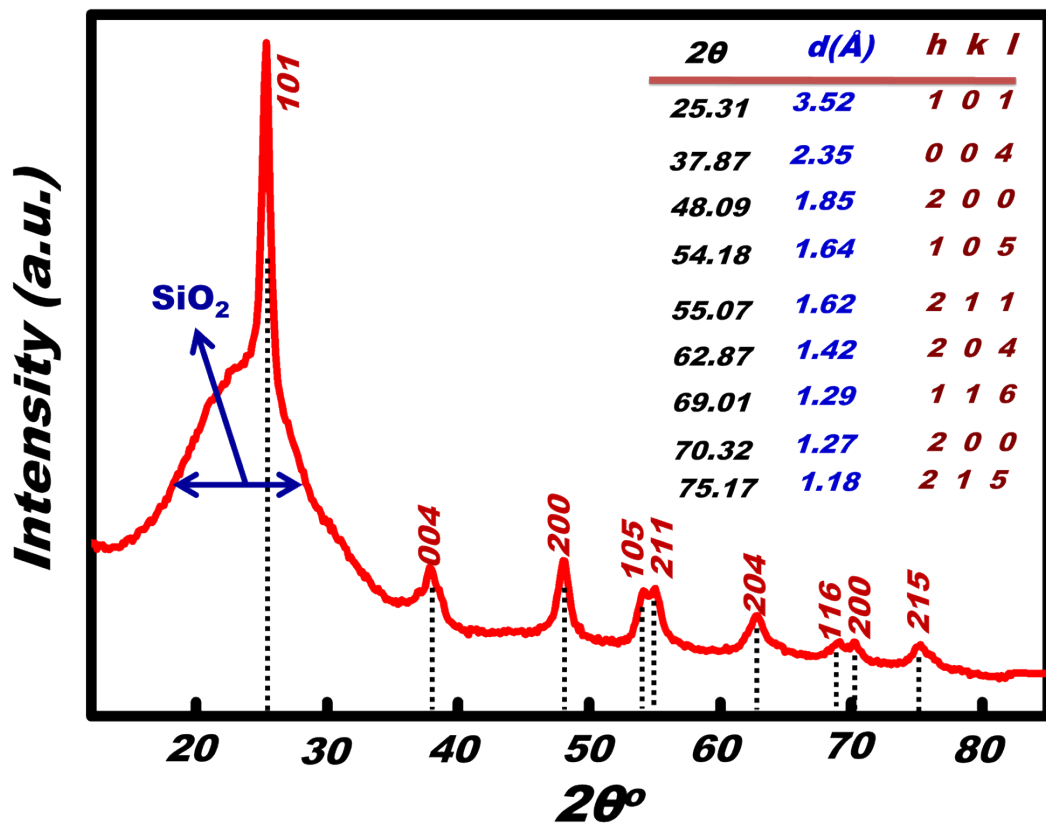


Figure S3:

Wide-angle XRD pattern of mesoporous $\text{TiO}_2\text{-SiO}_2$ nanotubes (TSN) after calcination at $500\text{ }^\circ\text{C}$ under air. The diffraction pattern indicated the formation of anatase phase of TiO_2 crystal with amorphous SiO_2 frameworks of TSN hybrid PAA membrane.

Supporting Information S4:

Separation of noxious SeO_3^{2-} using a wide-range of adsorbents

A number of adsorption assays of noxious SeO_3^{2-} anions were carried out using the PAA (porous anodic Al_2O_3 membrane), Al_2O_3 , TiO_2 , PAA- $\text{TiO}_2/\text{SiO}_2$ (TSN), $\text{TiO}_2/\text{SiO}_2$, and $\text{Al}_2\text{O}_3/\text{SiO}_2$, SiO_2 , and PAA- TiO_2 - SiO_2 -DPTC (TSN-MS) adsorbents at batch contact-time adsorption conditions of pH 2, and at room temperature. The uptake adsorption of noxious SeO_3^{2-} using these adsorbents was studied as a function of contact time (i.e. at 10 min, 2 and 5 hours, respectively) and noxious SeO_3^{2-} concentrations of 10, 45, 155, 813 and 1258 (see Table S1, Figure S4-1-3).

Our findings show that aside to the function of materials types, the contact time and DPTC-decorated PAA- TiO_2 - SiO_2 (TSN) play significant role in the enhancement of the adsorption uptake of noxious SeO_3^{2-} at a wide-range of feed solution concentration (i.e., 10-1258 ppb range). However, after 10 minutes of contact time adsorption assays, negligible uptake% in the range 0.03 to 13.2 % was determined using all adsorbents except PAA- TiO_2 - SiO_2 -DPTC (TSN-MS) that adsorb >> 98% of noxious SeO_3^{2-} . With 120 minutes of contact time adsorption assays, all adsorbents show slightly higher adsorption uptake in the range of 0.56 to 49.8%. In turn, the host capture TSN-MS shows capability to completely adsorb noxious SeO_3^{2-} anion and enables the suitable accommodation of the loaded noxious SeO_3^{2-} under longer time >> 2 hours without releasing to solution (Figure S4-1-3, Table S1). Figure (S4-3) shows the comparison in the uptake% between TSN and TSN-MS as a function time and noxious SeO_3^{2-} concentrations. Although the uptake % noxious SeO_3^{2-} using TSN was increased from 10% to 60% with time range of 10 min to 5 hours, the TSN-MS shows complete adsorption either at 10 minutes or at 5 hours of contact-time assays of noxious SeO_3^{2-} anion.

Under our adsorption/separation condition, in which the contact-time was 10 minutes, one can neglect the noxious SeO_3^{2-} uptake % of the membrane textural body of TSN scaffolds compared with the 98% uptake of DPTC-decorated TSN (TSN-MS). The exclusive segregation, in addition to the visual signaling response of SeO_3^{2-} target species, in the order of 10 minutes using TSN-MS indicates the following:

- 1) The immobilization of DPTC was dense and tightly decorated and coated the surfaces of the entire longitudinal TSN nanochannels of macroscopic membrane (as shown in BF-STEM mapping and elemental analysis distribution, see Figures 1 and 2);
- 2) Under further pressure-assisted approach, the DPTC coverage the surface area of TSN through the H-bonding interactions that preferably rearranged to form covalent Ti–O–S bonds, leading to high stability of TSN surface-bound DPTC ligand; and
- 3) Because of building TSN-MS design with mesoporous tubular structures inside PAA, the TSN-MS showed higher uptake % of a wide-range of noxious SeO_3^{2-} concentrations than that of bulk Al_2O_3 , TiO_2 , PAA- $\text{TiO}_2/\text{SiO}_2$ (TSN), $\text{TiO}_2/\text{SiO}_2$, and $\text{Al}_2\text{O}_3/\text{SiO}_2$ and SiO_2 metal oxide adsorbents, respectively, even at a long contact-time \gg 5 hours (see ESI, Table S1 and Figure S4-1-3).

Table (S1): Study the effect of different metal oxides on the adsorption process of SeO_3^{2-} under optimum conditions of batch contact-time adsorption of pH 2, 20 mL of feed solution, and 20 °C.

Material	Treatment	Adsorbent composition	Uptake%	
			10 min	2h
PAA membrane	--	Al_2O_3	4.87	70.9
PAA- SiO_2	Etching (5% H_3PO_4)	SiO_2	0.03	2.56
PAA- SiO_2	--	Al_2O_3 - SiO_2	0.14	11.65
PAA- TiO_2	Etching (5% H_3PO_4)	TiO_2	13.2	49.87
PAA- TiO_2 - SiO_2	Etching (5% H_3PO_4)	TiO_2 - SiO_2	7.38	36.78
PAA- TiO_2 - SiO_2	--	TSN	11.37	47.16
PAA- TiO_2 - SiO_2 /DPTC	--	TSN-MS	98.46	99.03

5 wt% phosphoric acid solution was used to etch the alumina matrix

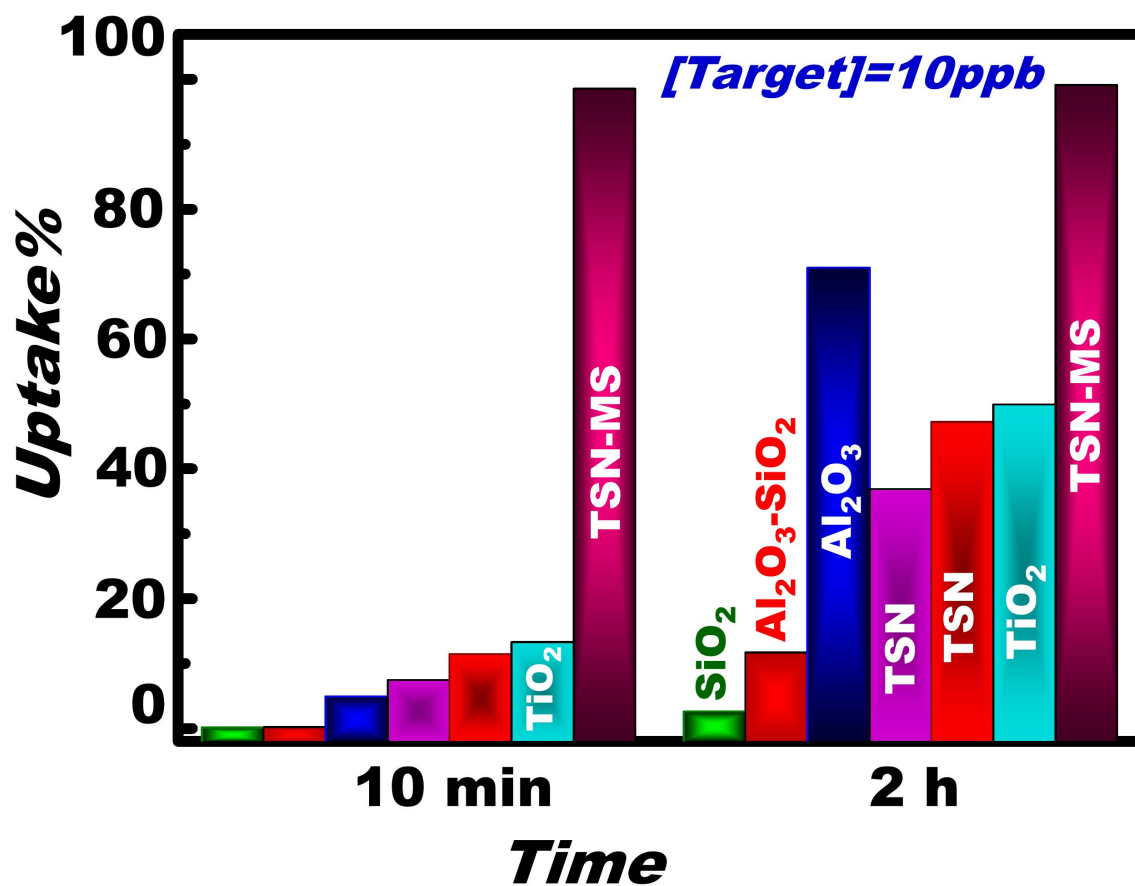


Figure (S4-1): Time dependence on the filtration/separation assays of SeO_3^{2-} of different metal oxides under the following condition: 10 ppb SeO_3^{2-} feed solution, (A) 10 min and (B) 120 min response time, pH 2, 20 mL of feed solution, 50 kPa vacuum pressure, and 25 °C. The SeO_3^{2-} solution was quantitatively measured by ICP-MS.

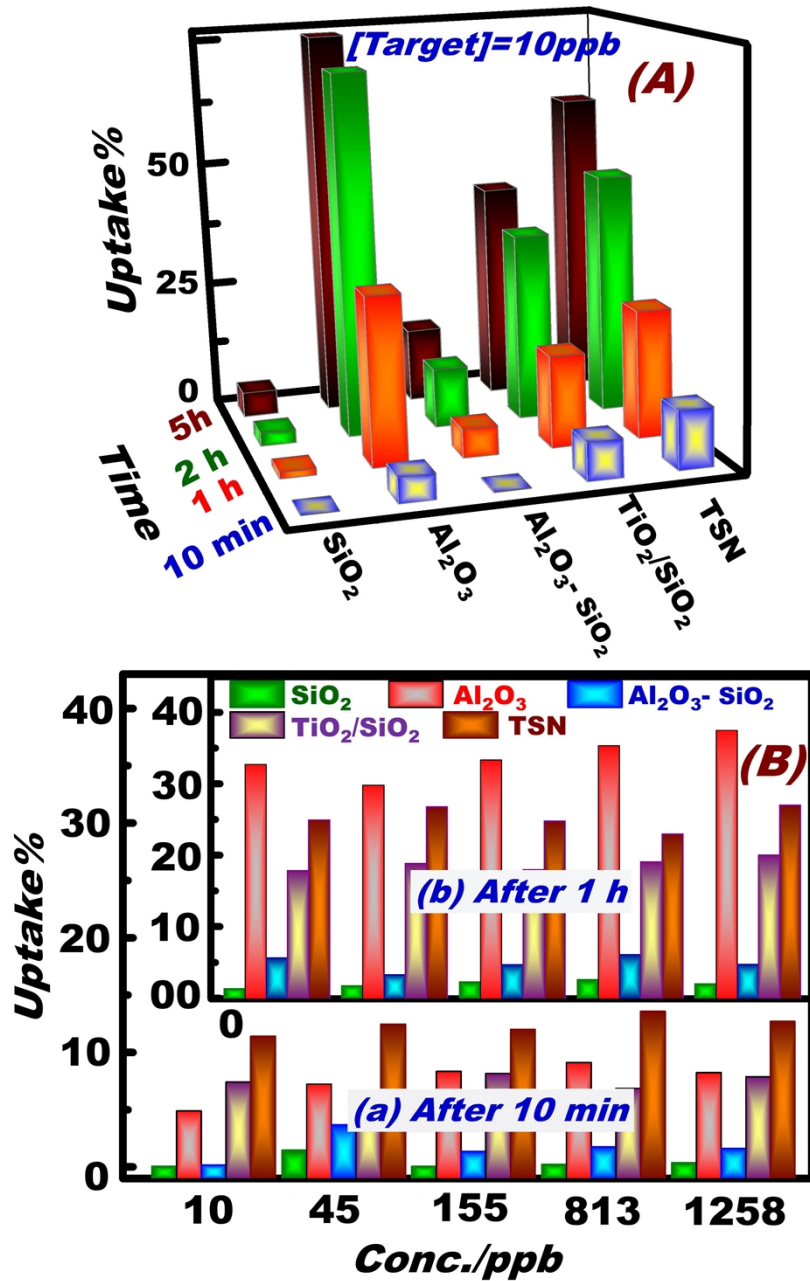


Figure (S4-2): (A) Time dependence and (B) concentration effect on the filtration/separation assays of SeO_3^{2-} of different metal oxides under the following condition: pH 2, 20 mL of feed solution, 50 kPa vacuum pressure, and 25 °C. The SeO_3^{2-} solution was quantitatively measured by ICP-MS.

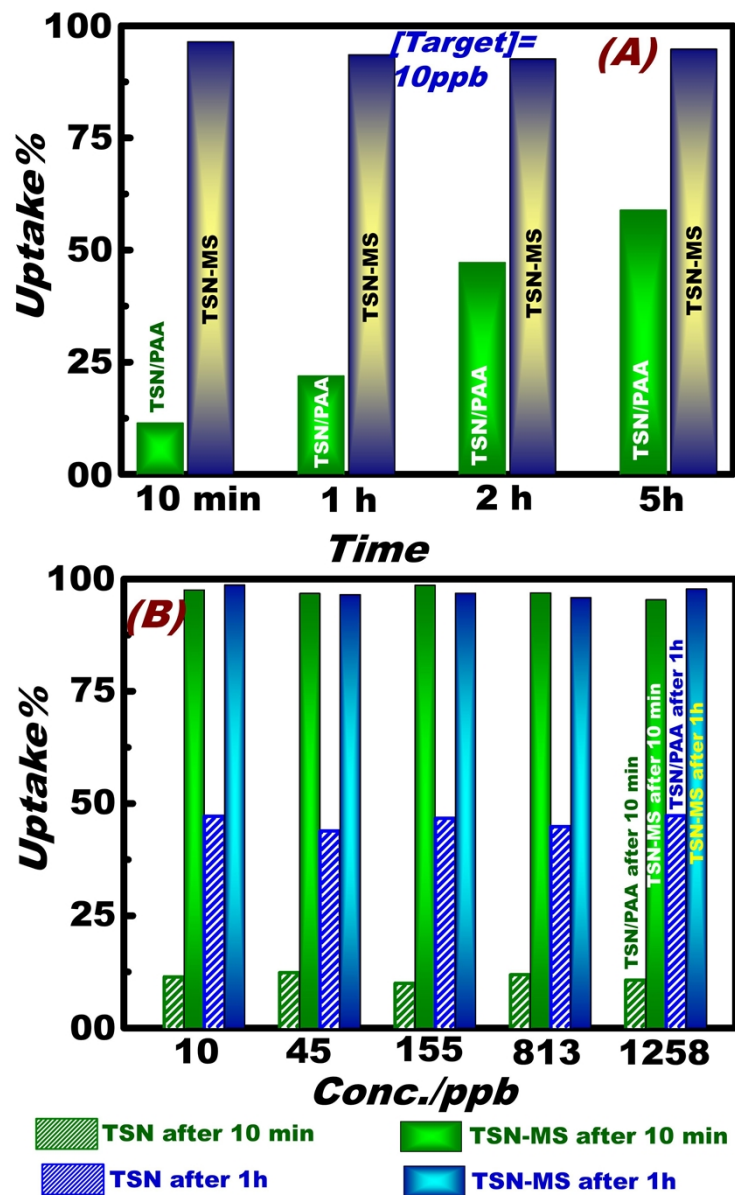


Figure (S4-3): The comparison between TSN/PAA and TSN-MS as a function of (A) Time dependence and (B) concentration effect on the filtration/separation assays of SeO_3^{2-} of under the following condition: pH 2, 20 mL of feed solution, 50 kPa vacuum pressure, and 25 °C. The SeO_3^{2-} solution was quantitatively measured by ICP-MS.

Supporting Information S5:

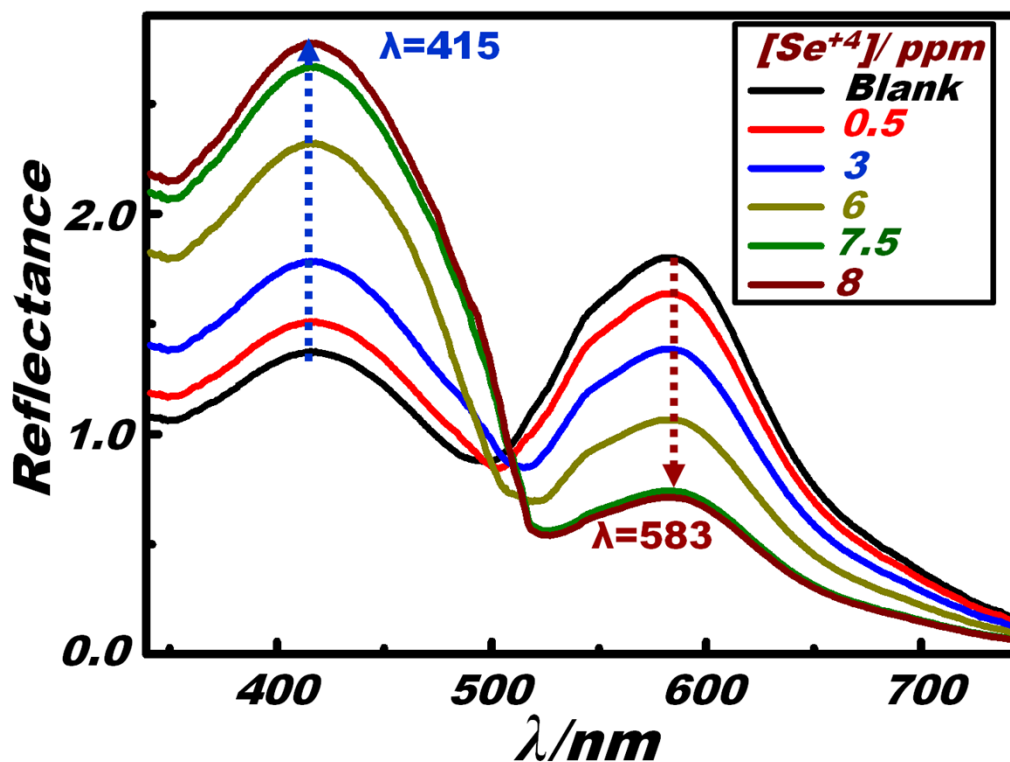


Figure (S5): UV-Vis spectroscopy of DPTC in solution shows signaling response spectra at λ_{max} of 415 and 583 nm, respectively, with addition of SeO_3^{2-} anion concentration range of 0.5-8.0 ppm at pH 2 and 25 °C.