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Photo-anodes based on TiO₂ and carbon dots for photo-electrocatalytical measurements

Humay Aliyeva,¹ Ari Gurel,¹ Sophie Nowak,¹ Stéphanie Lau,¹

Philippe Decorse,¹ Samiha Chaguetmi,^{1,2} Delphine Schaming^{1,} and Souad Ammar¹*

¹ Université Paris Diderot, Sorbonne Paris Cité, ITODYS, CNRS-UMR 7086, 75013 Paris, France.

² Université du 20 Août 1955 de Skikda, Faculté des Sciences, 21000 Skikda, Algeria

(*)Corresponding author: delphine.schaming@univ-paris-diderot.fr

Abstract

Wide band-gap semiconductor TiO₂ is an efficient anode material for photo-electrocatalytical (PEC) applications. Its light-sensitivity is limited to the UV but can be extended to the visible by chemical doping or chromophore sensitization. Moreover, its conductivity can be enhanced by coupling with carbon materials, which should limit back electron-hole recombination. In this context, we prepared hetero-nanostructures based on TiO₂ nanofibers supported on Ti sheet and impregnated with carbon dots (CDs), and used them as photo-anodes in photo-electrochemical cells. They showed a higher photocurrent than non-CD-impregnated photo-anodes, underlining the importance of CDs for water-splitting processing.

Keywords

TiO₂ nanofibers, carbon dots, photo-electrocatalysis

1. Introduction

Hydrogen production by solar light-driven water splitting is a promising technology. However, it requires photo-anodes which convert light energy into chemical energy efficiently. Several semiconducting nanomaterials have already been used as photo-electrodes. In particular, TiO₂ shows promise [1], due to its good electrical and light-dependent properties, its chemical stability, its low cost and its environmental safety. Nevertheless, work on improving its performance is in progress, principally by extending its activity to the visible range or by decreasing back electron-hole

recombination. Thus, TiO_2 has been modified by doping or functionalization [2, 3]. For example, carbon materials such as nanotubes [4], graphene [5-7], fullerene [8], etc. have been used to increase the photocatalytic properties of TiO_2 , because of their high electron mobility and their ability to promote the separation of photogenerated electron-hole pairs, enhancing charge-transfer processes [9-11]. Carbon dots (CDs) constitute a new class of carbon nanomaterials with no equivalent in other families of carbon-based nanomaterials [12-15]. They have the same fascinating physical properties as quantum-dots, but do not contain heavy metals, which makes them safer and more environmentally friendly. Their semiconductor-like electronic structure allows them to absorb visible light while their graphene-like crystallographic structure improves interfacial charge mobility [16] and separation [17]. Thus, CDs combine several important properties needed to enhance semiconducting properties in photo-assisted electrocatalysis applications.

Some studies have recently shown the capabilities of CDs to enhance photocatalytic properties of TiO_2 [18, 19]. In this letter, we investigate the effect of impregnation of TiO_2 nanofibers (NFs) by CDs on their photo-electrochemical (PEC) response, when immersed as anode materials in a standard PEC cell, by comparing their photocurrent to that of bare TiO_2 NFs. An important increase of the photocurrent has been observed in the presence of CDs, showing the capability of CDs to enhance photo-electrocatalytic properties of semi-conductors such as TiO_2 .

2. Experimental

TiO_2/Ti electrodes were obtained in treating Ti sheets in a 5 wt% aqueous oxalic acid solution at 100°C for 2 h, and then immersing them for 24 h in a solution of H_2O_2 (30 wt%) and NaOH (10 M) in a Teflon-lined stainless-steel autoclave at 80°C . CDs were synthesized using an aqueous solution (40 mL) of citric acid (1.68 g) and urea (1.44 g) in a Teflon-lined stainless-steel autoclave at 160°C for 4 h. CDs- TiO_2/Ti nanocomposites were prepared by impregnation of TiO_2/Ti sheets in a solution of CDs after acidification with HNO_3 .

High-resolution transmission-electron microscopy (HRTEM) and scanning-electron microscopy (SEM) were performed using microscopes operating at 200 and 5 kV, respectively. X-ray diffraction (XRD) was performed in grazing conditions using a $\text{Cu-K}\alpha$ X-ray source (1.5418 \AA). Raman spectra were recorded using a laser at 633 nm. High-resolution X-ray photoelectron spectroscopy (HR-XPS) was carried out with a monochromatic $\text{Al-K}\alpha$ X-ray source (1486.6 eV), with a spot size of $500 \mu\text{m}$ (15 kV, 150 W); spectra were acquired in the constant-analyzer energy mode with a pass energy of 40 eV.

The photo-responses of the two photo-anodes, TiO_2/Ti and CDs- TiO_2/Ti , were evaluated in a three-electrode PEC cell, under intermittent xenon lamp (150 W) illumination.

3. Results and discussion

On HRTEM micrographs, the CDs appear as 3-5 nm-sized spherical particles (Fig. 1A), with a well-resolved lattice spacing of 2.1 Å, matching the (100) crystal planes of graphite [20].

UV-visible absorption spectroscopy performed on a colloidal aqueous solution of CDs (Fig. 1B) indicates that CDs absorb principally in the UV range, with a shoulder in the visible range around 550 nm.

The XRD pattern of TiO₂/Ti (Fig. 1C) exhibits well-defined peaks matching perfectly the tetragonal TiO₂ anatase structure (ICDD no.00-021-1272). Additionally, its Raman spectrum (Fig. 1D) shows modes at 399, 517 and 638 cm⁻¹ corresponding to the B_{1g}, A_{1g}+B_{1g} and E_g vibrations, respectively, of the anatase phase [21]. Finally, SEM observation (Fig. 1E) confirms TiO₂ appears as entangled fibers less than 100 nm in diameter and several μm in length.

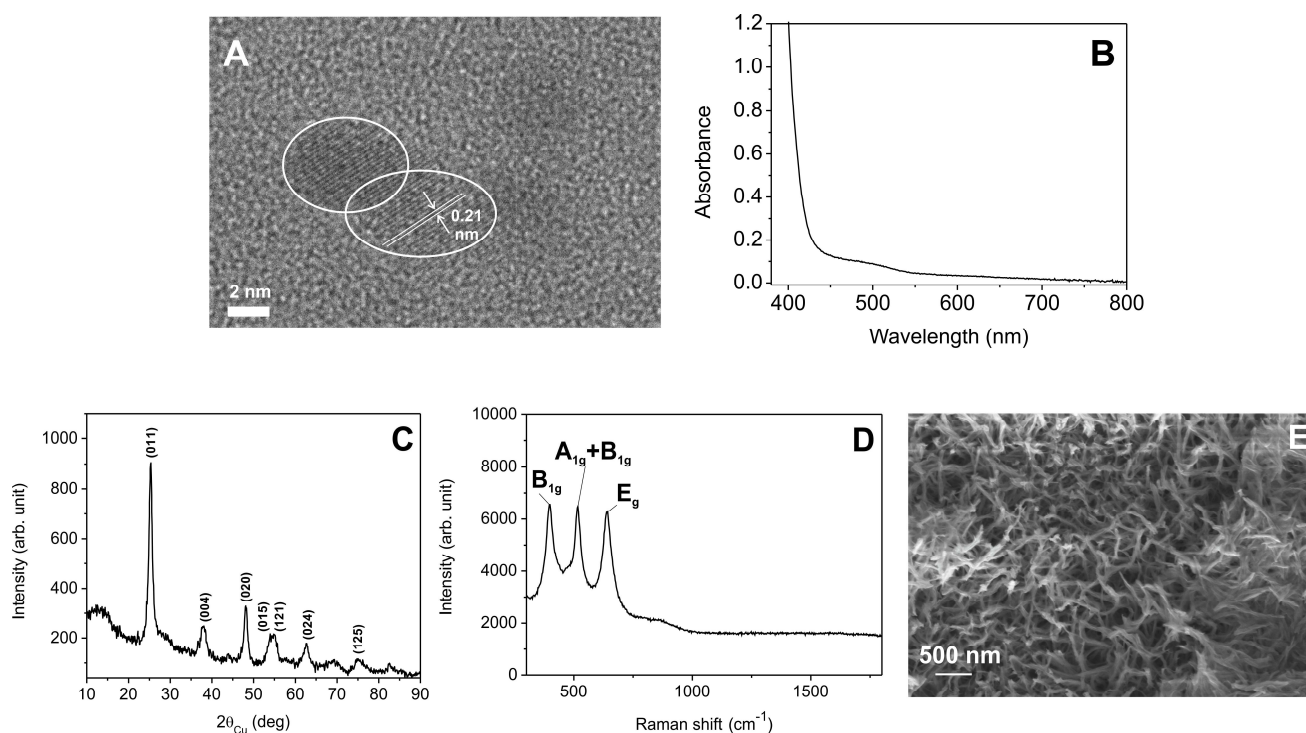


Figure 1. (A) HRTEM image and (B) UV-visible absorption spectrum of CDs; (C) XRD pattern, (D) Raman spectrum and (E) SEM image of TiO₂/Ti

The surface of the TiO₂/Ti sheet, initially white, becomes blue after impregnation by CDs, suggesting the presence of CDs, agglomerated on the surface of TiO₂ NFs and/or within their inter-porosity. The Raman spectrum of the resulting hetero-nanostructure (Fig. 2A) exhibits clearly the signature of both anatase and graphene-type phases. Indeed, a total of five bands were observed, three at 399, 517 and 638 cm⁻¹, assigned to crystalline TiO₂, and two at 1350 and 1550 cm⁻¹, assigned to CDs. The band at

1550 cm^{-1} , usually called the crystalline G-band, corresponds to the in-plane vibration of sp^2 carbon, and that at 1350 cm^{-1} , called the disordered D-band, is related to the presence of sp^3 carbon defects [20, 22].

The surface chemical compositions of TiO_2/Ti and $\text{CDs-TiO}_2/\text{Ti}$ were also investigated. $\text{Ti}2\text{p}$ HR-XPS spectra of the two samples exhibit the same signature: two Ti signals at 459.5 and 465.2 eV, assigned to classical binding energies of titanium in TiO_2 and corresponding to $2\text{p}_{3/2}$ and $2\text{p}_{1/2}$ Ti(IV), respectively (Fig. 2B). The $\text{C}1\text{s}$ HR-XPS spectrum of TiO_2/Ti (Fig. 2C) is consistent with previously reported XPS data for TiO_2 materials [17]. Three peaks with binding energies of 285.6, 287.5 and 289.6 eV, mainly attributed to the adsorption of organic residues, are observed. The first peak corresponds to C-C and C-H bonds. Those at higher energies correspond to C-O and C=O bonds from carbonates, leading to Ti-C-O and Ti-O-C bond [23, 24]. The $\text{C}1\text{s}$ HR-XPS spectrum of CDs consists of a strong peak at 284.8 eV, usually attributed to sp^2 carbon atoms [20], which is broadened and followed at higher energies by a small, broader peak assigned to C-O and C=O bonds, present at the surface of CDs. The $\text{C}1\text{s}$ of $\text{CDs-TiO}_2/\text{Ti}$ seems to be a combination of those of TiO_2/Ti and of free CDs. At low binding energies, the graphitic sp^2 (at 284.8 eV) and the aliphatic sp^3 (at 285.6 eV) signals are observed, related to the impregnated CDs and organic residues adsorbed at the surface of TiO_2 NFs, respectively. At higher energies, the intensity of the carbonate peaks is enhanced, due to the presence of CDs adsorbed at the surface of TiO_2 . The $\text{O}1\text{s}$ spectra of these samples confirm the former conclusions, since we can clearly distinguish the signature of both CDs and TiO_2 on the $\text{CDs-TiO}_2/\text{Ti}$ spectrum (Fig. 2D). Indeed, oxygen atoms from carbonates at the surface of CDs exhibit a typical signal at 532.0 eV, which is present in both free CDs and $\text{CDs-TiO}_2/\text{Ti}$ spectra. The oxygen atoms of the anatase lattice exhibit also a specific signature at 531.0 eV, which is present in the spectra of TiO_2/Ti and $\text{CDs-TiO}_2/\text{Ti}$. The peak at 530.3 eV observed in the CD spectrum corresponds to ITO, which has been used as substrate to deposit CDs for the XPS analysis.

As a consequence, Raman spectroscopy and XPS measurements confirm the presence of CDs at the surface of TiO_2 nanofibers. As a negative zeta potential has been measured for CDs, they should be linked at the surface of TiO_2 , which is positively charged after soaking in the acid bath, by electrostatic interactions.

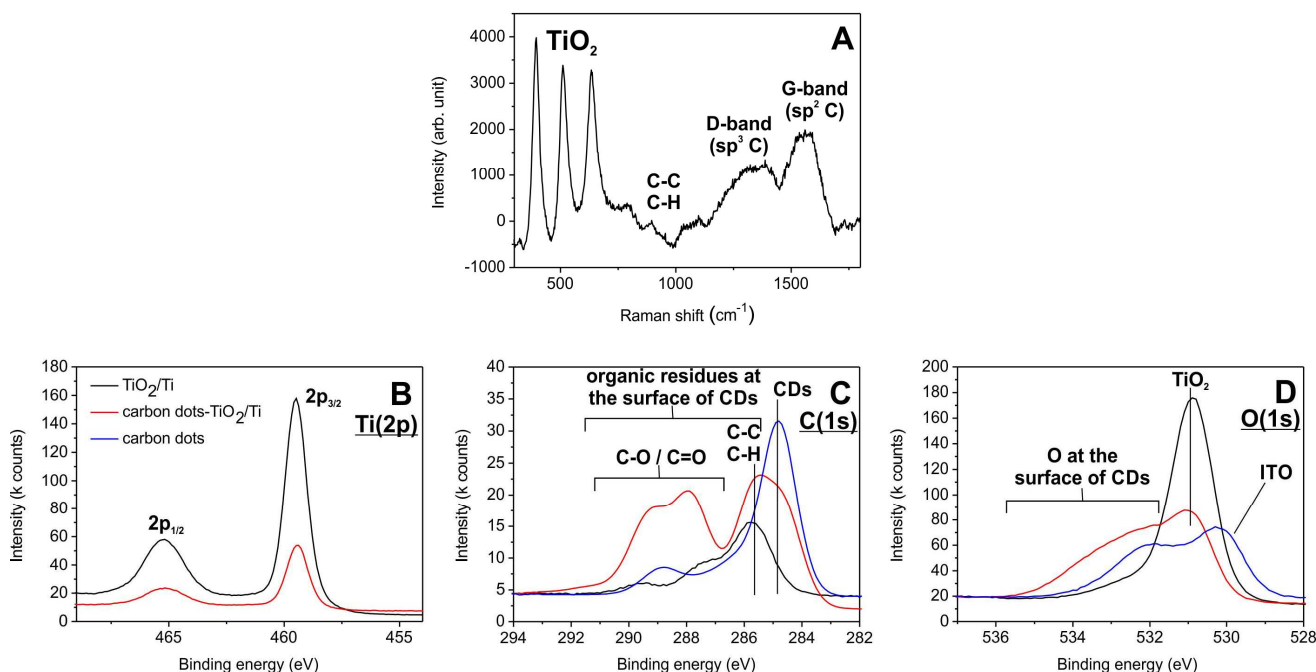


Figure 2. (A) Raman spectrum of CDs-TiO₂/Ti sheet; (B) Ti2p, (C) C1s and (D) O1s XPS spectra of CDs, TiO₂/Ti and CDs-TiO₂/Ti.

PEC properties of TiO₂/Ti and CDs-TiO₂/Ti were investigated by measuring the photocurrent produced during intermittent illumination, at different bias potentials. Firstly, we used an electrolyte of sulfites (Na₂SO₃) and sulfides (Na₂S) (Figs. 3A,B). This mixed electrolyte has already been found suitable for hydrogen production, because sulfides can be oxidized to disulfides at the anode and then be regenerated in solution by the reaction of the disulfides with sulfites [25]. With this electrolyte, at zero bias, the photocurrent density reached 90 $\mu\text{A}/\text{cm}^2$ on TiO₂/Ti, and increased to 160 $\mu\text{A}/\text{cm}^2$ at a 500 mV/SCE bias. Replacing TiO₂/Ti by CDs-TiO₂/Ti led to an approximately three-fold increase in the photocurrent density: 270 and 390 $\mu\text{A}/\text{cm}^2$ at 0 and 500 mV/SCE, respectively.

Such a synergetic effect of CDs with TiO₂ can be particularly valuable for hydrogen generation. In order to carry out water-splitting, we performed photocurrent measurements in Na₂SO₄, a non-electroactive electrolyte (Figs. 3C,D). As expected, the photocurrent measured was lower than in the previous experiment. Under these conditions, the photocurrent density reached 5 and 10 $\mu\text{A}/\text{cm}^2$ at 0 mV/SCE and increased to 8 and 21 $\mu\text{A}/\text{cm}^2$ at 500 mV/SCE, on TiO₂/Ti and CDs-TiO₂/Ti, respectively. This decrease in the photocurrent compared to the experiments performed with the previous electrolyte is due to the absence of electroactive species. As a consequence, the photocurrent measured is the result of the oxidation of water at the TiO₂/Ti or CDs-TiO₂/Ti photo-anodes (and, consequently, the reduction of protons at the platinum counter-electrode).

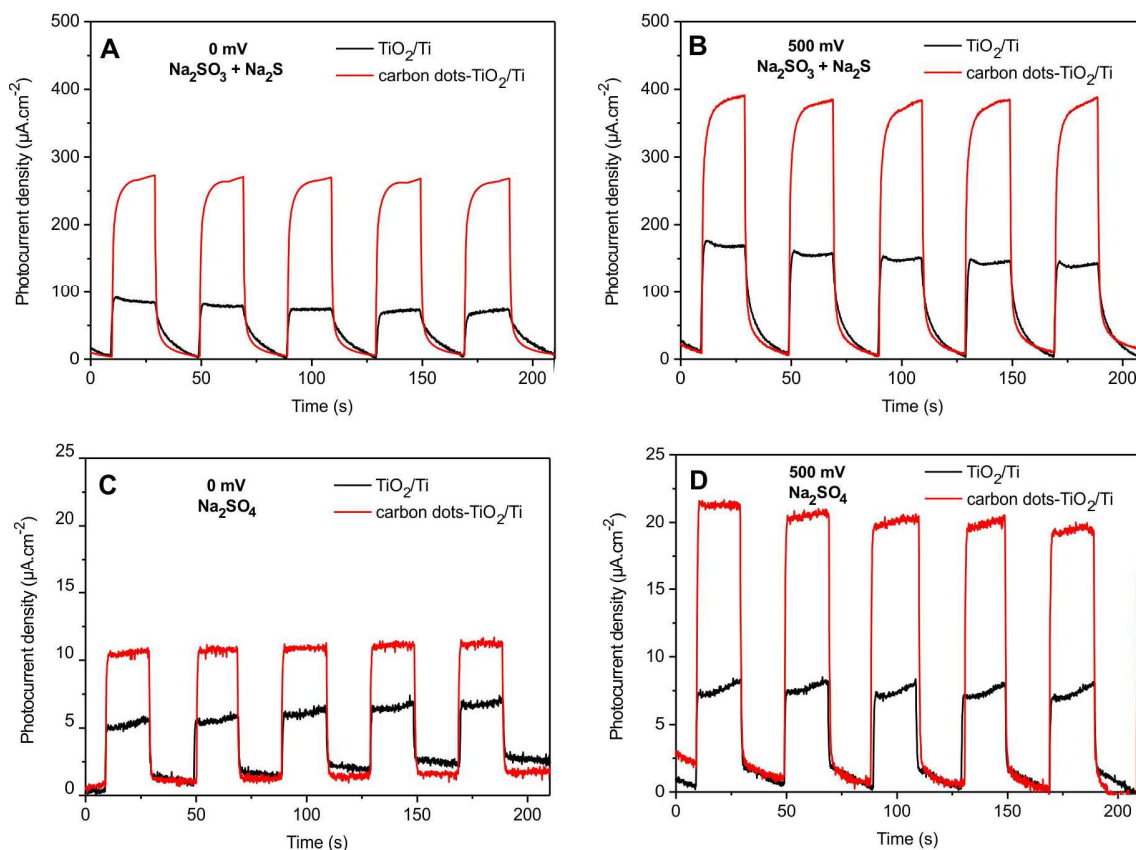


Figure 3. Photocurrent responses of TiO_2/Ti and $\text{CDs-TiO}_2/\text{Ti}$ using several electrolytes and bias potentials.

One can assume that CDs contribute in the generation of photo-electrons and that they promote interfacial charge-carrier separation. Charge transfer at the photo-anodes must be accompanied by water oxidation at the surface of both nanostructures. The enhancement of the photocurrent using CDs can be explained not only by a photosensitizing effect but also by a decrease in electron-hole recombination inside the TiO_2 . Characterization of the $\text{CD-TiO}_2/\text{Ti}$ electrodes has been again performed after photo-electrochemical assays, and no significant change has been observed, demonstrating the stability of the TiO_2 -based photo-anodes as already observed otherwise [26].

4. Conclusion

In summary, we have described the preparation of $\text{CDs-TiO}_2/\text{Ti}$ hetero-nanostructures based on the formation of TiO_2 nanofibers by the corrosion of Ti sheets and their subsequent impregnation by CDs. The PEC properties of the resulting electrode were measured, and a strong enhancement of the photocurrent was observed, compared to bare TiO_2/Ti . This enhancement is attributed to the

photosensitizing ability of the CDs and their interfacial charge-carrier separation contribution. These results are promising for hydrogen generation.

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