Short communication

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

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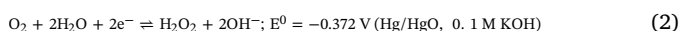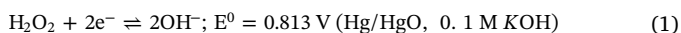
ARTICLE INFO

ABSTRACT

The charge-transfer characteristics of nanostructured carbon/TiO$_2$ electrodes are studied by cyclic voltammetry under photoelectrochemical conditions exploiting the electrooxidation and electroreduction of H$_2$O$_2$ in an alkaline medium. Films of composites were prepared by physically mixing TiO$_2$ with 5 wt% of either single-walled carbon nanotubes (SWCNTs) or reduced graphene oxide (rGO). In addition, a layer-by-layer rGO/TiO$_2$ electrode was prepared. Under dark conditions, both mixed SWCNTs and rGO facilitate H$_2$O$_2$ reduction. Under light irradiation, the blank TiO$_2$ electrode shows a cathodic photopotential, the SWCNT/TiO$_2$ an anodic photopotential, and the mixed rGO/TiO$_2$ an increased cathodic photopotential. This scenario unambiguously reveals a photo-electron 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 H$_2$O$_2$ redox reactions for unraveling the electron-donor or electron-acceptor character of carbon nanostructures in C/metal oxide electrodes is demonstrated.

1. Introduction

Hydrogen peroxide (H$_2$O$_2$) 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$_2$O$_2$, 3 ppm O$_2$), the potentials for H$_2$O$_2$ reduction and oxidation are respectively:

$$H_2O_2 + 2e^- \rightleftharpoons 2OH^-; E^0 = 0.813 \text{ V (Hg/HgO, 0. 1 M } KOH) \tag{1}$$

$$O_2 + 2H_2O + 2e^- \rightleftharpoons H_2O_2 + 2OH^-; E^0 = -0.372 \text{ V (Hg/HgO, 0. 1 M KOH)} \tag{2}$$

The potential of the reduction half-reaction is higher than the potential of the oxidation half-reaction, indicating that H$_2$O$_2$ is unstable by disproportionation. Moreover, H$_2$O$_2$ 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$_2$O$_2$ 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 semi-conducting 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$_2$O$_2$ 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$_2$O$_2$ 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)

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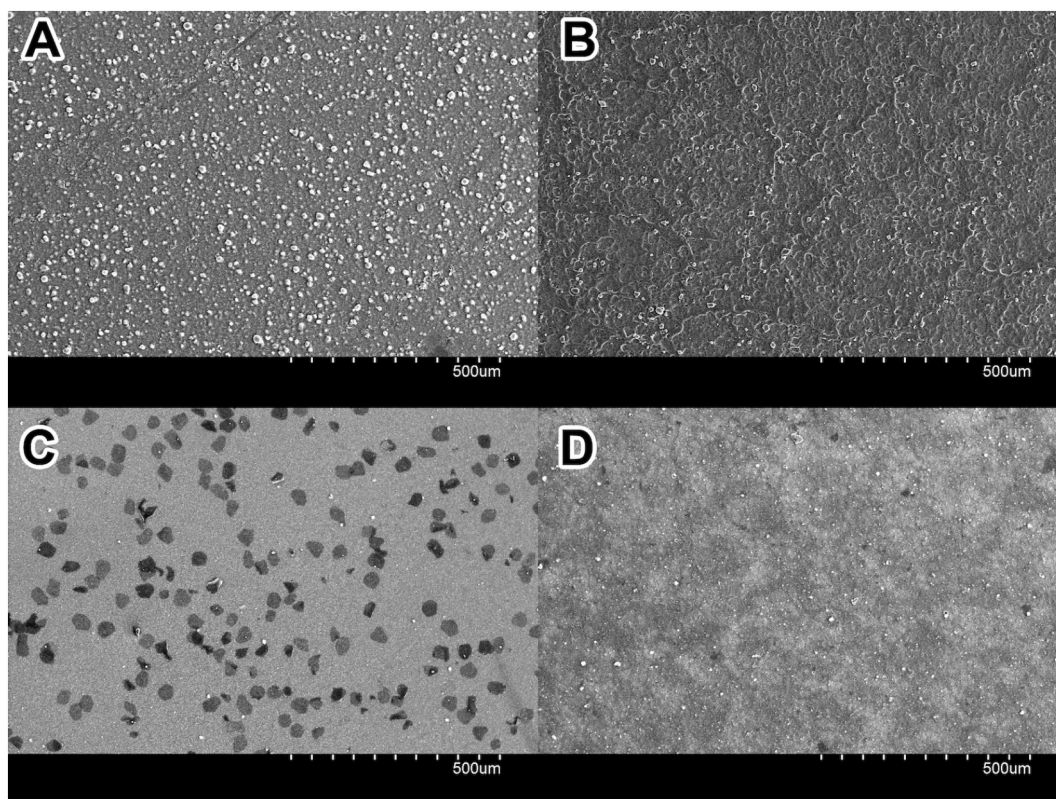 *E-mail address:* jhernandez@icb.csic.es (J. Hernández-Ferrer).

Fig. 1. SEM micrographs of the electrodes.

were used in this work. SWCNTs (Small diameter HiPCo™) 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, 2.5 × 1 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 mg·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 NaNO$_3$/ H_2SO_4/KMnO$_4$, cooling in 30% H_2O_2, filtration, resuspension in water at 0.5 mg·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.

2.3. 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 2 h 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/TiO_2 electrode. GO dispersion was spray-coated on a blank TiO_2 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 0.1 M KOH).

2.4. Electrochemical measurements

Voltammograms were performed using N$_2$-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 0.1 M H_2O_2. Photopotential was calculated according to:

$$V_{ph} = E_{light} - E_{dark} \tag{3}$$

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:

$$j_{ph} = \max(j_{light} - j_{dark}) \tag{4}$$