

COMMUNICATION

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

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UV irradiation of an ethanolic sol of TiO₂ nanoparticles produces a trapped Ti(III) centre and a noticeable Burstein shift. Direct evidence that the accumulated charges can drive the otherwise forbidden reduction of As(v) by conduction band electrons is presented.

Although TiO₂-valence band holes have powerful oxidation strength, the ability of conduction band (CB) electrons to drive useful reductions is limited by the fact that most inorganic and organic substrates are reduced at potentials more negative than the CB edge.¹ Hence, with the exception of the reduction of some nitro- and halogenated compounds and heavy metals (Cr(vi), Hg(II)), all of environmental significance, the cathodic process is usually restricted to the reduction of dissolved oxygen to avoid recombination and enhance photocatalytic oxidations.^{2–4} To overcome this limitation, it is possible to use sacrificial donors (R) that generate intermediates (R⁺) of strong reducing power,^{3,4} by reaction with photoinduced HO• radicals or holes, as schematically shown in reaction (1):



Common examples of sacrificial donors are primary or secondary alcohols, e.g. CH₃OH, (CH₃)₂CHOH, and carboxylic acids such as formic acid, which produce α-hydroxymethyl (R⁺ = •CH₂OH, •C(CH₃)₂OH or carboxyl radicals •CO₂[−]).

These intermediates have standard reduction potentials well above the CB, *E*₀ vs. NHE (CH₂O, H⁺/•CH₂OH) = −0.97 V, ((CH₃)₂CO, H⁺/•C(CH₃)₂OH) = −1.30 V and *E*₀ (CO₂/•CO₂[−]) = −1.8 V,^{5–7} and expand the range of the possible reductions.

On the other hand, the anaerobic UV irradiation of TiO₂ sols in the presence of these donors is known to result in electron accumulation. The number of electrons that each particle can hold in the steady state depends on the balance between the rate of generation and the rates of charge transfer and recombination under accumulation.⁸ Some of us have recently reported that TiO₂ colloids, prepared by the HCl catalyzed hydrolysis of a titanium alkoxide at a low water to titanium molar ratio, *h* = 6.5, display an unusually high electron storage capacity.⁹

It has been recognized that accumulation of electrons on semiconductor nanoparticles or hybrid metal–semiconductor heterostructures^{10–12} can promote reactions that occur at potentials more negative than the CB.^{13,14} However, the experimental evidence is very scarce,^{10,15,16} and, in most cases, it is very difficult to disentangle the actual mechanism by which the reduction takes place. It is apparent that electron accumulation can not only increase the reductive strength by moving the Fermi level of the semiconductor to more negative potentials, but may also support the occurrence of concerted multielectron transfer processes. Although the simultaneous transfer of two or more electrons is under continuous debate, recent experimental evidence¹⁷ and theoretical analysis^{18,19} indicate that the concerted mechanism cannot be discarded *a priori*. However, direct evidence in favour of successive or concerted electron transfer is very difficult to obtain and, to our knowledge, it is still a pending task in the elucidation of the heterogeneous photocatalytic mechanisms.²⁰

The results reported here show that As(v) can be reduced in the dark by electrons stored in alcoholic TiO₂ nanoparticles. Besides its environmental significance,^{21,22} As(v) is a good probe to assess the effectiveness of the accumulated electrons as the reported one electron reduction potential of this species, *E*₀ (As(v)/As(IV)) = −1.2 V vs. NHE,²³ lies well above the TiO₂ CB.

As reported elsewhere, the anaerobic irradiation of the ethanolic TiO₂ sols results in a typical blue coloration that is

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† Electronic supplementary information (ESI) available: Experimental details, a scheme showing the proposed coordination of the Ti(III) centre that accounts for the RT EPR signal and a figure displaying the EPR spectra of the samples before and after the removal of the stored charges by As(v) species. See DOI: 10.1039/c3cp51349a

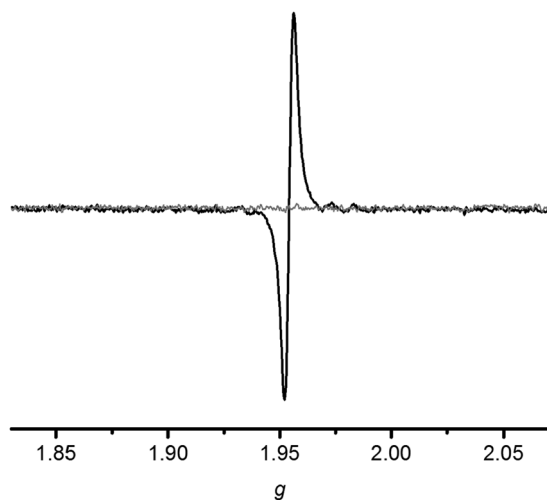


Fig. 1 RT EPR spectrum of a 3 mM TiO_2 sol ([ethanol] = 16.2 M, $[\text{H}_2\text{O}] = 2.8$ M and $[\text{HCl}] = 40$ mM) obtained before (grey line) and after (black line) anaerobic irradiation, respectively. Irradiation conditions are: $\lambda = 303 \pm 10$ nm, $P_0 = 3.64 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$.

detected as a broad band in the visible region between 400 and 800 nm.^{24,25} We have previously reported that the irradiated anaerobic samples of the synthesized colloids showed an intense EPR signal at $g = 1.9551$ (see Fig. 1), which can certainly be ascribed to a Ti(III) species.

Strikingly, and at variance with the common practice, the signal is detected at room temperature (RT, 298 K).^{26,27} It has been shown, through a detailed combined FTIR-EPR investigation,⁹ that coordination of bidentate ethoxide to the TiO_2 surface and replacement of surface hydroxyl groups by chloride ions are strongly correlated with the high electron storage capacity of this system. It is also apparent from the studies that chloride bonding lengthens spin relaxation times and becomes essential to facilitate the RT detection of Ti(III) species by reducing their normal line broadening. For completion we have included a scheme of a small hydrated 101 anatase cluster in the ESI† showing the proposed coordination of the Ti(III) centre that accounts for the RT EPR signal.

Fig. 2 shows the UV-Vis spectra obtained in a typical run by irradiation of a TiO_2 sol ([ethanol] = 16.2 M, $[\text{H}_2\text{O}] = 2.8$ M and $[\text{HCl}] = 40$ mM, for preparation see ESI†) at different photon doses.

Besides the appearance of the visible band, it is important to recall that the irradiation of this sol results in a clear blue shift in the semiconductor bandgap. This behaviour is referred to in the literature as the Burstein–Moss effect, and it is observed when a high electron concentration is attained in each nanoparticle.^{12,28} Under this condition, the optical absorption edge increases from the uncharged value, $E_g = E_{\text{CB}} - E_{\text{VB}}$, to the difference between the lowest unfilled level of the CB and the border of the valence band, $E_{\text{VB}}^{\text{13}}$.

The number of reducing species stored after irradiation can be determined by anaerobic titration in the dark with a suitable acceptor.²⁹ Methylene blue, MB, is usually employed for this purpose since the end of the titration reaction can be easily monitored by the emergence of the characteristic MB spectrum

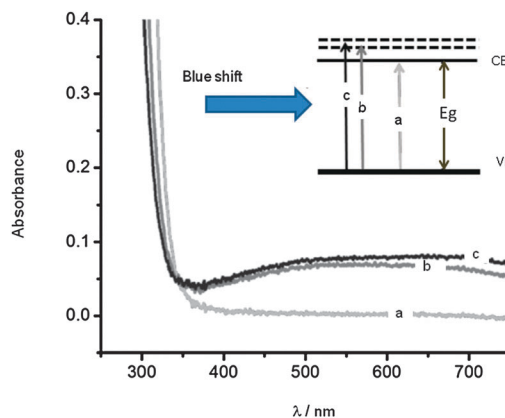
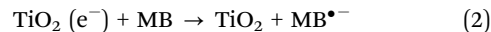


Fig. 2 UV-Vis spectra of a 3 mM TiO_2 sol ([ethanol] = 16.2 M, $[\text{H}_2\text{O}] = 2.8$ M and $[\text{HCl}] = 40$ mM) under a nitrogen atmosphere before (a) and after 20 and 40 minutes of irradiation ((b) and (c) curves, respectively). Irradiation conditions as in Fig. 1. The blue shift observed in the bandgap is accounted for by the progressive increment in the energy of the optical transition from E_g to higher values, schematized by the transitions b and c shown in the inset.

($\epsilon_{655\text{nm}} = 1.0 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) after all the reducing species have been removed. Assuming that $\text{TiO}_2(e^-)$ generically symbolizes the stored reducing species, the stoichiometry of the titration reaction can be represented by eqn (2) and (3).

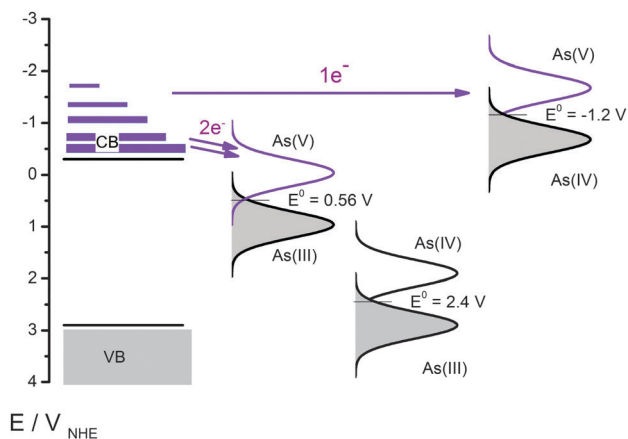


In the above equations, $\text{MB}^{\bullet-}$ is the short lived methylene blue anion radical, and MB^{2-} is the colourless reduced form of the dye.

Using the above methodology, it was determined that concentrations of MB as high as $220 \pm 20 \mu\text{M}$ are required to neutralize the reducing species stored in the irradiated 3.0 mM TiO_2 under the conditions of Fig. 2, once the steady state has been reached. The quoted MB consumption implies that the 3 mM sols can hold a high density of electrons (about $440 \mu\text{M}$). It should be stressed that these experiments were quite reproducible, and if the purged condition is carefully preserved, both the UV and the EPR spectra remain stable for hours, after interrupting the irradiation.

Thus, in another set of experiments, after achieving the steady state conditions, a small aliquot (between 20 and $50 \mu\text{L}$) of a degassed concentrated aqueous As(v) solution was injected into the 3 mL cell containing the accumulated electrons. The mixture was allowed to react in the dark for at least 30 minutes. The spectrophotometric arsenomolybdate technique (detection limit (DL): 0.01 mg L^{-1})³⁰ was used to determine As(v) concentrations in solution. The amount of reaction was evaluated from the difference between the As(v) concentrations determined after injecting the same aliquot of the purged As(v) solution into the 3 mL cell containing the pristine (without irradiation) and the pre-irradiated TiO_2 sol (after electron accumulation).

Preliminary experiments at different As concentrations (between 10 and $500 \mu\text{M}$) indicate an uncertainty of about 20% in As(v) consumption as a result of combined errors.



Scheme 1 Energy diagram of the As(v)-TiO₂ system. The standard redox potentials of the species are taken from ref. 20 and 21 and they ignore possible changes upon chemisorption. All the quoted values are vs. NHE at pH 0.

Thus, concentrations were adjusted to minimize error propagation. In a typical experiment, $80 \pm 8 \mu\text{M}$ ($(3.3 \pm 0.3) \times 10^{-4}$ moles of As per g of TiO₂) was consumed from a 210 μM As(v) solution. Additionally, after reaction with As(v), the UV-Vis spectrum of the system was completely restored to its initial form (black line in Fig. 2), and, also, the EPR spectra indicated that no trapped electrons remained in the sample (see Fig. S1 in the ESI†). Note that although in the described experiment reducible species are completely removed from the irradiated sample, the quoted As(v) consumption is considerably lower than the concentration of the stored charges. Particularly, we observed that nearly 5 electrons are consumed in the disappearance of a single As(v) molecule.

We have verified in separate experiments that As(III) can also be reduced by accumulated charges. Conversion of As(III) was determined using total reflection X-ray fluorescence (TXRF) spectroscopy³¹ (see ESI† for details).

The experimental findings can be discussed on the basis of the position of the potential energy bands of the semiconductor and the relevant aqueous standard reduction potentials for As(v) transformations at pH 0. As shown in Scheme 1, the two electron reduction of As(v) appears to be thermodynamically possible, since the redox couple E_0 (As(v)/As(III)) = 0.56 V is below the conduction band of TiO₂, E_{CB} (pH 0) = -0.3 V. However, the successive one electron reduction of As(v) to As(III) must overcome the high-energy As(IV) intermediate. According to the reports, the redox couple As(v)/As(IV) lies nearly 0.9 V above the CB of TiO₂.²³ Although the estimation uses the homogeneous redox potential for As(v)/As(IV) reduction, it seems to be unlikely that this highly unfavorable condition could be substantially modified as a result of As(v) chemisorption.

On the other hand, the successive transformation of As(IV) to As(III) and As(III) to As(0) appears to be favourable. Accordingly, though the potential for one electron reduction of As(III) to As(II) is not known, current evidence indicates that As(III) can be reduced by CB TiO₂ electrons in aqueous systems.²⁰ In contrast, As(v) reduction is not possible by heterogeneous photocatalytic

reactions over TiO₂ P25 suspensions in water in the absence of an electron donor capable of producing intermediates with high reducing power.²¹

In view of the above arguments, as soon as the high energy electrons are depleted or the number of stored electrons by a particle is not enough to support a concerted transfer, As(v) reduction becomes a forbidden process. However, when these conditions are met, less energetic stored electrons, if present, could still be used to complete the reduction of As(III) to As(0).

In the present approach, two experimental conditions, which are not frequently met in standard photocatalytic studies, favor electron accumulation and allow As(v) reduction. First, alkoxide and chloride coordination probably impede electron discharge and charge recombination by promoting a high degree of surface dehydroxylation.⁹ Diffuse reflectance infrared spectroscopy studies lend support to this argument by proving that the charge carrier annihilation rate increases with increasing surface hydration, *i.e.*, the extent of surface hydroxylation.^{32–34}

Second, the small size of TiO₂ nanoparticles dictates that a relatively low electron concentration in a particle may cause the semiconductor to become degenerate due to the quantization of the CB levels. This fact, in turn, results in the increase in the electron Fermi level as revealed by the Burstein–Moss shift observed in Fig. 2.

The current understanding of electron transfer processes occurring at the semiconductor interface is still limited.³⁵ Certainly, more theoretical and experimental research in this area is needed. However, the results presented herein undoubtedly demonstrate that electrons stored in TiO₂ nanoparticles can, under controlled conditions, drive otherwise forbidden reductions by the electrons of the conduction band. Unfortunately, we cannot discriminate the actual mechanism. Both the concerted multiple electron transfer processes which avoid the high-energy As(IV) intermediate and the stepwise successive one electron reduction under accumulation can account for the experimental findings reported herein.

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