Supporting Information for

Enhanced photocatalytic selectivity of noble metallized TiO_2 (Au-, Ag-, Pt- and Pd-TiO_2) nanoparticles for the reduction of selenate in water: Tunable Se reduction product $H_2Se_{(g)}$ vs. $Se_{(s)}$

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KEYWORDS: Photocatalysis, selenate, selenium, noble metal deposited TiO_2, photoreduction, direct Z-scheme

S1. Photocatalytic experimental set-up

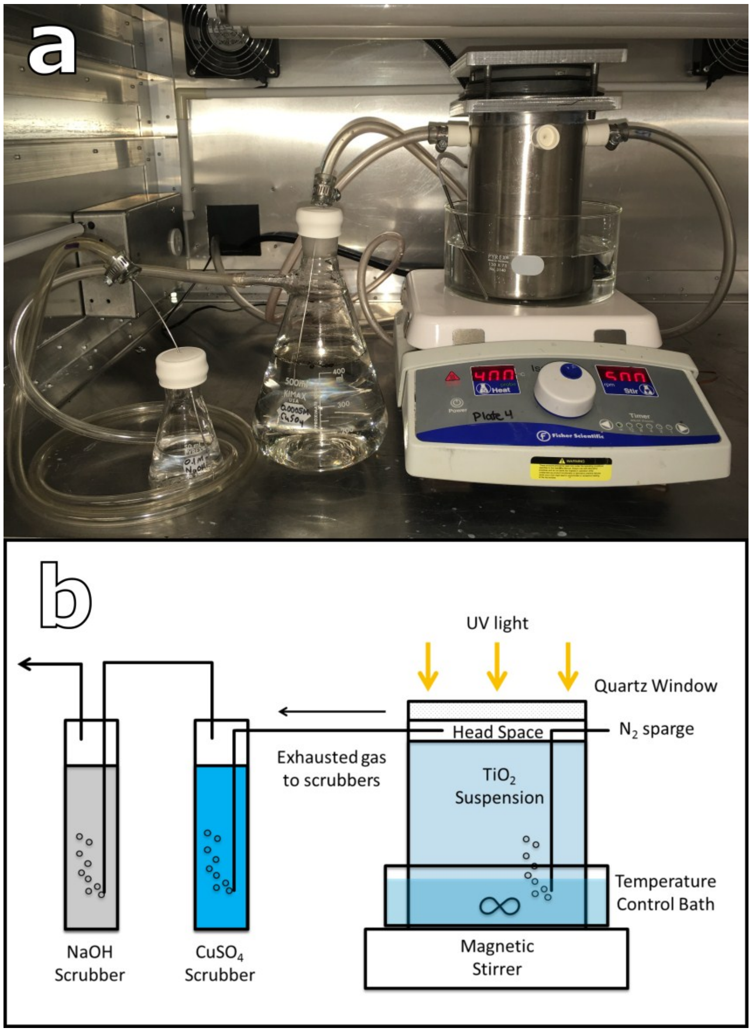

Figure S1. (a) Photograph and (b) schematic image of the batch photocatalytic reaction set-up for the reduction of selenium oxyanions in synthetic and real industrial FGDW.

S2. Noble metal deposited TiO_2

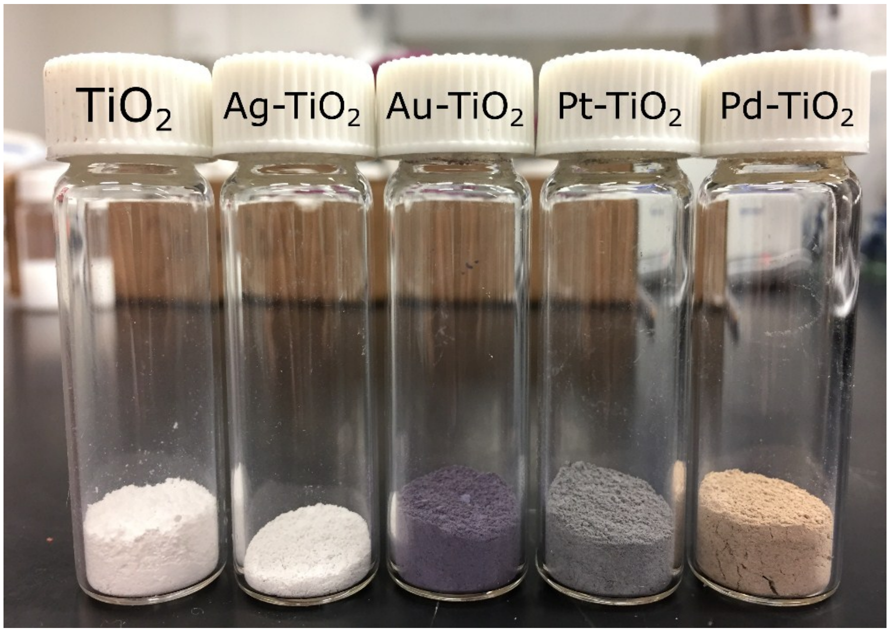

Figure S2. Photograph presenting the various colours of the final noble metal deposited TiO_2 photocatalysts. From left to right: TiO_2, Ag-TiO_2, Au-TiO_2, Pt-TiO_2 and Pd-TiO_2.

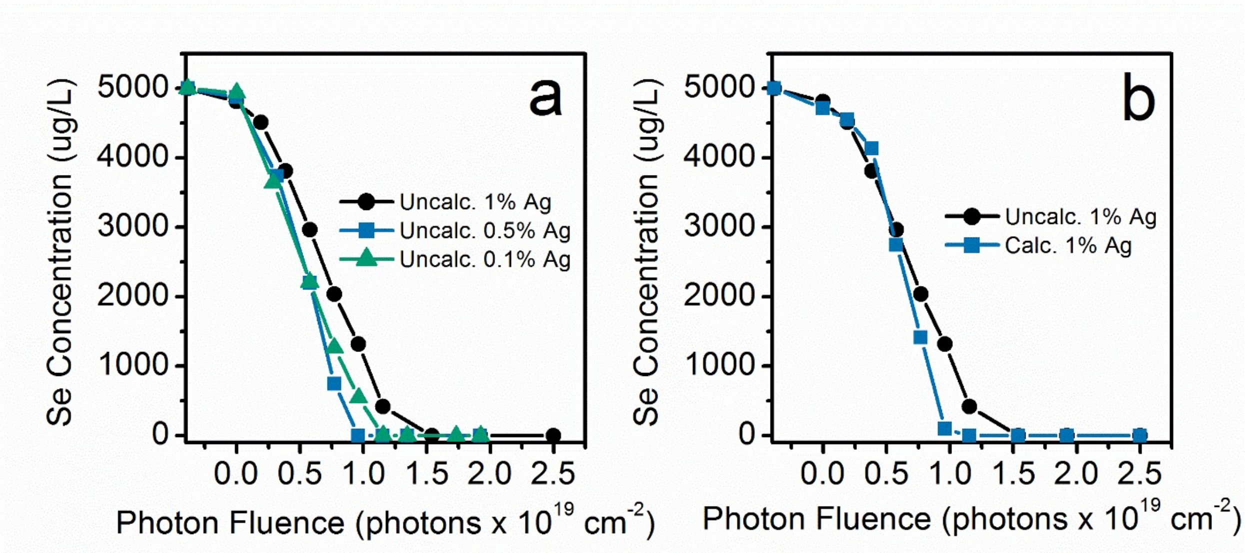

Figure S3. (a) Photocatalytic reduction of 5 mg/L (as Se) sodium selenate in MilliQ over varying concentrations of silver deposited on TiO_2 and (b) Photocatalytic reduction of 5 mg/L (as Se) sodium selenate in MilliQ over calcined and uncalcined samples of 1 wt% Ag-TiO_2.

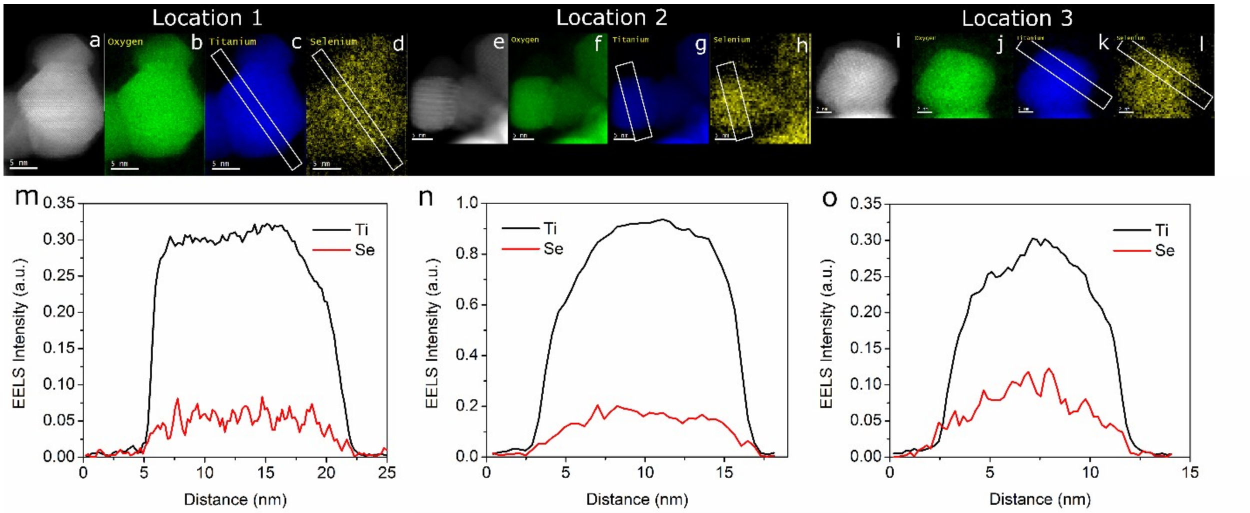

Figure S4. High resolution transmission electron microscopy (HR-TEM) with electron energy loss spectroscopy (EELS) for three separate locations on the TEM grid prepared with Se deposited onto TiO_2 after 1.0 photons $\times 10^{19}$ cm^{-2} of UV exposure. (a-d, e-h, i-l) HR-TEM, EELS O imaging, EELS Ti Imaging, EELS Se imaging, for location 1, 2 and 3 respectively and (m-o) EELS line scans for location 1, 2 and 3 respectively.

S3. $O_2^{\bullet-}$ / $^{\bullet}HO_2$ Radical Experiments

Experiments were conducted to reveal the variations in hydroperoxyl generation rate with the varying noble metal deposited TiO_2 samples. Dihydroethidium (DHE) at a concentration of 5×10^{-5} M was used to quantitatively detect superoxide (and consequently hydroperoxyl) radical ($O_2^{\bullet-}$ / $^{\bullet}HO_2$) generated by the TiO_2 photoreduction system. Unless otherwise stated, a 0.08 M DHE stock solution in DMSO was used and stored in the dark at –20°C for at most 2 days. Superoxide concentrations were indirectly determined by monitoring the increase in fluorescence intensity at 580 nm (ex. 480 nm), attributed to the formation of the superoxide-specific product 2-hydroxyethidium, at set time intervals [1–4]. When superoxide dismutase (SOD) was used, it was added prior to the dark adsorption period and the aforementioned DHE procedure was conducted without further modifications. Fluorescence spectra were recorded on a Photon Technology International QM-4SE fluorimeter and were smoothed using Origin Pro by removing Fourier components with frequencies higher than a particular cut-off frequency prior to integration of the area under the emission peak. A calibration curve for 2-hydroxyethidium was generated by reacting known amounts of DHE with potassium nitrosodisulfonate (Fremy's Salt), which has been demonstrated to yield the same superoxide-specific oxidation product [5,6]. The previously mentioned procedure for photoreduction experiments was adapted for this probe molecule, with DHE replacing selenium. Contrary to previous investigations where DHE was added immediately after stopping illumination [7], it was necessary to have DHE present during illumination because the half-life of superoxide and disproportionation of hydroperoxyl are significantly lower at low pH compared to alkaline conditions [8].

References

[1] B. Fink, K. Laude, L. McCann, A. Doughan, D.G. Harrison, S. Dikalov, Detection of intracellular superoxide formation in endothelial cells and intact tissues using dihydroethidium and an HPLC-based assay, Am. J. Physiol. Cell Physiol. 287 (2004) C895-902. doi:10.1152/ajpcell.00028.2004.

[2] H.M. Peshavariya, G.J. Dusting, S. Selemidis, Analysis of dihydroethidium fluorescence for the detection of intracellular and extracellular superoxide produced by NADPH oxidase, Free Radic. Res. 41 (2007) 699–712. doi:10.1080/10715760701297354.

[3] H. Zhao, S. Kalivendi, H. Zhang, J. Joseph, K. Nithipatikom, J. Vásquez-Vivar, B. Kalyanaraman, Superoxide reacts with hydroethidine but forms a fluorescent product that is distinctly different from ethidium: potential implications in intracellular fluorescence detection of superoxide, Free Radic. Biol. Med. 34 (2003) 1359–1368.

[4] J. Chen, S.C. Rogers, M. Kavdia, Analysis of kinetics of dihydroethidium fluorescence with superoxide using xanthine oxidase and hypoxanthine assay, Ann. Biomed. Eng. 41 (2013) 327–337. doi:10.1007/s10439-012-0653-x.

[5] F.R.M. Laurindo, D.C. Fernandes, C.X.C. Santos, Assessment of superoxide production and NADPH oxidase activity by HPLC analysis of dihydroethidium oxidation products, Methods Enzymol. 441 (2008) 237–260. doi:10.1016/S0076-6879(08)01213-5.

[6] J. Zielonka, H. Zhao, Y. Xu, B. Kalyanaraman, Mechanistic similarities between oxidation of hydroethidine by Fremy's salt and superoxide: stopped-flow optical and EPR studies, Free Radic. Biol. Med. 39 (2005) 853–863. doi:10.1016/j.freeradbiomed.2005.05.001.

[7] S. Thabet, F. Simonet, M. Lemaire, C. Guillard, P. Cotton, Impact of photocatalysis on fungal cells: depiction of cellular and molecular effects on Saccharomyces cerevisiae, Appl. Environ. Microbiol. 80 (2014) 7527–7535. doi:10.1128/AEM.02416-14.

[8] M. Hayyan, M.A. Hashim, I.M. AlNashef, Superoxide Ion: Generation and Chemical Implications, Chem. Rev. 116 (2016) 3029–3085. doi:10.1021/acs.chemrev.5b00407.