

Electronic Supplementary Information

Exploiting electron storage in TiO₂ nanoparticles for dark reduction of As(V) by accumulated electrons

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The Electronic Supplementary Information (ESI) includes:

(A) Materials and Methods

(B) SCHEME S1

Small hydrated 101 anatase cluster showing the proposed coordination of the Ti(III) centre to account for the RT EPR signal. See reference 9. Chloride ion (blue) replaces one OH ion, increasing the distortion of the octahedral symmetry of surface titanium (green). Oxygen, hydrogen and carbon atoms are symbolized by red, grey and yellow balls

(C) Figure S1:

Fig. S1: RT EPR spectrum of a 3 mM TiO₂ sol ([ethanol] = 16.2 M, [H₂O] = 2.8 M and [HCl] = 40 mM) with accumulated electrons: spectra obtained before (black line) and after (grey line) anaerobic As(V) addition. [As(V)]_{initial} = 2.1 × 10⁻⁴ M; [As(V)]_{final} = 1.3 × 10⁻⁴ M.

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Materials and Methods

Reagents: Phenylglyoxylic acid (Sigma) was recrystallized from carbon tetrachloride (Merck). All other chemicals were of the highest purity available and used as received: 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride, methylene blue, (Merck, for microscopy), sodium meta-arsenite (NaAsO_2 , Baker) and sodium arsenate dibasic 7-hydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, Baker), ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$, Stanton); potassium antimonyl tartrate ($\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot 1/2 \text{H}_2\text{O}$, Baker), sulphuric acid (Biopack), ascorbic acid (Anedra), oxalic acid dihydrate ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, Merck), 2-propanol ($\text{C}_3\text{H}_8\text{O}$ Biopack), Co(II) standard solution ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, ChemLab).

All solutions were prepared using ultra-pure water (resistivity $>18 \text{ M}\Omega \cdot \text{cm}$). HCl (Merck, p.a. 37%) were used to adjust the pH. Titanium(IV) ethoxide (Aldrich), and absolute ethanol (Cicarelli, p.a. 99.5%) were employed in the synthesis of TiO_2 sols.

Preparation of TiO_2 sols. TiO_2 colloids were prepared by controlled acid hydrolysis of the alkoxide under a low water to titanium molar ratio, $h = \text{H}_2\text{O}:\text{Ti} = 6.5$. Briefly, a stock solution obtained by dissolving 1 cm^3 of $\text{Ti}[\text{OCH}_2\text{CH}_3]_4$ in 20 cm^3 of absolute ethanol was carefully prepared and preserved from humidity. The colloid was synthesized by slowly adding the stock solution to 200 cm^3 ethanol-water mixture ($[\text{ethanol}] = 17.0 \text{ M}$; $[\text{H}_2\text{O}] = 0.10 \text{ M}$, $[\text{HCl}] = 0.028 \text{ M}$ maintained at $1 \text{ }^\circ\text{C}$. The sol was continuously stirred in the dark for 48-72 hours, to promote aging and a more stable and uniform size distribution. After this period, the solutions were concentrated at $35 \text{ }^\circ\text{C}$ under vacuum in a rotary evaporator, and used within a month.

Irradiation procedures. Photolysis were carried out in 3 cm^3 square quartz prismatic cells, (path length, $l = 1 \text{ cm}$). A high pressure Hg-Xe lamp coupled to a Kratos-Schoeffel monochromator was used to select the $303 \pm 10 \text{ nm}$ irradiation wavelength. Photon flux determinations were performed by actinometry using phenylglyoxylic acid.² Absorbed light photon flux was evaluated as $P_a = P_0 \times (1 - 10^{-A_{303}})$ using the incident photon flux, $P_a = 5.24 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ and the measured absorbance, A_{303} . Most of the experiences were performed using 3 mM TiO_2 sols, which gives $A_{303} \sim 4.5$.

² Defoin, A.; Defoin-Straatmann, R.; Hildenbrand, K.; Bittersmann, E.; Kreft, D.; Kuhn, H.J. *J. Photochem.* **1986**, *33*, 237. b) Kuhn, H. J.; Görner, H. *J. Phys. Chem.* **1988**, *92*, 6208.

Analytical determinations

Reduction of As(III) species by stored charges.

At variance with As(V) species, As(III) cannot be determined by a simple colorimetric technique. Thus, in order to quantify As(III) consumption by accumulated charges a different approach was used. Total As remaining in the liquid phase was evaluated by TXRF technique after removing TiO₂ nanoparticles and by precipitation and filtration. The hypothesis behind this procedure is that reduced As(0) dispersed or adsorbed in the semiconductor particles can be removed from the solution by filtration.

For this purpose, a convenient amount of a 0.1% w/v oxalic acid dihydrate solution in 2-propanol, was added to the samples. The precipitate was separated by filtration with cellulose acetate membrane (0.22 μm, Millipore). The colour of the precipitate depends on whether or not the TiO₂ sol had been previously irradiated. A grey-bluish solid was clearly discernible onto the semiconductor surface but solely in the samples treated with accumulated electrons. These results suggest the formation of As(0).

After this procedure, elemental analysis of total As and Ti in solution in was carried out using an X-ray fluorescence spectrometer with total reflection geometry (TXRF) S2-PICOFOX. The spectrometer consists of a tube with a Mo anode on 50kV and 600 μA and a 30mm² SDD detector with resolution of 160 eV. The acquisition time for each spectrum was 300 s. Co(II) standard solution (Co(NO₃)₂·6H₂O, ChemLab) was used as internal standard for analytical determinations (LD: 0.005 mg L⁻¹)¹.

In a typical experiment, (65 μM As(III)), we found that the concentration of total As (Ti) in the liquid phase was 9.75 ± 0.10 μM (187 ± 19 μM) and 0.65 ± 0.07 mM (187 ± 19 μM) in the blank and photolyzed samples. The results showed a similar and very efficient separation of the solid phase as the remaining Ti detected was about 6% of the original. However, a considerable loss of As was observed in the blank after the precipitation step, probably as result of As(III) chemisorption.

SCHEME S1

Small hydrated 101 anatase cluster showing the proposed coordination of the Ti(III) centre to account for the RT EPR signal. Chloride ion (blue) replaces one OH ion, increasing the distortion of the octahedral symmetry of surface titanium (green). Oxygen, hydrogen and carbon atoms are symbolized by red, grey and yellow balls

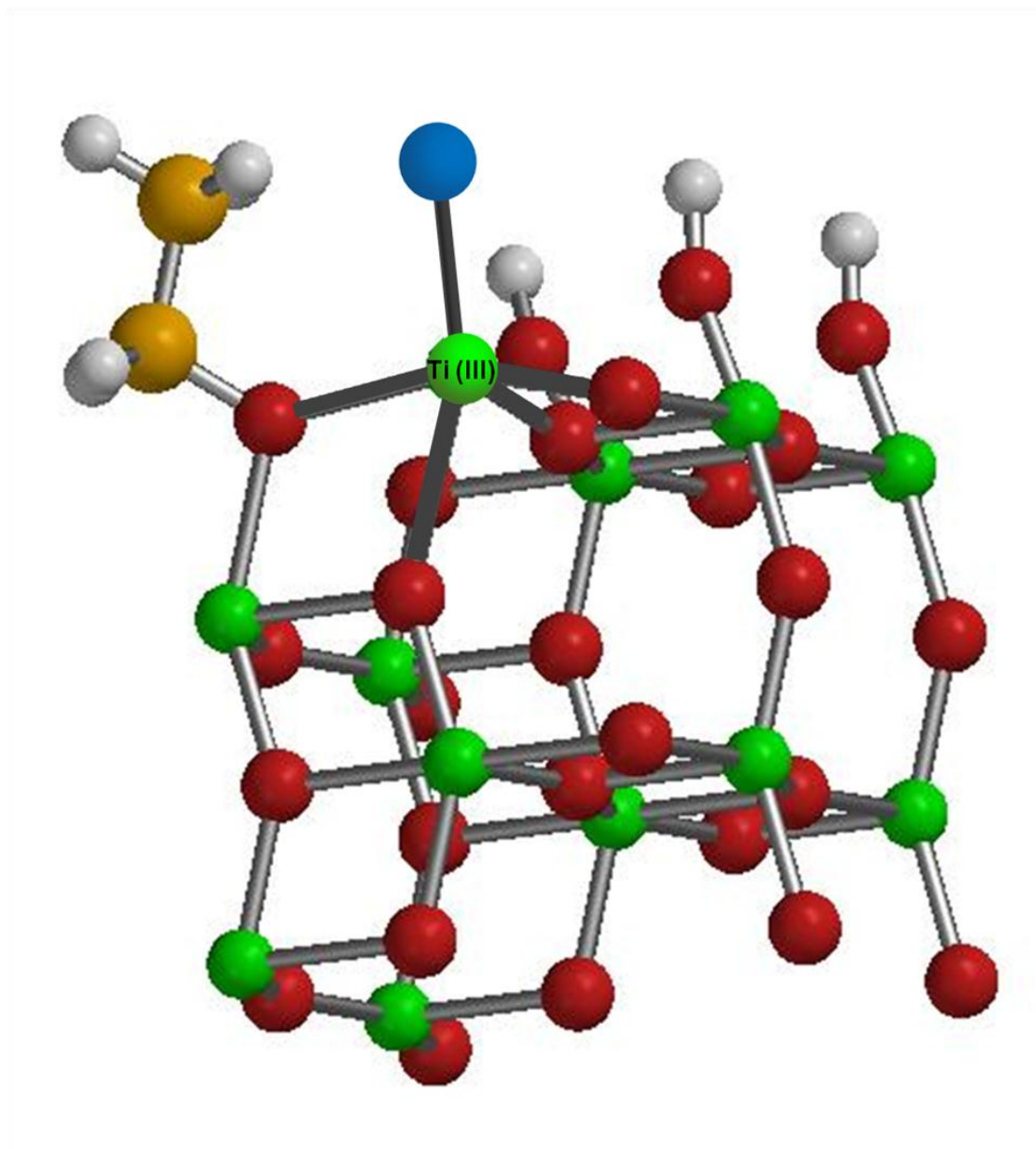


FIGURE S1

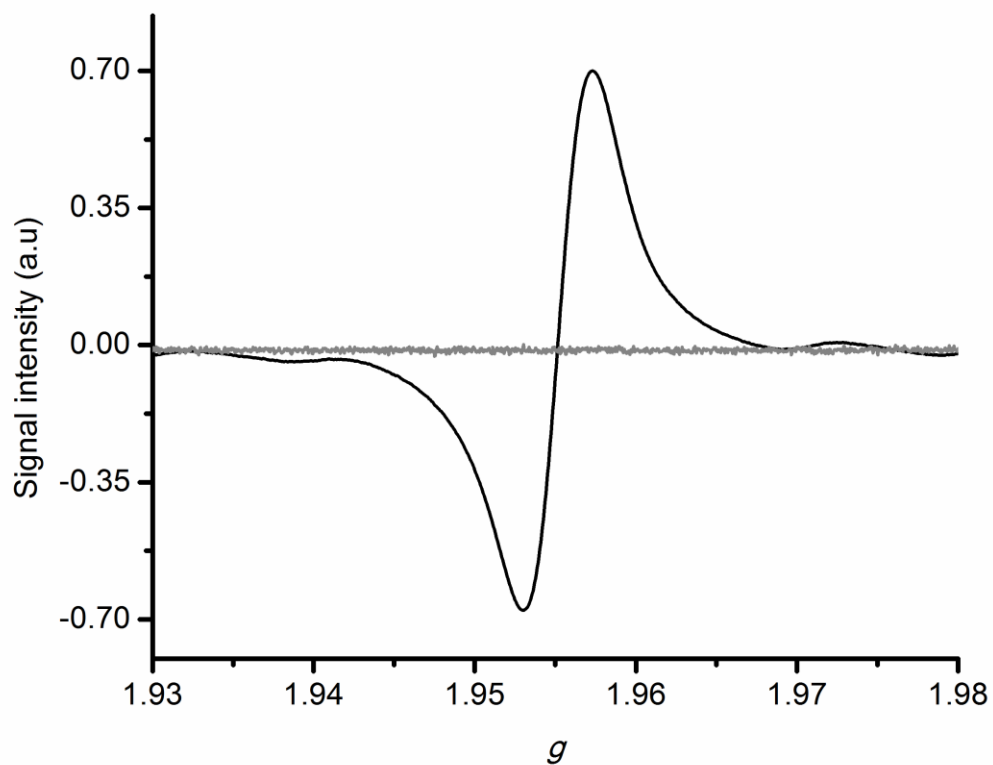


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