ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 123 (1999) 137–143

Journal of Photochemistry and Photobiology A:Chemistry

Homogeneous and heterogeneous photocatalytic reactions involving As(III) and As(V) species in aqueous media

H. Yang, W.-Y. Lin, K. Rajeshwar*

Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, TX 76019-0065, USA

Received 23 September 1998; received in revised form 8 February 1999; accepted 22 February 1999

Abstract

Thermodynamic considerations show that photogenerated holes in UV-irradiated TiO_2 can oxidize As(III) to As(V). Similarly, the photogenerated electrons can reduce As(V) to the elemental state. Experimental data are presented in verification of these expectations. An electron acceptor (e.g., O_2) is needed for the hole transfer pathway whereas the heterogeneous photocatalytic reduction of As(V) is facilitated by a hole scavenger such as methanol. The oxidation of As(III) to As(V) also proceeds in the dark when a large excess of H_2O_2 is present. However, this process is very facile with simultaneous UV irradiation of the peroxide. These data point toward the feasibility of a two-step pollution abatement scheme for the initial oxidation and subsequent immobilization of the toxic As(III) species. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Homogeneous and heterogeneous photocatalytic reactions; As(III) and As(V) species; Aqueous media

---

1. Introduction

Heterogeneous photocatalytic reactions in aqueous titania (TiO_2) suspensions have been extensively studied in recent years [1–6]. The vast majority of these studies have focused on organic substrates. As Table 1 shows, however, the range of inorganic substrates (especially main group elements) that have been examined in terms of their reactivity toward irradiated TiO_2 is much narrower. As part of a broader study on the reactivity patterns of inorganic species in aqueous TiO_2 suspensions, we describe herein the photocatalytic reactions of As(III) and As(V) species. Specifically, we show below that As(III) can be photooxidized to As(V) in alkaline TiO_2 suspensions. However, this process is not quite as facile as the UV/H_2O_2 homogeneous photocatalysis counterpart. In fact, the oxidation of As(III) can even be driven "in the dark" in the presence of a large excess of H_2O_2.

Interestingly, As(V) can also be photoreduced (to As) in acidic deoxygenated TiO_2 suspensions. This process is facilitated by hole scavengers such as methanol. Instances wherein a given substrate can undergo either a conduction band- or a valence band-mediated photoreaction pathway with TiO_2, depending on the solution pH and other variables, are not very common. In a broader vein, we are not aware of any previous study on the photocatalytic reactions of arsenic species in TiO_2 suspensions.

The present data have obvious environmental significance in that arsenic is toxic to plants, animals, and humans. Arsenic in the +3 oxidation state is ca. 60 times more toxic than As(V) [7]. On the other hand, reduction of As(V) to the elemental form serves to immobilize it, and thus constitutes a potentially useful approach to a pollution abatement scenario.

2. Experimental

All chemicals were at least of reagent grade and were used as received. The TiO_2 (Degussa P-25) was predominantly anatase and had a specific surface area of $\sim 60\ m^2\ g^{-1}$. The photoreactor was described previously [8,9] and a 400 W medium pressure mercury arc lamp was used. The nominal light flux inside the photoreactor was estimated by ferrioxalate actinometry [10] and was 1.83×10^{-5} einstein/min. Deionized water (Corning Megapure) was used in all the cases, and the nominal TiO_2 dose was 2 g/l. These suspensions were then adjusted to pH either ~ 3 or ~ 9 with HCl or NaOH, respectively.

The solutions were sparged with air or ultrapure N_2 as needed [8,9]. The gas flow also served to maintain the TiO_2 particles in suspension. Either As_2O_3 or $Na_2HAsO_4 \cdot 7H_2O$

---

*Corresponding author. Fax: +1-817-272-3808.

PII: S1010-6030(99)00052-0

Table 1
Inorganic species that have been studied in UV-irradiated TiO_2 suspensions in terms of photocatalytic conversion

Category	Examples
Transition metals	Cr, Mn, Fe, Co, Ni, Cu, Ru, Pd, Ag, Pt, Au, Hg
Other metals and main group elements	Tl, Pb, Bi, S
Complex anions	Cyanide and sulfite

was used as the source of As(III) and As(V), respectively. The solutions were initially equilibrated with TiO_2 in the dark (see below) prior to turning the light on. Aliquots were then withdrawn from the photoreactor at pre-specified intervals, filtered through a 0.45 μm filter (to remove the TiO_2 particles) and then tested for As(V) (see below).

Arsenic(V) was assayed either by ion chromatography or by UV–visible spectrophotometry. For the former, a Dionex Model 2000 instrument with suppressed conductivity detection fitted with an anion column (Model AS4A-SC) was used. The mobile phase was 25 mM $Na_4BO_7{\cdot}7H_2O$ (degassed by a helium sparge) and the regenerant was 0.036 N sulfuric acid. Alternatively, As(V) was derivatized with ammonium molybdate and Rhodamine B as per a reported procedure [11]. The UV–visible spectrum of the resultant complex was acquired on a Hewlett-Packard Model HP8452 diode array spectrometer. Beer's law plots were prepared using the measured absorbance of the complex at 604 nm [11]. The total arsenic levels were quantified by inductively-coupled plasma atomic emission spectroscopy [12].

The UV/H_2O_2 homogeneous photocatalysis process was carried out in the same photoreactor as above except that the As(III) solutions were dosed instead with requisite amounts of H_2O_2 (instead of TiO_2). This process was carried out under air purge of the solutions.

Finally, X-ray photoelectron spectroscopy (XPS) was performed on a Physical Electronics Model 5000C instrument; instrumental details are given elsewhere [13].

3. Results and discussion

3.1. Thermodynamic considerations and adsorption of arsenic species on the TiO_2 surface

Consideration of the Pourbaix diagram for arsenic at 25°C in an aqueous medium [14,15] reveals that predominant As(III) and As(V) species at pH 9 to be $H_2AsO_3^-$ and $HAsO_4^{2-}$, respectively. Similarly the dominant As(V) species at pH 3 is $H_2AsO_4^-$. Fig. 1 illustrates the approximate locations of the conduction and valence band edge locations for TiO_2 (anatase form) in the two solutions (pH 3 and pH 9) of relevance to this study. Also shown in the same energy diagram are the standard reduction potentials for the $As^{3+/5+}$ and $As^{0/5+}$ redox couples extracted from the literature [16], along with the potentials of other relevant redox reactions to be discussed below. From these data, we can deduce that the photogenerated holes (or hydroxyl radicals, see below) in TiO_2 will have sufficient energy to oxidize As(III) to As(V) in the pH 9 medium. Similarly, the photogenerated electrons in TiO_2 can reduce As(V) [to As(0), see below] in the pH 3 medium. However, competing with these electrons are dissolved O_2 molecules necessitating the arsenic solutions to be deoxygenated in the photoreduction case (see below).

Preliminary experiments revealed adsorption of both As(III) and As(V) species on the TiO_2 surface in the dark. The adsorption tendency was stronger in the acidic medium than in the pH 9 case. This is rationalizable in terms of electrostatic considerations wherein the negatively charged As species (see above) will be more strongly attracted to TiO_2 particles with a net positive charge. The surface charge on TiO_2 is known to be pH-dependent with the point of zero charge (PZC) located at ca. 6.0 [17]. Interestingly the present situation with As contrasts with that of another group V element, Bi previously studied [18]. In the latter case, the Bi species are positively charged and adsorption on the TiO_2 surface is favored in basic aqueous media [18].

No attempt was made in the present study to further quantify the As adsorption behavior on the TiO_2 surface. Instead, in all the experiments to be described below, sufficient time (ca. 40 min.) was merely given to allow the adsorption equilibrium to proceed to completion in the dark, before initiating the heterogeneous photocatalytic reactions.

3.2. Photocatalytic oxidation of As(III)

Fig. 2 shows how the As(V) levels evolve in an air-saturated pH 9 solution containing 525 μM arsenite. Four cases are shown including the results of control experiments. Specifically, in the absence of TiO_2 and in the dark, no conversion to As(V) occurred in deoxygenated solutions. In the presence of TiO_2 and in an air-saturated medium, the dark oxidation of As(III) to As(V) did occur (see Curve 3 in Fig. 2), albeit very sluggishly. That the very slow atmospheric oxidation of As(III) is triggered by TiO_2 (compare Curves 1–3 in Fig. 2) is interesting and could be the manifestation of a pre-concentration effect brought about by co-adsorption on the TiO_2 surface of both As(III) species and O_2 molecules. Further speculation, however, is not warranted by the data on hand.

In the presence of UV light, TiO_2 and an electron scavenger (O_2 in this case), the oxidation of As(III) to As(V) is reasonably facile and is complete within ca. 30 min. (Curve 4 in Fig. 2). Concomitantly, this photocatalytic reaction is inhibited when the solution is sparged with N_2. Thus in the absence of an electron scavenger, the photogenerated electron-hole pairs simply recombine.

In the absence of TiO_2, the dark oxidation of As(III) [to As(V)] can be triggered by H_2O_2 in an air-saturated pH 9 solution (Fig. 3). However, a large excess of peroxide is

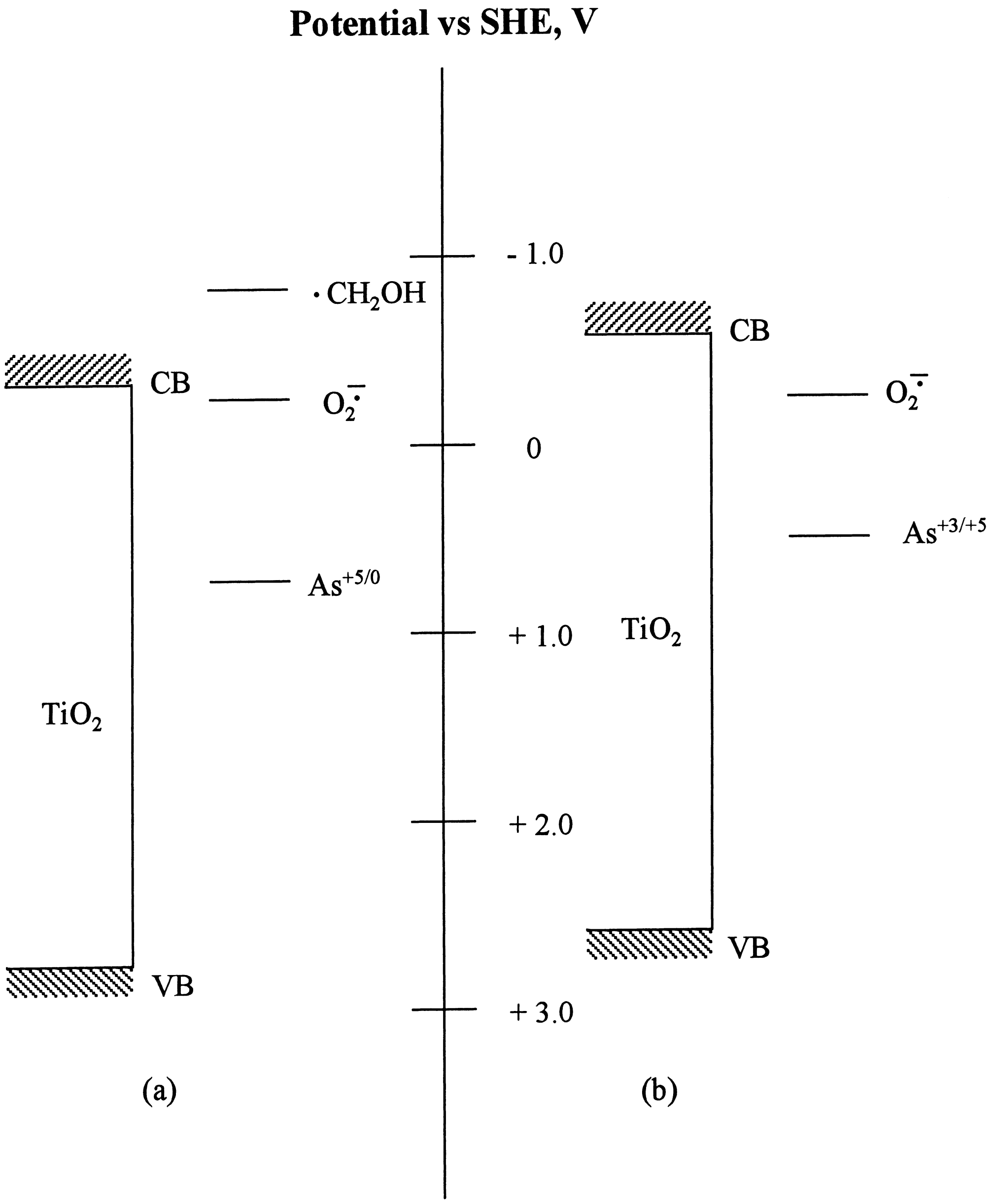

Fig. 1. Comparisons of the approximate locations of the valence and conduction band edges (VB and CB) of anatase TiO_2 (energy band-gap: ~3.2 eV) in pH 3 (a) and pH 9 (b) media and corresponding energy levels of various redox species in solution. All the potentials are quoted with respect to the standard hydrogen electrode (SHE).

needed to completely oxidize the As(III) species in the dark. Note that the reaction:

$$AsO_3^{3-} + H_2O_2 \rightarrow AsO_4^{3-} + H_2O \qquad (1)$$

requires a reactant stoichiometry of only 1:1. We attribute the much higher level of peroxide required, to the base-catalyzed decomposition of H_2O_2 [19]:

$$H_2O_2 + HO_2^- \rightarrow H_2O + O_2 + OH^-. \qquad (2)$$

In the presence of UV light and H_2O_2, however, the oxidation is very facile (Fig. 4), and is completed in less than 10 min. Further, the initial H_2O_2 level is also not critical here as in the dark case. This is because a steady-state concentration of hydroxyl radicals (see below) is established in the reaction system that is largely determined by the incident photon flux.

Thus, the homogeneous UV/H_2O_2 photocatalysis reaction is more efficient than its heterogeneous UV/TiO_2 counterpart (Fig. 2) for the oxidation of As(III). The rather dramatic effect of light (compare Figs. 3 and 4) underlines the fact that hydroxyl radicals (generated from the photolysis of H_2O_2, [6,20]) are more potent oxidants than H_2O_2 itself (or more precisely, its conjugate base, HO_2^-, under the conditions relevant to Fig. 3). We presume that $^{\bullet}OH$ radicals are also involved in the UV/TiO_2 case, although the data presented in Fig. 2 do not suffice to establish whether the

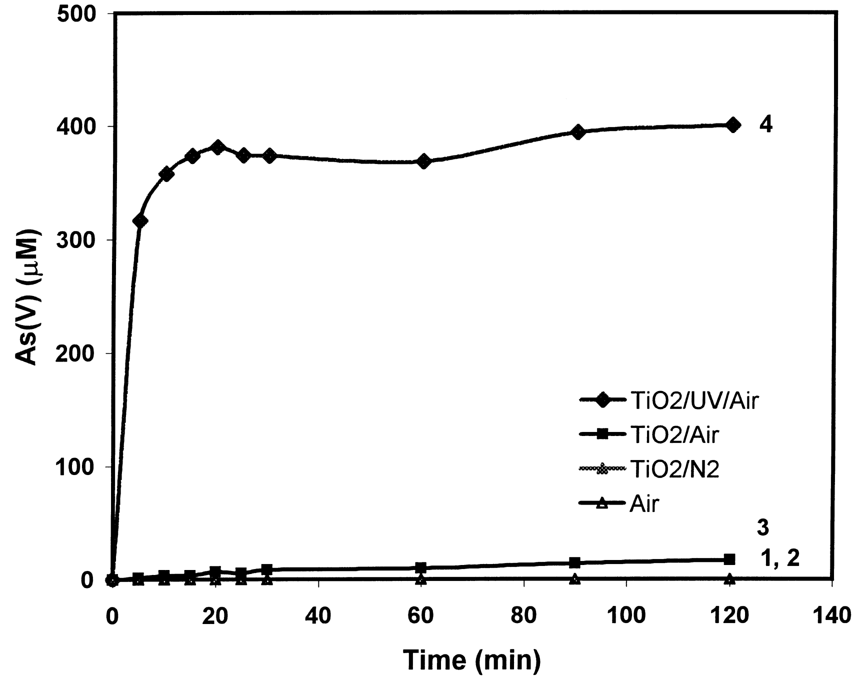

Fig. 2. Evolution of As(V) in a pH 9 solution initially containing 525 μM sodium arsenite (i.e., arsenic in the +3 oxidation state). Curves 1 and 2 are "dark" control data showing the absence of As(III) oxidation in a deoxygenated solution with TiO_2 present or in air-saturated solution with no TiO_2 present. Curve 3 is also a "dark" run with TiO_2 and an air-saturated solution. Curve 4 contains the corresponding data with UV-illumination. The lines are simply drawn through the data points for visualization here in this figure and in Figs. 3 and 4 below.

As(III) species are directly oxidized by the photogenerated holes or "indirectly" by the $^{\bullet}OH$ radicals. Indeed, this is an outstanding issue in the heterogeneous photocatalysis field [3,6], and one that may be further complicated by its sensitivity to the specific chemical nature of the substrate.

3.3. Photocatalytic reduction of As(V)

One crucial advantage that the UV/TiO_2 process has (relative to the UV/H_2O_2 counterpart) is that the photogenerated electrons in TiO_2 can be put to use for reducing

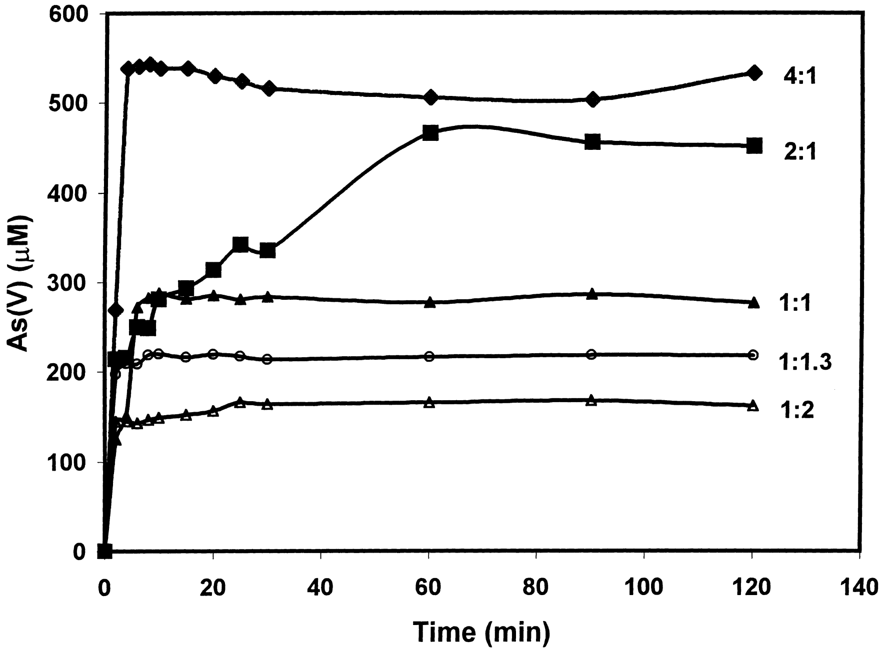

Fig. 3. Evolution of As(V) "in the dark" with time in an air-saturated pH 9 solution initially containing 525 μM sodium arsenite and dosed with H_2O_2 as shown. The numbers in the figure refer to the H_2O_2:As(III) mole ratio.

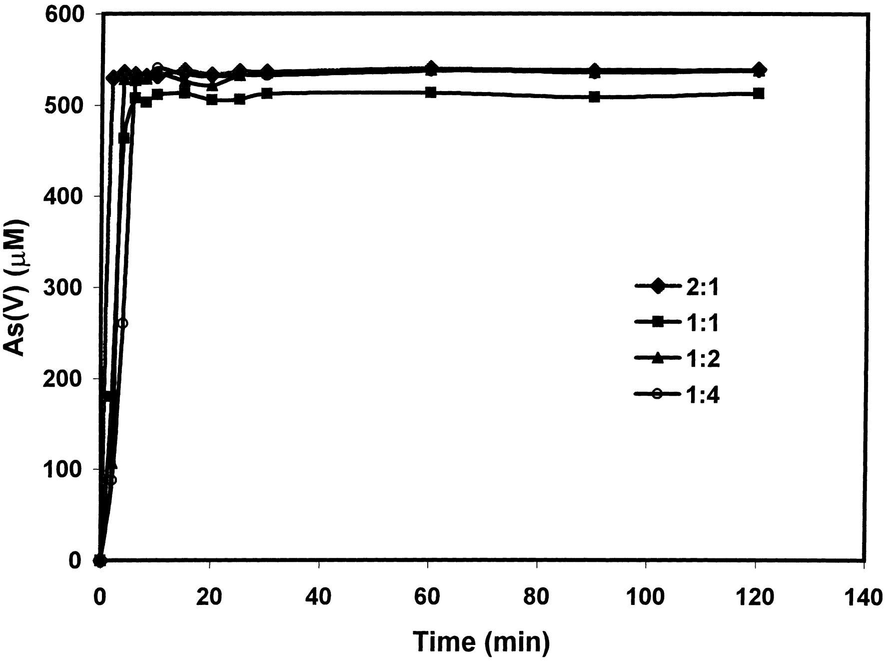

Fig. 4. As in Fig. 3 but with UV-irradiation of the solutions.

targeted solution and/or adsorbed species. Obviously, photoreduction reactions are largely precluded in the UV/H_2O_2 approach. Thus we and others [8,9,21–23] have previously shown that inorganic species such as Cr(VI), Ni(II), and Pb(II) can be photoreduced in deoxygenated and UV-irradiated TiO_2 suspensions.

Preliminary experiments revealed a progressive decrease in As(V) levels in UV-irradiated TiO_2 deoxygenated suspensions ranging in pH from ∼3 to ∼7. However, the rate of decrease was also small in solution of pH higher than ∼3, again presumably due to electrostatic factors of the sort discussed earlier. Thus, all further experiments were performed at this pH. Fig. 5 shows

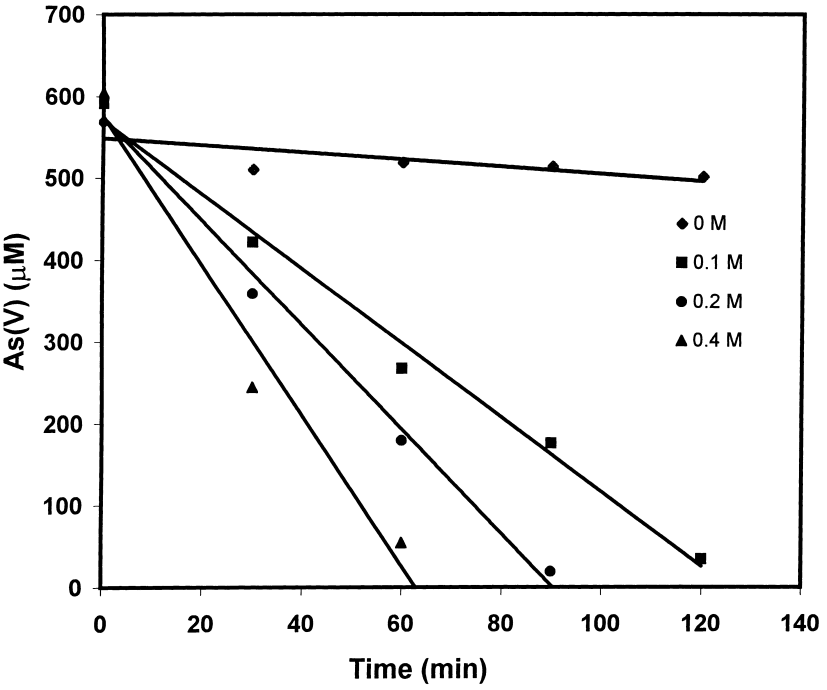

Fig. 5. Reduction of As(V) in a TiO_2-dosed deoxygenated pH 3 suspension under UV-irradiation with and without methanol added as a hole scavenger. The lines are least-squares fits of the data points.

that the photoreduction rate is greatly enhanced in the presence of a hole scavenger such as methanol. This increase in rate can be interpreted in terms of two possible effects on addition of methanol. First, electron-hole recombination would be suppressed and the kinetics of the conjugate electron reaction pathway would be improved by addition of a facile hole capture agent [24]. Recall that in the absence of this agent, the photogenerated holes would have to be consumed via a (more sluggish) 4 e-pathway leading ultimately to water oxidation. Second, α-hydroxy radicals are created in the presence of methanol via H-atom abstraction [25]:

$$\mathrm{TiO_2} \xrightarrow{h\nu} \mathrm{e^-} + h^+ \quad (3)$$

$$h^+ + \mathrm{H_2O} \rightarrow {}^{\bullet}\mathrm{OH} + \mathrm{H^+} \quad (4)$$

$${}^{\bullet}\mathrm{OH} + \mathrm{CH_3OH} \rightarrow {}^{\bullet}\mathrm{CH_2OH} + \mathrm{H_2O} \quad (5)$$

These radicals are highly reducing and thus have sufficient energy to reduce As(V) species (see Fig. 1).

For example, the redox potential corresponding to ${}^{\bullet}\mathrm{CH_2OH}$ lies at −0.98 versus SHE [26–28] (see Fig. 1). Free radicals derived from other alcohols have similar reducing power.

We believe that photoreduction of As(V) occurs both via direct reduction by the photogenerated electrons in $\mathrm{TiO_2}$ as well as by the radical-mediated route. Indeed both these pathways are thermodynamically possible (see Fig. 1) although the direct reduction is kinetically not facile (see the methanol-free data in Fig. 5). The competition between the direct and indirect (i.e., radical-mediated) electron-transfer pathways is addressed in a separate study [29].

What is the product of the photocatalytic reduction of As(V)? First, the initially white $\mathrm{TiO_2}$ suspensions turned progressively grey when the As(V) solutions were photoreduced. Second, ICP-AES assay of the total As content of a solution initially containing ~800 μM, after photoreduction revealed negligible arsenic levels. Third, the greyish $\mathrm{TiO_2}$ powders after photocatalysis were subjected to XPS analyses. A survey spectrum is contained in Fig. 6. Aside from the expected Ti and O signals and the ubiquitous Cls signal, an arsenic peak [30] was also present. A high-resolution scan of this As 3d peak in the 35–60 eV binding energy region revealed a profile consistent with the species in its elemental form [30].

Therefore, we have the following picture for the photocatalytic reduction of As(V). The arsenate species are strongly adsorbed on the $\mathrm{TiO_2}$ surface. In fact, the reaction kinetics (especially at low methanol concentrations) obey a zero-order rate law consistent with the adsorbed state of the substrate. Photoreduction either by the electrons in $\mathrm{TiO_2}$ or by radicals created in the presence of methanol results in the reduction of As(V) to elemental As.

As mentioned in Section 1, we are not aware of any previous study involving either As(III) or As(V) in irradiated $\mathrm{TiO_2}$ suspensions. However, photoreduction of Bi(III) to metallic Bi was recently reported in illuminated $\mathrm{TiO_2}$ (Degussa P-25) suspensions [18].

4. Summary and concluding remarks

The present study has shown that a given substrate can undergo either a conduction-band (electron) or a valence-

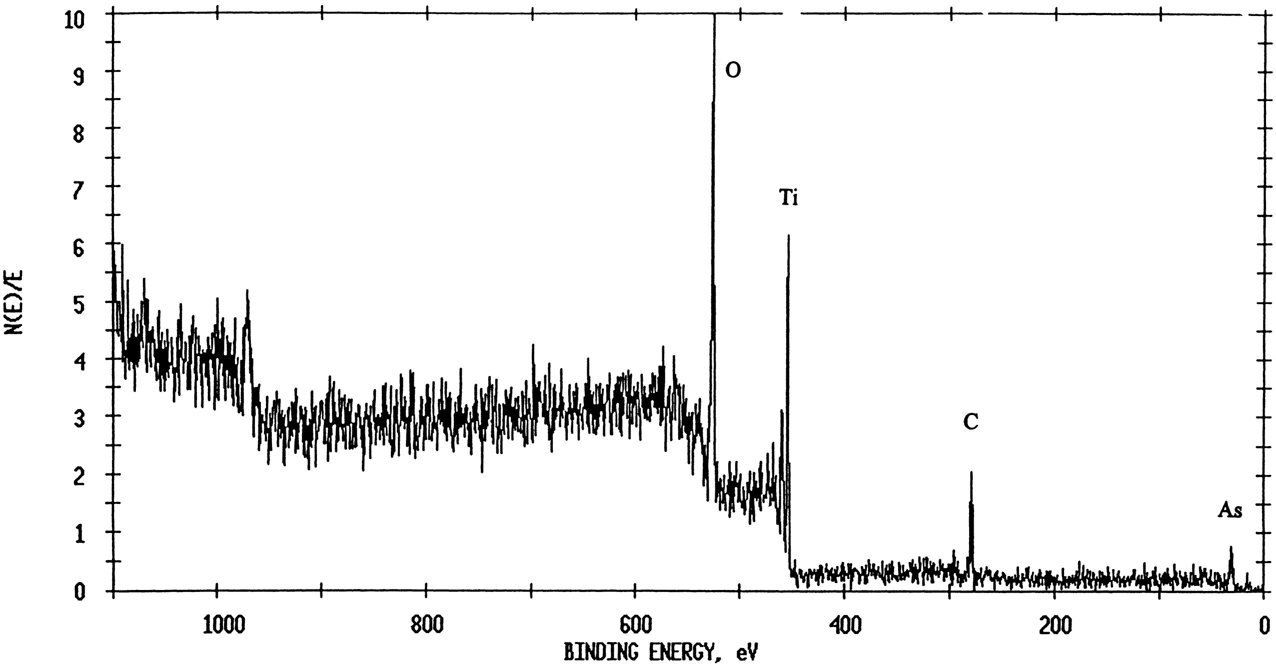

Fig. 6. Survey XPS spectrum of a $\mathrm{TiO_2}$ sample after photocatalytic reduction as in Fig. 5.

band (hole) heterogeneous photocatalytic pathway depending on the solution pH and other variables. For example, a low pH, a deoxygenated medium, and a hole scavenger are needed for the former pathway. For the hole transfer case, a high solution pH and an electron scavenger (e.g., O_2) are pre-requisites. In fact, the arsenic case provides a rather nice illustration of the inherent symmetry of the conjugate electron and hole reactions in UV-irradiated TiO_2 [24]. The present data may also have relevance to environmental remediation scenarios. For example, an initially toxic As(III)-containing waste stream can be photoconverted to the (less toxic) As(V) state either via UV/TiO_2 or by the (more facile) UV/H_2O_2 route. The pH of the stream can then be adjusted to an acidic level and the As(V) subsequently immobilized as the elemental species onto the TiO_2 support in a second abatement stage. Use of the UV/H_2O_2 process in the first stage would require neutralization or consumption of all the initial peroxide. Otherwise, any residual peroxide, being a facile electron scavenger, would interfere with the subsequent UV/TiO_2 photocatalytic reduction of As(V). Finally, the arsenic can be dislodged from TiO_2 and the latter reused as outlined by us earlier for the Cr(VI) case [8].

Acknowledgements

This study was supported, in part, by a grant from the US Department of Energy, Office of Basic Energy Sciences. We thank the two reviewers for constructive criticism of an earlier version of this paper. Finally, we are grateful to Ms. Gloria Madden for assistance with paper preparation.

References

[1] E. Borgarello, N. Serpone, M. Barbeni, C. Minero, E. Pelizzetti, E. Pramauro, Chim. Ind. (Milan) 68 (1986) 53.
[2] P.V. Kamat, Chem. Rev. 93 (1993) 267.
[3] K. Rajeshwar, J. Appl. Electrochem. 25 (1995) 1067.
[4] K. Rajeshwar, Chem. Ind. 17 (1996) 454.
[5] D.M. Blake, Bibliography of Work on the Heterogeneous Photocatalytic Removal of Hazardous Compounds from Water and Air, NREL/TP-430-22197, January (1997).
[6] K. Rajeshwar, J.G. Ibanez, Environmental Electrochemistry, Chapter 6, Academic Press, San Diego, 1997.
[7] J.F. Ferguson, J. Gavis, Water Res. 6 (1972) 1259.
[8] W.-Y. Lin, C. Wei, K. Rajeshwar, J. Electrochem. Soc. 140 (1993) 2477.
[9] W.-Y. Lin, K. Rajeshwar, J. Electrochem. Soc. 144 (1997) 2751.
[10] C.G. Hatchard, C.A. Parker, Proc. Roy. Soc. A235 (1956) 518.
[11] K. Palanivelu, T.V. Ramakrishna, Ind. J. Technol. 28 (1990) 67.
[12] T.D. Martin, C.A. Brockhoff, J.T. Creed, S.E. Long, Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma Atomic Emission Spectroscopy, Revision 3.3, US Environmental Protection Agency, Cincinnati, OH, April, 1991.
[13] C.S.C. Bose, K. Rajeshwar, J. Electroanal. Chem. 333 (1992) 235.
[14] M. Pourbaix, Atlas of Electrochemical Equilibria, Pergamon, Oxford, 1966.
[15] W.R. Cullen, K.J. Reimer, Chem. Rev. 89 (1989) 713.
[16] A.J. Bard, R. Parsons, J. Jordan (Eds.), Standard Potentials in Aqueous Solution, Marcel Dekker, New York, 1985.
[17] G.A. Parks, Chem. Rev. 65 (1965) 177.
[18] Y. Inel, D. Ertek Haciu, J. Chem. Soc., Faraday Trans. 89 (1993) 129.
[19] W.C. Schumb, C.N. Satterfield, R.L. Wentworth, Hydrogen Perioxide, Reinhold, New York, 1955, p. 473.
[20] S. Lunak, P. Sedlak, J. Photochem. Photobiol A 68 (1992) 1.
[21] M.R. Prairie, L.R. Evans, B.M. Stange, S.L. Martinez, Environ. Sci. Technol. 27 (1993) 1776.
[22] T. Rajh, A.E. Ostafin, O.I. Micic, D.M. Tiede, M.C. Thurnauer, J. Phys. Chem. 100 (1996) 4538.
[23] F. Forouzan, T.C. Richards, A.J. Bard, J. Phys. Chem. 100 (1996) 18123.
[24] K. Rajeshwar, J.G. Ibanez, J. Chem. Educ. 72 (1995) 1044.
[25] M. Kaise, H. Nagai, K. Tokuhashi, S. Kondo, S. Nimura, O. Kikuchi, Langmuir 10 (1994) 1345.
[26] V.J. Lilie, G. Beck, A. Henglein, Ber Bunsenges – Ges. Phys. Chem. 75 (1971) 458.
[27] R. Baba, R. Konda, A. Fujishima, K. Honda, Chem. Lett. (1986) 1307.
[28] D.W. Bahnemann, J. Monig, R. Chapman, J. Phys. Chem. 91 (1987) 3782.
[29] C.R. Chenthamarakshan, H. Yang, C.R. Savage, K. Rajeshwar, Res. Chem. Intermed., in press.
[30] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Mulder, G.E. Mattenberg, Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer Corporation (Physical Electronics Division), 1979, p. 90.