Charge-transfer characteristics in carbon nanostructure/metal oxide photoelectrodes efficiently probed by hydrogen peroxide

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Abstract

The charge-transfer characteristics of nanostructured carbon/TiO₂ electrodes is studied by cyclic voltammetry under photoelectrochemical conditions exploiting the electrooxidation and electroreduction of H₂O₂ in an alkaline medium. Films of composites were prepared by physically mixing TiO₂ with 5 wt.% of either single-walled carbon nanotubes (SWCNTs) or reduced graphene oxide (rGO). In addition, a layer-by-layer rGO/TiO₂ electrode was prepared. Under dark conditions, both mixed SWCNTs and rGO facilitate H₂O₂ reduction. Under light irradiation, the blank TiO₂ electrode shows a cathodic photopotential, the SWCNT/TiO₂ an anodic photopotential, and the mixed rGO/TiO₂ an increased cathodic photopotential. This scenario unambiguously reveals a photoelectron acceptor behavior for SWCNTs and a photohole acceptor performance for rGO. The latter one also agrees with the photoactivity observed in the layer-by-layer electrode. Overall, the value of H₂O₂ redox reactions for

unraveling the electron-donor or electron-acceptor character of carbon nanostructures in C/metal oxide electrodes is demonstrated.

Keywords: titanium dioxide; carbon nanotube; graphene oxide; cyclic voltammetry; photoelectrochemistry

1. Introduction

Hydrogen peroxide (H_2O_2) is often considered as a strong oxidizing agent with a very high standard potential. Specifically, under the conditions of this work (pH=13, 0.1 M H_2O_2 , 3 ppm O_2), the potentials for H_2O_2 reduction and oxidation are respectively:

The potential of the reduction half-reaction is higher than the potential of the oxidation half-reaction, indicating that H_2O_2 is unstable by disproportionation. Moreover, H_2O_2 can act both as an electron[1] or a hole scavenger[2], depending on the considered electrochemical system. In fact, on TiO_2 surfaces H_2O_2 has been previously employed as an electron acceptor to improve the oxidation of organic compounds[3-5], as well as to facilitate advanced sensing applications[6]. It has also been used as a complementary electron source to enhance the performance of photoanodes [7], which in turn, from a conceptual point of view, underlines its ability to accept photo-generated holes [8, 9]

On the other hand, carbon nanomaterials, including carbon nanotubes and graphene in their different varieties, may work as electron or hole acceptors when they form composites with photoactive semiconducting materials. Carbon nanotubes usually behave as electron acceptors and improve the photoactivity of TiO_2 at low nanotube contents[10]. For graphene, both electron[11] and hole acceptor[12, 13] behavior have

been observed, depending on the characteristics of the material and the conditions of the experiments. Therefore, it is difficult to generalize the charge transfer behavior of graphene in complex systems with different configurations and kinetics. In this work we exploit for the first time the double redox reaction of H_2O_2 on carbon nanomaterial/semiconducting metal oxide composites and demonstrate its unique value for elucidating the charge transport characteristics of highly-purified single-walled carbon nanotubes (SWCNTs) and reduced graphene oxide (rGO) in TiO_2 composites. The energy levels of the H_2O_2 molecule and its relatively fast reaction kinetics appear to be highly suitable for understanding the pathway of photogenerated charges in these systems.

2. Experimental methods

2.1. Materials and equipment

Commercial TiO_2 nanoparticles (Aeroxide P25, Evonik Degussa) were used in this work. SWCNTs (Small diameter HiPCoTM) were purchased from NanoIntegris, Boisbriand, Canada. Graphite flakes were purchased from Aldrich (Ref. 332461). NaOH (reagent grade) was purchased from Sigma-Aldrich and extra-pure 30% H_2O_2 from Fisher. FTO substrates (70-100 Ω/sq , 80 nm thickness, 2.5x1 cm^2 pieces) were purchased from SOLEMS ASAHI. A graphite rod (CYMIT Química) was used as the counter electrode. Photoelectrochemical measurements were performed in a three-electrode cell with a quartz window, using an AUTOLAB PGSTAT302N. Illumination was carried out using a 150 W Xe arc lamp (LOT-Oriel GmbH, Germany). Scanning electron microscopy was carried out in a SEM EDX Hitachi S-3400 N microscope.

2.2. Aqueous inks of carbon nanomaterials

The SWCNT powder material was ultrasonically dispersed in a surfactant at $1 \text{ mg} \cdot \text{mL}^{-1}$, and purified by ultracentrifugation[14]. The SWCNT concentration in the supernatant dispersion was measured by optical absorption.

Graphene oxide (GO) was synthesized from graphite flakes by a modified Hummers method including an overnight reflux in $\text{NaNO}_3/\text{H}_2\text{SO}_4/\text{KMnO}_4$, cooling in 30% H_2O_2 , filtration, resuspension in water at $0.5 \text{ mg} \cdot \text{mL}^{-1}$, and exfoliation in an ultrasound bath[15]. The rGO ink was prepared by reaction of the GO dispersion with hydrazine under reflux conditions at pH 9, followed by dialysis, in order to remove excess reagent and products.

2.2. Electrode preparation

Blank TiO_2 films were prepared by spray-coating 1 mL of a TiO_2 suspension in absolute ethanol (2 mg/mL) onto approximately 1 cm^2 of the FTO substrate. The films were treated at 450°C for two hours in N_2 atmosphere. Three different C/ TiO_2 electrodes were prepared:

- i) A SWCNT/ TiO_2 electrode, which contained approximately 5 wt.% SWCNTs, by mixing the SWCNT supernatant with the TiO_2 dispersion. The films were washed in water to remove traces of remaining surfactant.
- ii) An rGO/ TiO_2 electrode, which contained 5 wt.% in rGO, by mixing the rGO ink with the TiO_2 dispersion.

These two electrodes were also treated at 450°C in N_2 atmosphere.

iii) A layer-by-layer (L-)rGO/TiO₂ electrode. GO dispersion was spray-coated on a blank TiO₂ electrode. The average thickness of the GO layer was 20 nm as probed by profilometry (Bruker DektakXT Stylus). Finally, the GO layer was electrochemically reduced applying four potentiodynamic cycles between -0.040 and -1.440 V (Hg/HgO 0.1M KOH).

2.4. Electrochemical measurements

Voltammograms were performed using N₂-purged 0.1 M NaOH as the supporting electrolyte, a Hg/HgO (0.1 M KOH) reference electrode and a graphite counter electrode. The scan rate was 20 mV/s, and the second cycle is presented here in all the cases. The photoactivity was tested in 0.1M H₂O₂. Photopotential was calculated according to:

$$V_{ph} = E_{light} - E_{dark} \quad (\text{eq. 5})$$

where E_{light} and E_{dark} are the zero current voltage with and without illumination respectively. The maximum photocurrent density j_{ph} is calculated at both the anodic and cathodic branches of the voltammograms, as the largest difference of the current density between light and dark conditions:

$$j_{ph} = \max(j_{light} - j_{dark}) \quad (\text{eq. 6})$$

3. Results and discussion

3.1 SEM micrographs.

SEM images show a homogeneous TiO₂ layer with larger aggregates on its surface (figure 1A). For the SWCNT/TiO₂ electrode (figure 1B), a homogeneous surface is observed. The absence of aggregates of TiO₂ and SWCNTs is indicative of a rather

uniformly composed material. The rGO/TiO₂ electrode (figure 1C) is characterized by individual rGO sheets, homogeneously dispersed throughout the TiO₂ matrix. Contrarily, the L-rGO/TiO₂ electrode (figure 1D) looks very similar to the TiO₂ one, but “blurred” by the rGO layer, which appears as a uniform and homogeneous top-layer.

3.2. Dark voltammetry in NaOH

The electrodes were characterized by cyclic voltammetry, in dark conditions, in 0.1 M NaOH (Figure 1). Blank TiO₂ exhibits the typical electrochemical behavior that can be found in the literature[16]. The main characteristic of the SWCNT/TiO₂ electrode is the presence of large cathodic/anodic peaks in the TiO₂ bandgap region that can be associated to charge accumulation in the proximity of SWCNTs, due to the availability of new electronic states in the proximities of the TiO₂ conduction band[10]. In contrast, the rGO/TiO₂ voltammogram resembles the blank TiO₂ electrode. The layer-by-layer L-rGO/TiO₂ electrode experiences an increase in the electrode capacitive character and in the faradaic cathodic current for water reduction ($\sim -1.4\text{V}$), which can be attributed to an improvement in the electrical conductivity of the system[17], due to the presence of the top rGO layer.

3.3. Voltammetry in H₂O₂

CVs were carried out at a high concentration of H₂O₂, both under dark conditions and xenon lamp illumination (Figure 2). Forward and backward scans of each voltammogram are identical, not revealing any hysteresis loop. The curves (Figure 2) show negative and positive branches, according to the consumption of H₂O₂ by reduction to OH⁻ (Eq. 1) and oxidation to O₂ (Eq. 2) respectively. For blank TiO₂ in dark conditions (Figure 3A, 3B), the zero-current potential is located at -0.224 V, which

is near the oxidation potential of hydrogen peroxide. Therefore, according to the classical mixed potential theory[18], H_2O_2 electro-oxidation is faster than H_2O_2 electro-reduction. However, under illumination the electrode develops an activity in the cathodic branch (Figure 2B). Even though H_2O_2 might undergo photochemical reactions in liquid phase[19, 20], previous studies have shown that the main source of photoactivity refers to the reaction of H_2O_2 on TiO_2 surfaces, rather than to homogeneous photocomposition processes of H_2O_2 [3, 4].

The presence of SWCNTs changes substantially the response of TiO_2 . Under dark conditions (Figure 3B), anodic current decreases, cathodic current increases, and zero-current potential is 44 mV more positive than for TiO_2 alone. Therefore, the SWCNT/ TiO_2 electrode shows an improved behavior for H_2O_2 electro-reduction. Apparently, SWCNTs might provide additional electronic states that help the electron transfer to the H_2O_2 molecule in the dark. Under illumination (Figure 2B), the SWCNT/ TiO_2 electrode develops a clear photoanodic activity.

For the rGO/ TiO_2 electrode in dark conditions (figure 3B), there is a decrease in the anodic value of the current, and an increase in the cathodic branch, compared to TiO_2 alone. The trend is analogous to that observed for the SWCNT/ TiO_2 electrode, and the different currents are most likely associated to variations in the electronic states provided by the carbon nanomaterials. Zero-current potential for the rGO/ TiO_2 electrodes does not change significantly compared to the TiO_2 electrode. Under illumination, rGO/ TiO_2 remains as photocathode (Figure 3C), contrary to the behavior of the SWCNT/ TiO_2 electrode.

In the L-rGO/ TiO_2 electrode, the continuous rGO layer blocks the direct contact between the TiO_2 and the electrolyte, thus entirely changing the electrode-electrolyte interphase. The H_2O_2 electro-oxidation is favored in the dark (Figure 3B), while H_2O_2

electro-reduction is hindered with respect to the composite rGO/TiO₂ electrode. Under illumination, the photoanodic process is slightly favored (Figure 3C).

In summary, the electrochemical behavior in H₂O₂ under dark conditions depends on the electrode configuration (composite or layered), rather than on the type of carbon nanostructure itself (SWCNT or rGO). Both carbon nanomaterials perform similarly in the dark, while behaving totally different under light irradiation. This suggests that electronic levels from the valence band of the carbon nanomaterials are involved in charge transfer under dark conditions, while the conduction band levels of SWCNTs may play a role when electrons are excited to the TiO₂ conduction band. The effects of light irradiation are further discussed in the following paragraphs.

3.4. Photopotential and photocurrent density in H₂O₂

V_{ph} and j_{ph} for all the electrodes are plotted in Figure 3D and 3E. Positive V_{ph} and negative j_{ph} indicate the ability of the electrode to work as a photocathode (H₂O₂ photoreduction), while negative V_{ph} and positive j_{ph} are associated to a photoanode behavior (H₂O₂ photooxidation). Blank TiO₂ shows a negative (cathodic) photocurrent ($-93 \mu A \cdot cm^{-2}$), together with a positive V_{ph} (+37 mV) indicating that H₂O₂ is able to extract photogenerated electrons from the TiO₂ conduction band.

The photoresponse of the electrode changes considerably after the addition of SWCNTs. Unlike blank TiO₂, the SWCNT/TiO₂ electrode behaves as a photoanode, yielding a high positive j_{ph} ($+79 \mu A \cdot cm^{-2}$) and negative V_{ph} (-217 mV). Therefore, H₂O₂ is able to react rapidly with the photogenerated holes on TiO₂ surfaces, while the photoelectrons from the TiO₂ conduction band are transferred to the SWCNT trap states, thus hindering recombination. This observation agrees with the presence of

electronic levels near the TiO_2 accumulation region (conduction band) in the reference voltammogram (Fig. 2). In previous experiments with water and methanol [10], even though SWCNTs showed photoelectron accepting properties, they did act as recombination centers. It seems that recombination rate was faster than water and methanol photooxidation, and photocurrent was completely blocked in the SWCNT/ TiO_2 electrode. However, a high oxidation photocurrent for H_2O_2 seems to confirm the role of SWCNTs as electron acceptors, further implying that H_2O_2 oxidation is faster than recombination.

The V_{ph} for mixed rGO/ TiO_2 increases compared to TiO_2 (+45 and +37 mV, respectively), indicating an improvement in charge separation. The positive photopotential is associated with the accumulation of positive charges in the electrode. The rGO additive thus improves the amount of accumulated photoholes and reveals an hole-acceptor behavior. Also, cathodic photocurrent is higher for rGO in the potential range between -0.15 and -0.35 V (figure 3B). However, maximum cathodic j_{ph} for rGO/ TiO_2 is lower than for TiO_2 (-48 and -64 $\mu\text{A}\cdot\text{cm}^{-2}$, respectively). The photoelectrons are not easily transferred to the electrolyte, indicating that rGO eventually may act as recombination center.

In the L-rGO/ TiO_2 electrode the sign of V_{ph} changes. The rGO layer hinders the direct contact between TiO_2 and the electrolyte, blocking the photoelectron transfer from TiO_2 to H_2O_2 . The cathodic photocurrent nearly disappears due to the blocking effect, while an anodic photocurrent appears, reaching +16 $\mu\text{A}\cdot\text{cm}^{-2}$. Therefore, the rGO material acts as an acceptor of photoholes and allows the transport of holes from the electrode to the solution. The L-rGO/ TiO_2 response is compatible with the hole acceptor behavior of rGO previously observed in the mixed rGO/ TiO_2 electrode.

Figure 3 clearly shows that H_2O_2 can be used to unravel charge transfer mechanisms of the different carbon nanostructures and confirm that SWCNTs act as electron acceptors while rGO acts as a hole acceptor from photoexcited TiO_2 . Furthermore, the photoactivity of rGO in a layer-by-layer configuration qualitatively agrees with the one observed in the mixed composite electrode. The exterior layer of carbon nanomaterials hinders the TiO_2 contact with the solution, and may even change the cathodic/anodic character of the electrode.

4. Conclusions

Photoelectrochemical study of the double H_2O_2 redox reaction can be employed for the analysis of the charge transfer behavior of carbon nanostructures in C/ TiO_2 composites. This strategy is particularly useful since H_2O_2 photooxidation is faster than electron/hole recombination processes. The results, particularly photopotential measurements, reveal a photoelectron acceptor behavior in the case of SWCNT-based electrodes under light irradiation and a photohole acceptor behavior for rGO-based electrodes. Hole accepting properties of rGO also agree with the behavior of a layer-by-layer rGO/ TiO_2 electrode.

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Figure captions

Figure 1. SEM micrographs of the electrodes.

Figure 2. Cyclic voltammograms in dark conditions, 0.1M NaOH.

Figure 3. (A-C) Cyclic voltammograms in 0.1M H₂O₂. (D, E) Photopotential and maximal photocurrent obtained by cyclic voltammetry in 0.1M H₂O₂.

Figure 1

Figure 2

Figure 3