Electron trap states and photopotential of nanocrystalline titanium dioxide electrodes filled with single-walled carbon nanotubes


Abstract

Hybrid film electrodes were made of nanocrystalline titanium dioxide (TiO$_2$) and various percentages of single-walled carbon nanotube (SWCNT) fillers up to 5.5 wt%. A complete photoelectrochemical study was performed in both alkaline and acidic conditions by cyclic voltammetry, potentiostatic photocurrent measurements, and open circuit potential measurements under ultraviolet-visible irradiation. Dark voltammograms show a transition from a capacitive to a resistive behavior in the TiO$_2$ accumulation region upon increasing SWCNT percentages. In addition, the energy levels of deep electron traps change inside the TiO$_2$ band-gap. The new peak positions correspond to the reduction potentials of SWCNTs, and their associated charge capacities increase with the SWCNT percentage. The modifications observed in dark experiments directly impact on the shape profile of cyclic voltammograms under irradiation. As a consequence, reduction potentials of SWCNTs appear near the cathodic peaks of certain water oxidation intermediates, and may be interacting with them. On the other hand, open circuit photopotentials reach maximum values for small SWCNTs percentages around 0.02 wt%. An increase in potentiodynamic and potentiostatic photocurrents is observed for the electrode containing 0.02 wt% SWCNTs, compared to reference TiO$_2$ in acidic conditions.

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Introduction

Wide band-gap semiconductors such as TiO_2 are being investigated for clean energy production and environmental applications, including photovoltaic cells and photocatalytic advanced oxidation processes. More specifically, thin films made of nanocrystalline TiO_2 have demonstrated improved properties due to their small particle size and high specific surface area. A fundamental understanding of the electronic properties of those film systems has been achieved by electrochemical methods. In particular, cyclic voltammetry measurements have been performed on TiO_2 films for the study of their electronic density of states, which is typically reflected in a charge accumulation region and certain trap states. Moreover, the detection of electronic states and intermediate species by electrochemical methods provides insights on reaction mechanisms, which are a topic of intense debate, particularly in the water oxidation reaction. Great differences in the TiO_2 energy levels and photocatalytic activity are found depending on the crystalline structure, particle morphology, and other external conditions such as electrolyte additives, oxygen purge, and pH. 

The preparation of nanostructured carbon/TiO_2 hybrids has been extensively studied in the literature. Carbon nanotubes and graphene have been tested for transparent conducting electrodes, electron transport layers, hole transport layers, and as electron acceptors. Both carbon nanotubes and graphene can decrease electron/hole recombination, improving the photocatalytic behavior of TiO_2 under selected conditions. In particular, it has been shown by us and other research groups that 0.1-8 wt% of single-walled carbon nanotubes (SWCNTs) added to TiO_2 are effective for the photocatalytic degradation of model pollutants. The mechanism of the photoactivity improvement has been typically explained by the electron acceptor character and transport properties of carbon nanotubes. However, a comprehensive understanding of those complex systems is far from being reached.

In the present work, we aim to elucidate the characteristics of the SWCNT/TiO_2 system by means of photo-electrochemical methods, including cyclic voltammetry, potentiostatic photocurrent and open circuit photopotential measurements, in both alkaline and acid environments. For the sake of reproducibility, we try to simplify the system as much as possible, using commercial well-characterized materials and standard experimental procedures, including the electrode preparation, cell design, nitrogen purge, and light source. Our results confirm the role of SWCNTs as electron acceptors, but also describe for the first time other particular features of the hybrid
system that affect the TiO$_2$ energy levels and the photoactivity. More specifically, potentiodynamic measurements show a shift in the TiO$_2$ electron trap energies, together with an increase in their associated peak intensities, after the addition of small amounts of SWCNTs. Also, it is demonstrated that open circuit photopotentials increase to a maximum for low SWCNT percentages. Finally, some mechanistic aspects of water and methanol photooxidation are evidenced and discussed in connection with the presence of SWCNTs and the effects caused in TiO$_2$.

Results and discussion

Reference TiO$_2$ dark voltammetry
Aeroxide® P25 TiO$_2$ is often utilized as a comparative sample in the photocatalytic degradation of organic pollutants since it is commercially available worldwide and it demonstrates among the best efficiencies, both in suspension and when the catalyst is deposited on a substrate.[26,27] On the other hand, the electrochemical characteristics of nanocrystalline TiO$_2$ electrodes have been widely studied in the literature.[4] Here, we briefly summarize our measurements on a blank P25 TiO$_2$ electrode in order to identify, in the next section, the changes undergoing with SWCNT addition. Electrodes were prepared from a TiO$_2$/ethanol suspension by spray-coating on conducting fluorinated tin oxide (FTO)/glass substrates. Electrode characterization details are included in the Supporting Information. Figure 1 shows cyclic voltammograms for the TiO$_2$ electrode at pH 2 and pH 13. All the measurements were effected at a typical scan rate of 20 mV s$^{-1}$. The following features can be observed:

i) A charge accumulation region appears below -1V vs. Ag/AgCl at pH 13 or below -0.1V at pH 2. It is related to the TiO$_2$ conduction band (CB), and is located at the most negative potentials, respectively for both pHs. The transition to the charge accumulation region occurs through an exponential decay that has been related to defect states just below the CB lowest limit.[28]

ii) The separation between accumulation regions at pH 2 and pH 13 is given by approximately 0.07/pH unit, thus being 120 mV wider than that expected from the Nernst equation. This fact has to be explained by the action of processes that somehow affect the surface acid-base equilibrium, for example cation intercalation.[6]
iii) The band gap region appears at potentials > -1 V vs. Ag/AgCl at pH 13 or > -0.2 V at pH 2. It is a wide region of low currents that covers most of the measurement potential window, and is associated to the forbidden states of TiO$_2$ band gap.

iv) Intra band gap states. Figure 1.b shows the region around -0.9/-0.5 V vs. Ag/AgCl at pH 13 and -0.2/0.2 V at pH 2. Here and whenever a comparison between potentials at different pH is needed, the values are transformed into the reversible hydrogen electrode (RHE) scale, applying the equation:

$$V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.059 \cdot \text{pH} + 0.210$$

(1)

A cathodic/anodic peak is detected between 0.2 and 0.4 V vs. RHE (Fig. 1b), which is typically related to intra band gap states and is supposed to play an important role in photoinduced processes.[6] The origin of these deep traps has been assigned to non-stoichiometric atoms on TiO$_2$ nanoparticle surfaces and crystal grain boundaries.[5] Different peak potentials for pH 2 and pH 13 reflect the influence of surface chemistry on the electron trap energies, and shows how protonation/deprotonation of surface atoms locally modifies the surface energy.

**SWCNT/TiO$_2$ dark voltammetry**

We investigate now the effect of progressively increasing the amounts of SWCNTs in TiO$_2$. Accordingly, the required volumes of a purified SWCNT aqueous suspension were added to the TiO$_2$/ethanol mixture for spray-coating on FTO electrodes. Characterization details of selected SWCNT/TiO$_2$ electrodes are included in the Supporting Information. Two changes from pure TiO$_2$ can be observed in dark voltammograms at pH 13, respectively involving the charge accumulation region and the deep trap features inside the band gap. First, the charge accumulation region at negative potentials (< -0.2 V vs. RHE) is significantly altered (Figure 2). The maximum in the anodic scan (positive current densities) shifts from -0.46 V vs. RHE for blank TiO$_2$ to -0.35 V vs. RHE for the 2.5%SWCNT/TiO$_2$ electrode, while it is not observed at all for the 5.5%SWCNT/TiO$_2$ sample. Concurrently, the cathodic branch progressively reaches lower current densities. These changes in the charge accumulation region indicate the transition from a capacitive to a resistive behavior.[28] For the 5.5%SWCNT/TiO$_2$ sample, no charge accumulation region is observed anymore at pH 13. However, the shape of the voltammogram at pH 2 is completely different, and remains nearly symmetric for the 5.5%SWCNT/TiO$_2$ electrode (Figure 2.g).
Secondly, prominent features appear inside the TiO\textsubscript{2} band-gap region at potentials between 0.1 and 0.3 V vs. RHE (Figure 2). Apparently, the positions of the new peaks can be related to the SWCNT reduction potentials, which have been previously measured and calculated by different researchers.\textsuperscript{[29,30]} For example, the reduction potentials for (12,1), (11,3), (10,5), and (9,7) SWCNTs, which are present in the HiPco material (Supporting Information), were determined by Hirana et al.\textsuperscript{[29]} to be in the range of 0.20 to 0.27 V vs. RHE, in good agreement with our data (Table 1). The interaction between SWCNTs and TiO\textsubscript{2} leads to SWCNT reduction peaks with a higher intensity than that previously observed by Hodge et al.\textsuperscript{[31]} in pure SWCNT electrodes.

The effect of SWCNTs on the TiO\textsubscript{2} intra-band gap states is clarified by measurements on SWCNT/TiO\textsubscript{2} electrodes with very small amounts of SWCNTs (Figure 3). The TiO\textsubscript{2} deep traps downshifted from -0.65 V vs. Ag/AgCl to -0.68/-0.75 V at pH 13 with the addition of 0.02 or 0.1 wt% SWCNTs, while they upshifted from -0.11/-0.14 V to -0.02/0.01 V at pH 2. In both cases, TiO\textsubscript{2} trap positions are different from those of SWCNTs features so electrons apparently migrate towards SWCNTs and not anymore to TiO\textsubscript{2} surface sites. Moreover, the direction of the shift depends on pH, indicating an influence of surface chemistry on the electron trap energy.

At higher SWCNT percentages, differences between cathodic and anodic peak voltages become wider than for low SWCNT percentages (Figure 3). Moreover, the anodic peak intensity substantially decreases at pH 2, indicating a modification in charge transfer kinetics between deep traps and the TiO\textsubscript{2} conduction band.\textsuperscript{[32]} Following Bertoluzzi et al.,\textsuperscript{[32]} it can be stated that electron release from intra band gap trap states, also called the detrapping process, is hindered when SWCNT percentages increase in the SWCNT/TiO\textsubscript{2} electrode.

**SWCNT/TiO\textsubscript{2} voltammetry under irradiation**

Figure 4 shows cyclic voltammetry measurements under light irradiation at pH 13 and pH 2 on blank TiO\textsubscript{2} and SWCNT/TiO\textsubscript{2} electrodes. For blank TiO\textsubscript{2} (Figure 4.a), currents due to water photooxidation can be observed in the anodic scan, at positive current densities, with onset potentials at -0.80 V and -0.22 V for pH 13 and pH 2 respectively.

The anodic reactions taking place can be generically written as:

\[
4\text{OH}^- - 4e^- \rightarrow \text{O}_2↑ + 2\text{H}_2\text{O} \quad \text{at pH 13} \quad (2)
\]

\[
2\text{H}_2\text{O} - 4e^- \rightarrow \text{O}_2↑ + 4\text{H}^+ \quad \text{at pH 2} \quad (3)
\]
The photocurrent in alkaline medium is higher than in the acidic pH. On the other hand, the cathodic scan at pH 13 shows a quite intense band centered at -0.8/-0.9 V, which is due to the reduction of persistent intermediate states of water oxidation. These states were first observed by Wilson,[33] and then confirmed by others,[34,35] and according to the current understanding they should be associated to surface peroxo species.[9] Wilson states are not observed at pH 2, demonstrating that different oxidation mechanisms with different kinetics govern under acidic conditions.[6,36-38]

The addition of SWCNTs to the TiO$_2$ electrode does not substantially change the onset potentials for water photooxidation in the anodic scan (Figure 4, Table 2). At pH 13, the cathodic peak due to Wilson states overlaps with the SWCNT reduction peak that was observed in dark voltammograms. This phenomenon is evidenced by an upshift in the cathodic peak position, together with the rise of the corresponding SWCNT anodic feature. We suggest that SWCNTs may compete with the surface sites of Wilson states as radical scavengers, since it is known from polymerization experiments that carbon nanotubes may capture radicals.[39] However, the role of SWCNTs is unclear, as the evolution of Wilson states with increasing SWCNT percentages cannot be totally unraveled due to its superposition with SWCNT reduction peaks.

The addition of SWCNTs to the TiO$_2$ electrode above a 0.1 wt% causes a progressive disappearance of the photocatalytic current. Actually, voltammograms for the 5.5%SWCNT/TiO$_2$ electrode under irradiation are nearly identical to those in dark conditions (Figure 4.d). This effect is usually assigned to two possible contributions: i) a light blocking effect which decreases the light intensity on TiO$_2$, and most important ii) the role of SWCNT networks as recombination centers.[21,23]

Methanol addition to the electrolyte under irradiation causes great changes in the voltammograms (Figure 5). The saturated photocurrent is very high at pH 13, in agreement with previous reports.[40] Two onset potentials can be distinguished in the anodic scan for both alkaline and acidic conditions (Table 2). The onset potential at the most positive voltages is nearly identical to that observed for water oxidation without methanol. Therefore, the other onset potential at the most negative voltages may be intuitively assigned to methanol oxidation. The products of the anodic methanol oxidation range from methyl aldehyde and formic acid to the most oxidized species CO$_2$.[41] It can be deduced from cyclic voltammetry that photooxidation of water and methanol follow different reaction mechanisms and does not interfere with each other. In fact, it has been suggested that alcohol photooxidation does not progress through
OH· radicals, but it directly occurs on the photocatalyst surface.\[^{[41]}\] Actually, it is evident from our voltammograms that both reactions do not need the same reactive sites on the catalyst surface, since the photocurrent due to water oxidation is not much lower than in the experiments without methanol. The addition of small amounts of SWCNTs to the TiO\(_2\) electrode does not qualitatively alter the voltammogram profiles in the presence of methanol (Figure 5), although causes some variations in the photopotential and photocurrent, as it will be discussed below.

Another feature to be remarked in the voltammograms at pH 13 is the extinction of cathodic Wilson states with the presence of methanol. Clearly, the mechanism of methanol oxidation is linked to the intermediates that are responsible for Wilson features, which indeed may not be necessary for the progress of water oxidation. Regarding SWCNT reduction features in the presence of methanol, they are also observed for the highest SWCNT percentages (not shown).

**SWCNT/TiO\(_2\) photopotential and photocurrent**

Potentiostatic photocurrent and photopotential measurements were subsequently registered after cyclic voltammetry for all the studied systems. Open circuit potential provides an estimate of surface charge distribution in the electrode. Thus, the photopotential correlates with the amount of charge carriers with respect to the dark state. As a general trend, photopotentials at pH 13 are higher than at pH 2, and also increase with methanol addition, particularly at pH 13. The evolution of photopotential with increasing SWCNT percentages is represented in Figure 6. Small amounts of SWCNTs cause increments in the photopotential under all the studied conditions, but especially in the alkaline medium. The photopotential reaches a maximum value for 0.02 or 0.1 wt% SWCNT, depending on the electrolyte conditions, and then progressively decreases below the level of blank TiO\(_2\). This evolution of photopotentials is reminiscent of many literature results on degradation of organics with SWCNT/TiO\(_2\) photocatalysts.\[^{[21-23]}\] It can be hypothesized that individual SWCNTs have a positive influence as electron acceptors, while a charge recombination effect predominates in connected SWCNT networks.

According to the photopotential results, the addition of small amounts of SWCNTs to the TiO\(_2\) photoelectrode should improve its photoactivity if all the other kinetic factors are favorable. In fact, a 13.8% increase in the potentiostatic photocurrent was measured for the 0.02%SWCNT/TiO\(_2\) electrode at pH 2 with methanol (Figure 7), demonstrating
that the presence of SWCNTs can improve the TiO$_2$ photoactivity under selected environment conditions.

Conclusions
We performed an electrochemical study of SWCNT/TiO$_2$ hybrid electrodes that provides new insights on the effect of SWCNTs as additives, especially regarding modifications in the electronic states. In dark voltammograms, SWCNTs cause a substantial distortion of the TiO$_2$ accumulation region at pH 13, inducing a transition from a capacitive to a resistive behavior. However, this transition is not observed at pH 2, indicating that charge leaking through the SWCNTs is hindered by surface protonation, and showing the decisive influence of the environment on the system electronic response. It is also demonstrated by cyclic voltammetry in dark that the peak voltage of TiO$_2$ intra-bandgap traps is modified in the SWCNT/TiO$_2$ electrodes, and their charge capacity increases with the SWCNT percentage. Therefore, electrons are preferentially trapped on SWCNT surfaces and not on TiO$_2$ surface defects. Moreover, the energy levels of the SWCNT acceptors well agree with the calculated and measured reduction potentials of SWCNTs.

All the features that are induced by SWCNTs in dark voltammograms are also observed under light irradiation, jointly with the characteristics due to TiO$_2$ photoactivity. The cathodic peaks of certain water oxidation intermediates, identified as the Wilson states, fall near the reduction potentials of SWCNTs, and are shifted by the presence of the SWCNTs, possibly indicating an interaction between the SWCNTs and the intermediates. The addition of small SWCNT percentages to TiO$_2$ electrodes does not qualitatively modify voltammograms in methanol. Electrode photopotentials reach a maximum value at low SWCNT percentages (0.02-0.1 wt%) in all the studied conditions. This increase in photopotential provides an improved effective photoactivity under appropriate environmental conditions.

Experimental Section

Materials and equipment
Commercial TiO$_2$ nanoparticles (Aeroxide® P25) were obtained from Evonik. HiPco SWCNTs were purchased from NanoIntegris Technologies Inc., Boisbriand, Quebec, Canada. Sodium dodecyl sulfate (SDS, L3771), ethanol (absolute), and methanol
(analytical reagent) were respectively purchased from Sigma-Aldrich, Panreac, and Fisher Scientific.

A 400 W tip (Hielscher UP400S) working at 0.5 cycles and 60% amplitude was utilized for ultrasound treatments. Centrifugation was carried out in a Beckman Coulter L-100 XP ultracentrifuge provided with a SW55Ti 3671 rotor and Beckman centrifugation tubes Ref. 326819. Optical absorbance was measured in 2 mL cuvettes with 1 cm optical path using a Shimadzu UV-2401PC spectrometer.

Fluorinated tin oxide (FTO) substrates (70-100 Ω/sq, 80 nm thickness on 1 mm glass) were purchased from Solems S.A., Palaiseau, France. A Sagola Premium 475 spray gun was utilized for spray-coating. All the electrochemical measurements were performed in a three electrode cell provided with a quartz window, using an AUTOLAB PGSTAT302N. A graphite rod obtained from CYMIT Quimica was used as the counter electrode. Illumination was carried out using a 150 W Xe arc lamp by LOT-Oriel GmbH, which simulates the solar spectrum in the ultraviolet and visible regions.

**Electrode preparation**

The FTO substrates (2.5x1 cm²) were bath sonicated in isopropanol for 5 min. For the preparation of blank TiO₂ films, 1 mL of a 2 mg mL⁻¹ TiO₂ suspension in ethanol was sprayed onto ~ 1 cm² of the substrate. Then, the films were sintered at 450ºC for 2h in a tubular quartz reactor under nitrogen.

The preparation of electrodes with SWCNTs (SWCNT/TiO₂ samples) was carried out by first dispersing the SWCNTs in an aqueous medium and purifying the dispersion for the total removal of amorphous carbon and catalyst metal particles. In a typical experiment, 10 mg of SWCNTs were tip-sonicated for 1h in 10 mL of a 0.5% SDS aqueous solution. To avoid heating, the vial was kept in an ice bath during ultrasonication. Then, the dispersion was purified by ultracentrifugation at 40500 rpm (200,000 xg) for 90 min. The supernatant was carefully decanted and the sediment was discarded. The final SWCNT concentration was measured by optical absorption measurements, considering an extinction coefficient of 22.7 mL mg⁻¹ cm⁻¹ at 850 nm. An appropriate volume of the purified SWCNT ink was added to 1 mL of a 2 mg mL⁻¹ TiO₂ suspension in ethanol, and sprayed on ~ 1 cm² of the substrate. The electrodes were immersed in ultrapure water for 4h to remove the SDS surfactant, and finally sintered at 450ºC for 2h in a nitrogen atmosphere, according to the protocol applied to the blank TiO₂ sample.
Electrochemical measurements

A reference electrode of Ag/AgCl, 3M NaCl ($E^o = 0.210$ V vs. SHE) was utilized for the experiments. A nitrogen purge was utilized to avoid interferences of the oxygen reduction reaction. Experiments were performed in aqueous media at two different pHs. The alkaline environment ($\text{pH} = 13$) consisted of a 0.1M NaOH solution. The acidic environment ($\text{pH} = 2$) was obtained by 0.01M HCl, and 0.09M NaCl was added, making the total ionic strength equal to that in the alkaline experiments. In experiments with methanol, it was added to the electrolyte in a final concentration of 0.1M. Three electrochemical tests were performed, first in water and then with methanol, subsequently and in the following precise order:

Cyclic voltammetry (potentiodynamic experiments)

The potential window ranged from -1.5 to 0 V (vs. Ag/AgCl, 3M NaCl) at pH 13, and from -0.7 to 0.7 V at pH 2. The scan rate was of 20 mV s$^{-1}$. Several cycles were performed to detect the possible presence of irreversible phenomena. As a general observation, the second cycle was totally reproducible and thus is the one presented here. For voltammetry under irradiation, light was applied continuously during the whole cycle.

Photocurrent measurements under potentiostatic conditions

A bias potential of 0 V (vs. Ag/AgCl, 3M NaCl) at pH 13 and 0.7 V at pH 2 was applied, which respectively corresponds to the maximum voltage values in the cyclic voltammogram. Intermittent irradiation and dark periods of 15 s were applied during 5 min.

Open circuit potential measurements (zero current)

The cell was allowed to stabilize under dark conditions, and then the electrode was illuminated for 1 min. The photopotential ($V_{ph}$) was calculated as the difference between dark and illumination voltages.

Acknowledgements

The authors thank the Institute for Biocomputation and Physics of Complex Systems (BIFI) for the centrifugation laboratory. This work has been funded by MINECO and

Keywords: nanotubes; nanoparticles; film; semiconductor; voltammetry

References

**Figure 1.** A) Cyclic voltammogram in dark for bare P25 TiO$_2$ in alkaline and acid media. B) Enlargement of the low current density region in the RHE voltage scale.
Figure 2. Cyclic voltammograms in dark at pH 13 (a-f) and pH 2 (g): a) TiO$_2$, b) 0.02%SWCNT/TiO$_2$, c) 0.1%SWCNT/TiO$_2$, d) 0.5%SWCNT/TiO$_2$, e) 2.5%SWCNT/TiO$_2$, f-g) 5.5%SWCNT/TiO$_2$. 
Figure 3. Cyclic voltammogram in dark at pH 13 and pH 2: a) TiO$_2$, b) 0.02\%SWCNT/TiO$_2$, c) 0.1\%SWCNT/TiO$_2$, and d) 5.5\%SWCNT/TiO$_2$. 
Figure 4. Cyclic voltammograms under illumination at pH 13 and pH 2: a) TiO$_2$, b) 0.02%SWCNT/TiO$_2$, c) 0.1%SWCNT/TiO$_2$, and d) 5.5%SWCNT/TiO$_2$. 
Figure 5. Cyclic voltammograms under illumination at pH 13 and pH 2 with methanol: a) TiO$_2$, b) 0.02%SWCNT/TiO$_2$, and c) 0.1%SWCNT/TiO$_2$. 
**Figure 6.** Photopotential ($V_{ph}$) at zero current for SWCNT/TiO$_2$ electrodes in different media: a) pH 2, b) pH 2 + methanol, c) pH 13, and d) pH 13 + methanol.

**Figure 7.** Photocurrent density ($j_{ph}$) for SWCNT/TiO$_2$ electrodes after 4.25 min of intermittent irradiation in different media: a) pH 2, b) pH 2 + methanol, c) pH 13, and d) pH 13 + methanol. Bias voltage is either 0 V or 0.7 V (vs. Ag/AgCl, 3M NaCl) for measurements at pH 13 and pH 2 respectively.
### Table 1
Anodic (E<sub>a</sub>) and cathodic (E<sub>c</sub>) main peak positions in volts (vs. RHE), from dark cyclic voltammograms measured in both alkaline and acidic media.

<table>
<thead>
<tr>
<th>Sample</th>
<th>E&lt;sub&gt;a&lt;/sub&gt; (pH 13)</th>
<th>E&lt;sub&gt;c&lt;/sub&gt; (pH 13)</th>
<th>E&lt;sub&gt;a&lt;/sub&gt; (pH 2)</th>
<th>E&lt;sub&gt;c&lt;/sub&gt; (pH 2)</th>
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<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.34</td>
<td>0.33</td>
<td>0.22</td>
<td>0.18</td>
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<tr>
<td>0.02%SWCNT/TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.30</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>0.26</td>
<td>0.25</td>
<td>0.34</td>
<td>0.34</td>
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<td>0.1%SWCNT/TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.31</td>
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</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.25</td>
<td>0.30</td>
<td>0.32</td>
</tr>
<tr>
<td>0.5%SWCNT/TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.21</td>
<td>0.20</td>
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</tr>
<tr>
<td>1.0%SWCNT/TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.24</td>
<td>0.24</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>2.5%SWCNT/TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.26</td>
<td>0.18</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>5.5%SWCNT/TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.36</td>
<td>---</td>
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<td>---</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td>0.14</td>
<td>0.08</td>
<td>0.26</td>
</tr>
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</table>

### Table 2
Onset potentials E<sub>o</sub> [V] (vs. Ag/AgCl, 3M NaCl) from cyclic voltammograms in light.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH 13</th>
<th>pH 13 + MeOH&lt;sup&gt;a&lt;/sup&gt;</th>
<th>pH 2</th>
<th>pH 2 + MeOH&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-0.80</td>
<td>-1.11/-0.86</td>
<td>-0.22</td>
<td>-0.41/-0.20</td>
</tr>
<tr>
<td>0.02%SWCNT/TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-0.80</td>
<td>-1.09/-0.83</td>
<td>-0.15</td>
<td>-0.42/-0.14</td>
</tr>
<tr>
<td>0.1%SWCNT/TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-0.81</td>
<td>-1.09/-0.83</td>
<td>-0.17</td>
<td>-0.42/-0.14</td>
</tr>
<tr>
<td>0.5%SWCNT/TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-0.83</td>
<td>-1.11/-0.84</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1.0%SWCNT/TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-0.83</td>
<td>-1.09/-0.83</td>
<td>---</td>
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</tr>
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</table>

<sup>a</sup>Two contributions are clearly observed in the anionic scan of the experiments with methanol (MeOH).
The photoactive carbon nanotube/semiconductor system for an electrochemist: cyclic voltammetry unravels amplified nanotube reduction peaks; photopotentials reach maximum values for small carbon nanotube percentages.