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Photocatalytic properties of carbon nanotubes/titania nanoparticles composite layers deposited by electrophoresis

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ABSTRACT

A large-scale use of nanotechnology for photocatalysis-based water purification requires to identify simple, reliable and low cost processes for the production of the photocatalytic materials.

To this aim we have investigated the possibility to deposit, by electrophoresis, composite layers formed by multi-walled carbon nanotubes (MWCNTs) and anatase-type titanium dioxide nanoparticles (np-TiO_2), with different weight ratios. This method allows one to obtain photocatalytic layers on any conductive substrates that in principle can be re-used several times. The photocatalytic efficiency for each C-nanostructure/np-TiO_2 composite layer is evaluated by measuring the degradation of methylene blue (MB) dye induced by the light of a solar simulator or UVA/blue light irradiation. The morphology and the composition of the deposited layers are studied by scanning electron microscopy and energy dispersive X-ray analyses, respectively, while photoluminescence spectra were acquired in order to explain the different photocatalytic behaviors observed for each material.

1. Introduction

Photocatalytic processes are widely recognized as a suitable solution for problems connected to several contexts such as environmental health, biological, pharmaceutical and medical applications, food industry, wastewater and effluents treatment, plant protection applications and drinking water disinfection [1].

Common photocatalytic materials are semiconductor oxides [2]. Among these materials, the most widely used in water splitting technique and in photocatalysis is titanium dioxide (TiO_2) because of its easy availability, long-term stability and relative non-toxicity [3,4,5].

One of the limiting factor of TiO_2 photocatalytic activity is the fast electron–hole recombination times (10^{-9} s) with respect to typical time scale of chemical interactions (10^{-8}/10^{-3} s) induced by the photocatalyst surface on the molecules in contact with it [5,6]. A lot of strategies have been proposed to overcome these limitations. One of these approaches is to increase the lifetime of the electron–hole pair by trapping the electrons, and this can be achieved by integrating TiO_2 with transition metal ions or heavy metals [7,8] or carbonaceous materials [9,10]. Among carbon based materials, nanotubes (CNTs) are widely used, coupled with TiO_2 [11,12,13], for the improvement of the photocatalytic efficiency of the semiconductor oxides. In many works, mixed CNT–TiO_2 nanoparticle powders are dispersed in solution [11,12], but this process has some drawbacks, such as the permanency of the photocatalytic materials in the solution and the difficulty to reuse the same photocatalyst more than once.

The deposition of nanomaterials with photocatalytic properties on a suitable substrate, without significant release of CNTs and nanoparticles in the water to be purified, would allow to go beyond these problems.

In this work, we have used electrophoretic deposition (EPD) to deposit TiO_2 nanoparticles and multi-walled Carbon Nanotubes (MWCNTs) composite layers on Pt/SiO_2/Si substrates. EPD is a cost-effective method usually requiring a simple equipment allowing to fabricate uniform coatings with excellent macroscopic homogeneity.

The photocatalytic properties of mixed layers, with different MWCNTs/TiO_2 weight ratios, and TiO_2 nanoparticles are compared by using the photocatalytic discoloration of Methylene Blue (MB) under UV–vis irradiation provided by a solar simulator. The composite layers were characterized by scanning electron microscopy (SEM), Energy Dispersive X-ray analysis (EDX), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and

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photoluminescence (PL) measurements in order to explain the different photocatalytic behaviors observed for each material.

2. Experimental

Anatase TiO_2 nanoparticles (np-TiO_2) with an average diameter of 21 nm were acquired from Sigma-Aldrich. Multi-walled carbon nanotubes (MWCNTs) were purchased from Sigma-Aldrich (95% C purity, diameter of 20–30 nm) and were subsequently chemically treated to functionalize the MWCNTs surfaces by a procedure described in Ref. [14].

2.1. Preparation of MWCNT/np-TiO_2 samples

We have prepared mixed MWCNT/np-TiO_2 solutions in acetone with different weight ratios (MWCNT:TiO_2) equal to 0:1 (sample named TM00), 1:10 (TM10), 1:4 (TM25), 1:2 (TM50), 3:4 (TM75), always keeping constant the TiO_2 concentration at 4.76 mg/l. The reference solution is prepared by dispersing only np-TiO_2 in acetone. Each solution was sonicated for 25 min.

Electrophoretic depositions (EPD) were performed by applying a DC voltage of 30 V between two electrodes immersed in the MWCNT/np-TiO_2 solutions: the cathode is a Si substrate with a 77 nm SiO_2 layer and a 100 nmPt layer deposited on top (Pt/SiO_2/Si) and the anode is a Mo foil of the same size of the cathode. The distance between the two electrodes was 2.5 mm and the deposition time was set at 5 min. The electrodes were dipped at an angle of 30° with the normal to the surface solution. The volume of fresh solution was kept constant at 2 ml for each deposition in order to fix the same initial content of TiO_2 at $9.5 \cdot 10^{-3}$ mg for each deposition process. TiO_2 nanoparticles dispersed in acetone show a negative charge and, under an electric field, move towards the anode, where they are, finally, deposited. In the case of the MWCNTs, the negative charge derived from the functionalization process leads to the deposition on the anode too. After the EPD process, the Pt/SiO_2/Si substrate was carefully extracted and dried in air in horizontal position for 3 h on a hot plate at 70 °C. Each process produces a deposited area of about 0.5 cm^2.

2.2. Characterization

SEM (Zeiss Supra35 FE-SEM) was used to characterize the morphology of the deposits. The weight ratio of the elements (Ti, C and O) deposited on the substrates was evaluated by EDX (Oxford Instruments – Aztec, 80 mm^2 X-Max SDD) inside the SEM chamber.

Photoluminescence intensity measurements were performed on all the samples in order to evaluate the electron–hole pair recombination [12,15]. Room temperature photoluminescence (PL) measurements were obtained by using a 325 nm He–Cd laser chopped through an acousto-optic modulator at a frequency of 55 Hz. The PL signal was analyzed by a single grating monocromator and detected by a Hamamatsu photomultiplier tube in the visible range. The photocatalytic activity of the samples was evaluated by the degradation of Methylene Blue (MB) (initial concentration $3.8 \cdot 10^{-5}$ M in DI water) under light irradiation by a solar simulator based on a 150 W xenon lamp equipped with a back reflector, optical collimators and a filter at AM1.5G conditions. The samples were placed at the bottom of beakers with the same size filled with 2 ml of MB. The area of the photo-active surface of each sample was kept constant at 0.5 cm^2. A beaker with the same amount of MB without any catalyst samples was irradiated under the same conditions and used as a reference.

Ultraviolet-visible (UV–vis) absorbance spectra of the solutions after irradiation were acquired by an UV/vis AGILENT Cary 50 spectrophotometer in a wavelength range between 200 and 800 nm and the degradation of MB was evaluated by the Lambert–Beer law via the absorbance of the MB peak at 664 nm. Raman scattering was excited by the 514.5 nm radiation of an Ar^+ laser and analyzed by a Jobin Yvon 450 mm focal length monochromator equipped with a CCD camera detector cooled at 77 K. The incident laser beam was focused by a 100 × objective. X-ray Photoelectron Spectroscopy (XPS) characterization was performed by using a Kratos AXIS-HS Spectrometer. Radiation Al Kα of 1486.6 eV was used with the conditions of 10 mA and 15 keV and a pass energy of 40 eV for both survey and high resolution spectra.

3. Results and discussion

3.1. Characterization of MWCNT/Np-TiO_2 samples

The choice of acetone as a solvent for the preparation of the solutions derives from some experimental evidences: acetone favors the dispersion of the MWCNTs powder that usually in water tends to precipitate forming large agglomerates. TiO_2 nanoparticles are also dispersed in acetone in order to mix them with the solution containing MWCNTs and perform a joined deposition [16]. The Raman spectra of the MWCNTs/np-TiO_2 composite layer deposited by electrophoresis confirm the presence of anatase titania and MWCNT. Fig. 1 shows the Raman spectrum of sample TM75. The three peaks between 300 and 700 cm^{-1} are specific of anatase TiO_2. The peak position of the D and G bands of the MWCNTs are at 1365 and 1597 cm^{-1}, respectively. The I_D/I_G ratio is about 1.3. These features are the same for all the other samples (not shown).

Fig. 2 shows the SEM images of composite layers with different MWCNT/np-TiO_2 weight ratios obtained by electrophoresis. The deposit covers the whole substrate surface immersed in the solution and it is uniformly distributed as checked by SEM analysis in different regions of the sample. The deposit is constituted by TiO_2 nanoparticles entangled with MWCNTs, forming agglomerates that can even reach a micrometer size. In the sample containing only np-TiO_2, the Pt surface of the substrate is not completely covered by the deposition and uncovered Pt regions of few tens of squared nanometers are visible between the aggregates of TiO_2 particles (Fig. 2a). The presence of carbon nanotubes, even at the lowest concentration used in this work, is helpful to achieve a continuous and uniform layer on the surface region of the electrode dipped in the solution during the EPD. The presence of MWCNTs in a solution of acetylacetone containing anatase np-TiO_2

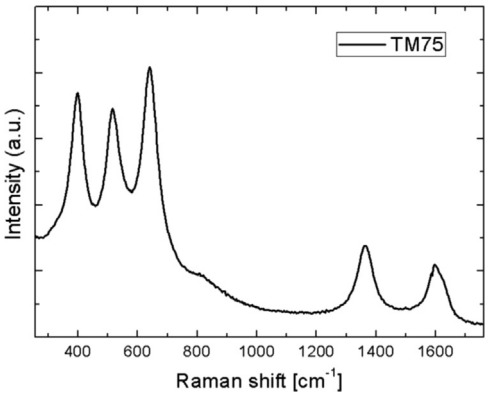

Fig. 1. Raman spectrum of the MWCNTs/np-TiO_2 composite layer deposited by EPD with mass ratio of 0.75:1 (sample TM75). The three peaks between 300 and 700 cm^{-1} are specific of anatase TiO_2. The D and G bands of the MWCNTs are at 1365 and 1597 cm^{-1}, respectively. The I_D/I_G ratio is 1.32. These features are the same for all the other samples.