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New Nanocomposite Materials by Incorporation of Nanocrystalline TiO_2 Particles into Polyaniline Conductive Films

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This work is focused on the combination of two building-blocks, nanocrystalline TiO_2 particles and polyaniline conductive films (PAni). The preparation of new nanostructured composite materials, displaying electron- and proton-conductive properties, to be used for the fabrication of new and superior energy storage devices was envisaged. The semiconducting TiO_2 nanoparticles were obtained by means of a hydrothermal route. The PAni films were prepared on glassy carbon electrodes by electrochemical polymerization, under potential dynamic conditions. After characterization by X-ray diffraction, transmission electron microscopy or scanning electron microscopy and electrochemical techniques, the nanocrystalline particles were immobilized in the polymer matrix. The incorporation of the TiO_2 was achieved using two distinct approaches: during the polymer growth or by deposition over previously prepared PAni films. The results demonstrate that the PAni morphology depends on the experimental conditions used during the polymer growth. After TiO_2 immobilization, the best electrochemical response was obtained for the nanocomposite structure produced through the TiO_2 incorporation after the PAni film synthesis. The modified electrodes were structurally and morphologically characterized and their electro-catalytic activity towards the hydrogen evolution reaction was analyzed. A new electrochemical performance related with the oxidation of molecular hydrogen entrapped in the PAni-TiO_2 matrix was observed for the modified electrode after TiO_2 incorporation. This behavior can be directly associated with the synergetic combination of the TiO_2 and PAni, and is dependent on the amount of the semiconductor.

KEY WORDS: Polyaniline (PAni); Nanosized TiO_2; Nanocomposites; Hydrogen trapping

1. Introduction

There is an increasing need to develop novel functional and structural materials with superior performance for technological applications. One of the most used methods for accomplishing this purpose is the synergetic combination of two or more components in order to prepare materials with improved and innovated properties. The development of new materials at a nanometer scale has given rise to a group with enough technological and scientific interest, the nanomaterials class. These materials generally have dimensions less than 100 nm and greater than 0.1 nm. They have chemical and physical properties different from those of the corresponding bulk materials which make them very attractive for new promising industrial applications.

Nanocrystalline TiO_2 is often used for technological photo and electro-catalytic applications, due to their size-dependent and easy tunable properties[1,2]. Based on the electrochemical properties, several applications have been reported for TiO_2, such as photo and electro-catalysis[3−5] polymer electrolyte membrane fuel cells[6], solar cells[7] and biosensors fabrication[8]. Also, polyaniline (PAni) is one of the most investigated conducting polymers due to its straightforward synthesis, good environmental stability, reversible redox behavior and wide range of potential applications[9−11]. This work is focused on the combination of these two building-blocks, TiO_2 nanocrystalline particles and a PAni film, aiming at the preparation of new nanostructured composite materials displaying new and interesting electro-active properties.

In this work, TiO_2 nanocrystalline particles have been obtained by means of a hydrothermal route and the PAni films have been prepared on glassy carbon electrodes (GCE) under potentiodynamic control. The TiO_2 incorporation was performed using two distinct methodologies: during the polymer growth and by drop-casting over a previously prepared PAni film. The TiO_2 nanoparticles and the PAni-modified electrodes, before and after

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TiO_2 incorporation, have been morphologically and structurally characterized and their electro-catalytic activity towards the hydrogen evolution reaction was carefully analyzed.

2. Experimental

All reagents were of analytical grade (Aldrich and Fluka) and were used as received without further purification. The solutions were prepared with Milli-Q ultra-pure water.

2.1. Materials and methods

2.1.1. TiO_2 synthesis. The TiO_2 sample was prepared using an amorphous precursor prepared using a procedure previously reported[12]. 50 mL of a titanium trichloride solution (10 wt% in 20−30 wt% HCl) was diluted in a ratio of 1:2 in a standard HCl solution (37%). A 4 mol/L ammonia aqueous solution was added drop-wise to the violet dark solution, under vigorous stirring, until complete precipitation of a white solid. The resulting suspension was kept overnight at room temperature and then filtered and washed several times with deionized water.

The nanocrystalline TiO_2 was obtained by means of a hydrothermal method, by using a suspension of ~3 g of this precursor, in *ca.* 60 mL of water[13]. The samples were prepared at 200 °C using an autoclave dwell time of 6 h. After cooling, the suspensions were filtrated and the solid was washed systematically with water. Afterward, the white solid was dried and stored.

2.1.2. Electrochemical polymerization. The electrochemical experiments were carried out with a computer-controlled CHI620A electrochemical workstation in a conventional three-electrode system using a platinum foil as counter electrode and a saturated calomel electrode (SCE) as a reference. All potentials are reported with respect to the SCE. The redox potential of the SCE is +0.244 V versus SHE at 25 °C. The working electrode was a glassy carbon (GCE, geometric area $A_{GC} = 0.38$ cm^2). When required, the GCE electrodes were modified with nanocrystalline TiO_2. The immobilization was performed overnight by a drop-cast methodology, typically 30 μL of a 1 mg mL^{-1} TiO_2 suspension, at room temperature.

The GCE-PAni modified electrodes were prepared via aniline (Ani) electrochemical polymerization[14]. The Ani potentiodynamic polymerization was performed by cyclic voltammetry, between −0.20 and +0.80 V for 5 cycles, then the anodic limit was taken down to 0.75 V for 2 cycles, and afterwards to 0.70 V for 40 cycles (PAni film) or 30 cycles (PAniI film). The scan rate was 20 mV s^{-1}, during the first two steps and then, only for the PAni film, adjusted to 80 mV s^{-1} during the last step. The electrolyte was a 0.5 mol/L H_2SO_4 aqueous solution containing 0.1 mol/L aniline, previously distillated. After preparation, the polymeric films discharge was performed at −0.20 V, during 500 s, using the electrolyte solution without monomer.

Two distinct procedures have been used for the GCE-PAni/TiO_2 production: by monomer polymerization in the presence of a TiO_2 nanoparticles aqueous suspension and by placing a drop of a TiO_2 aqueous suspension on the previous modified GCE-PAni electrode surface and subsequently dried overnight.

All the electrochemical characterization measurements have been performed in 0.1 mol/L H_2SO_4 electrolyte solutions. The solutions were prepared with ultra-pure water and were deoxygenated for *ca.* 20 min with a nitrogen flow before use.

2.2. Characterization

X-ray powder diffraction (XRD) was performed using a Philips X-ray diffractometer (PW 1730) with automatic data acquisition (APD Philips v3.6B), using Cu$K\alpha$ radiation ($\lambda = 0.15406$ nm), working at 40 kV/30 mA. The diffraction patterns have been collected in the range $2\theta = 7°-60°$ with a 0.02° step size and an acquisition time of 2.0 s/step. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) observations have been carried out using a JEOL 200CX microscope operating at 200 kV and a field emission gun − scanning electron microscope JEOL-7001F (FEG-SEM), operating at 10−15 kV, respectively.

3. Results and Discussion

3.1. Nanocrystalline TiO_2 characterization

The TiO_2 nanocrystalline powder's structure was characterized by XRD. Fig. 1(a) shows the XRD spectrum, indicating the presence of a crystalline material; the *anatase* was the only identified crystalline phase. The particle size was estimated as being 14.77 nm, by using the Scherrer formula. This value is in accordance with that obtained through measurements on the TEM images (Fig. 1(b)). From the TEM image analysis it is possible to conclude that the sample is homogeneous and the TiO_2 particles are spheroidal.

After immobilization in the GCE electrode surface, the electrochemical characterization of the nanocrystalline TiO_2 particles has been performed by cyclic voltammetry. Fig. 2 shows the GCE-TiO_2 electrode electrochemical response, e.g. current

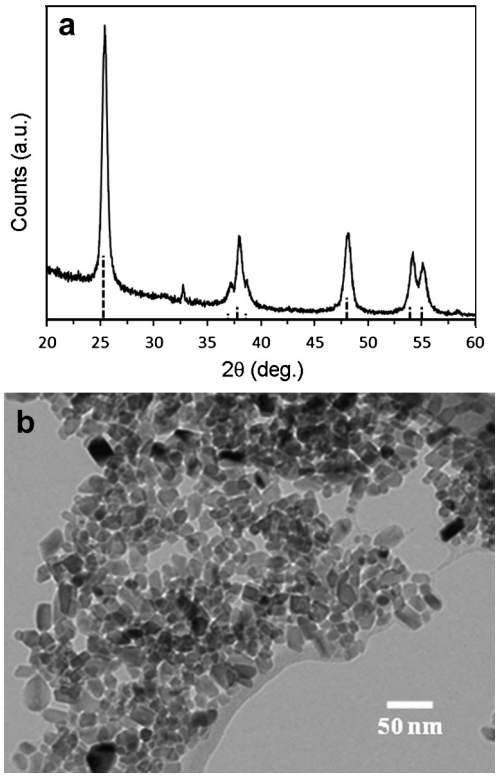

Fig. 1 XRD pattern of the nanocrystalline TiO_2 sample prepared (a) and TEM image of the nanocrystalline TiO_2 particles prepared (b).