

Photochemical Quartz Crystal Microbalance Study of the Nanocrystalline Titanium Dioxide Semiconductor Electrode/Water Interface: Simultaneous Photoaccumulation of Electrons and Protons

Buford I. Lemon and Joseph T. Hupp*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208

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Photochemical quartz crystal microbalance (PQCM) studies of nanocrystalline titanium dioxide films show evidence of charge-compensating cation intercalation during photolytically induced accumulation layer formation. The manifestation and magnitude of mass uptake (intercalation) are dependent, respectively, on the illumination and intensity of illumination provided. Isotope experiments performed in H₂O and D₂O unambiguously identify the cations as protons and deuterons. The experiments extend earlier experiments with dark TiO₂ (and other metal oxide semiconductors) that have implicated cation intercalation as the primary process involved in charge compensation under accumulation conditions.

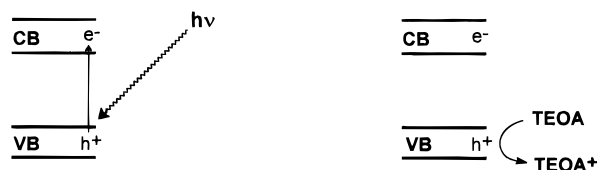
Introduction

High-area, thin-film metal oxide semiconductors have attracted tremendous recent attention in the electrochemical and photoelectrochemical community because of their potential utility in photovoltaic,¹ photocatalytic (environmental remediation),² electrochromic,³ and battery applications.⁴ The ultimate success of these applications relies on understanding the essential chemical and physical factors that define the energetics of the interface, including band-edge energetics. Photocatalytic usefulness and photovoltaic efficiency, for example, depend strongly on the energetic positions of the band edges relative to targeted contaminants and sensitizing dyes, respectively.

Recent electrochemical quartz crystal microbalance (EQCM) studies of TiO₂, SnO₂, and ZnO⁵ have provided significant new information regarding conduction band-edge energetics. These studies have shown that accumulation of conduction band electrons⁶ is accompanied by cation intercalation: protons in the case of water, small electrolyte cations in the case of aprotic solvents. The cations provide local charge compensation for the accumulated electrons, where the charge compensation/intercalation process appears to play a central role in determining the conduction band-edge energy. The studies also show that the compensation/intercalation phenomenon functions essentially independently of the well-known surface adsorption/desorption (acid/base) equilibrium that governs ζ potentials and open-circuit surface charges. As such, the intercalation effect represents an independent mechanism⁵ for generating rather extensive pH⁷ and electrolyte compositional control⁸ over band-edge positions (interface energetics).

The existing EQCM⁵ and related studies^{8,9} have emphasized accumulation layer formation via dark electrochemical means. To assess the possible importance of ion intercalation under photochemical conditions, we initiated a study of the illuminated nanocrystalline TiO₂ (anatase) electrode/solution interface where a photochemical quartz crystal microbalance method (PQCM) was employed. Accumulation layers were generated photochemically by a combination of suprabandgap illumination ($\lambda < 380$ nm) and a solution species hole scavenger. These electrodes are similar to those used in previous experiments in our lab⁵ and comparable to those employed in photovoltaic and photocatalytic studies. PQCM has been used previously to study

SCHEME 1



reactions and interactions at light-sensitive electrodes. Rajeshwar and co-workers have used this technique to study photo-corrosion of CdSe electrodes while Kuwabata et al. have studied charge-compensating anion egress processes accompanying the mediated photoreduction of polyaniline coatings.¹⁰ The PQCM experiments described here clearly show that photochemical intercalation of protons readily occurs under conditions where electron accumulation is known to occur.

Experimental Section

TiO₂ film preparation has been previously reported.¹¹ Briefly, TiO₂ sols consisting of 5 nm crystallites (as confirmed by TEM) were prepared via the acidic hydrolysis of titanium isopropoxide (Aldrich). The sols were then concentrated to 50 g/L and surfactant (Triton X-100, 1 drop/mL) was added to facilitate film formation from the sols. Films were prepared by spin-coating sol onto the conductive gold portion of masked 5 MHz quartz crystal resonators (ICM, Inc.). Between 5 and 10 coats were applied before firing the electrode in air at 400 °C for 1 h. This preparation gave films with electrochemistry and UV-vis spectra matching those in the literature.¹²

PQCM measurements were performed on an EQCM apparatus previously described.⁵ Briefly, it consisted of a homemade oscillator circuit, a Philips PM6681 frequency counter, and a 100 W quartz-tungsten halogen lamp (Oriel) to provide bandgap illumination. A color glass filter (CVI) to remove unwanted wavelengths and reduce heating of the gold substrate was also employed. Data were collected with a PC using Timeview software. The quartz crystal oscillator/semiconductor film was placed in the bottom of an electrochemical cell designed to permit direct illumination of the semiconductor surface. Cell solutions consisted of purified distilled water (Millipore Milli-Q system) or D₂O (Aldrich) with added triethanolamine (1 drop/mL) as hole scavenger. Solutions

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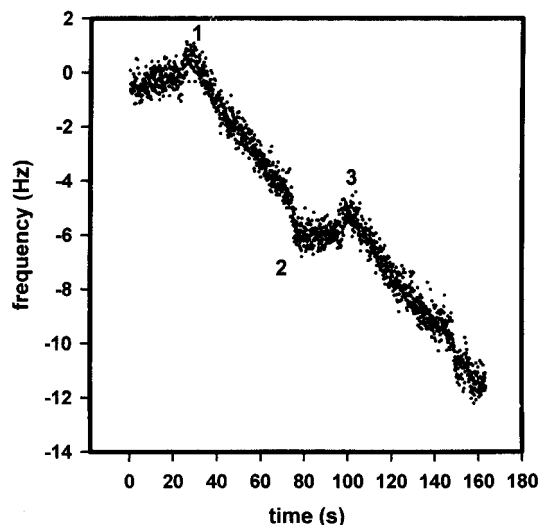


Figure 1. PQCM of TiO_2 : suprabandgap illumination is initiated at points 1 and 3 and terminated at point 2.

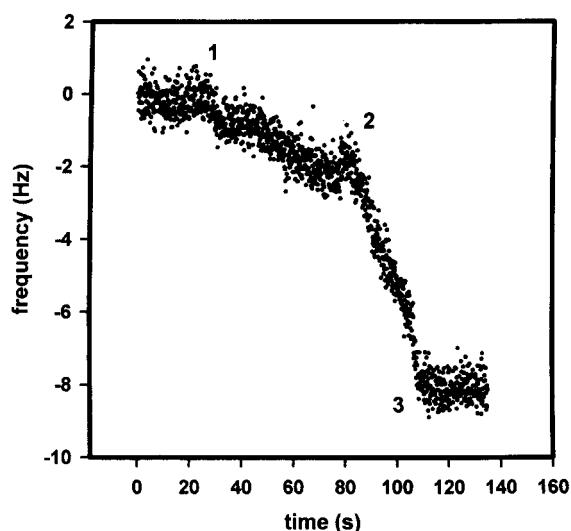


Figure 2. PQCM intensity effects: TiO_2 illumination is initiated at point 1 and increased at point 2.

were deoxygenated by bubbling with nitrogen immediately prior to each experiment.

Results and Discussion

Previous experiments have indicated that electrochemically induced accumulation layer formation in TiO_2 is accompanied quantitatively by intercalation of charge-compensating cations.^{5a} In the current experiments, accumulation layers were instead generated photochemically by illuminating TiO_2 in the presence of triethanolamine (TEOA). Electron-hole pairs are produced, followed by rapid hole scavenging by TEOA as shown in Scheme 1.¹³ QCM monitoring of the electrode (Figure 1) shows that (1) illumination at constant light flux is accompanied by an immediate steady decrease in oscillation frequency, (2) termination of photolysis is accompanied by an abrupt cessation of frequency shifts, and (3) restoration of photolysis also restores the frequency decrease effect. From the Sauerbrey equation,¹⁴ oscillator frequency decreases correspond directly to mass increases. From Figure 1, the mass increases clearly are correlated with illumination of the interface. By analogy to EQCM behavior on the same electrode, we attribute the mass uptake to charge-compensating cation intercalation accompanying the photochemical formation of an electron accumulation layer.

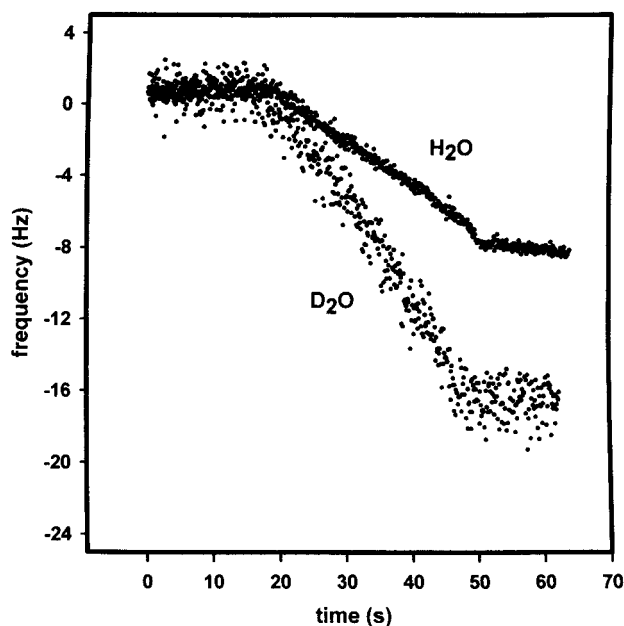


Figure 3. PQCM of TiO_2 in H_2O and D_2O , both containing TEOA.

To probe the process further, intensity-dependent experiments were performed. Figure 2 shows the results of such an experiment. Point 1 corresponds to the initial illumination of the electrode. At point 2 the intensity is increased, resulting in an increase of the rate of mass uptake.¹⁵ Point 3 indicates the point where illumination was ceased. Control experiments on bare gold electrodes or TiO_2 -coated electrodes subjected to subbandgap illumination failed to produce such results. In any case, the results in Figure 2 are consistent with Scheme 1: increased light intensity (photon flux) should lead to an increased rate of accumulation layer formation and, therefore, an increased rate of intercalation.

Finally, comparative $\text{H}_2\text{O}/\text{D}_2\text{O}$ experiments were undertaken in order to establish the identity of the intercalating cation. Because electrolytes were not intentionally included in PQCM solutions, the possibilities appear to be limited to H^+ , H_3O^+ , and the conjugate base of TEOA (with probable steric constraints^{5a} on intercalation of the latter). Figure 3 shows the results of an isotope experiment. The key finding is that mass uptake, while clearly occurring in both light and heavy water, occurs twice as rapidly in the latter. The intercalating ions, therefore, can be unambiguously identified as protons and deuterons.

Conclusions

Photochemical "accumulation" of protons accompanies the accumulation of electrons at suprabandgap-illuminated titanium dioxide/water interfaces. The findings suggest the possible mechanistic generality of recent observations⁵ of charge-compensating cation intercalation at *dark* $\text{TiO}_2/\text{water}$, $\text{SnO}_2/\text{water}$, and ZnO/water interfaces. In addition, the new experiments raise interesting questions concerning reactivity at dye-sensitized interfaces where dye sensitization represents yet another way of placing excess electrons into conduction bands or nearby localized states. We have recently suggested that anomalous back-electron-transfer reactivity patterns at dye-sensitized titanium dioxide/water interfaces could be explained via a sequential electron transfer/proton transfer scheme.¹⁶ The current results on photointercalation of protons lend significant support to these mechanistic speculations.

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