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Photoelectrochemical properties of hierarchical nanocomposite structure: Carbon nanofibers/TiO_2/ZnO thin films

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ABSTRACT

The basic objective of this work is related to the research on the design of hierarchic multilayer systems with the assumed final functionality utilized for microelectronics and photovoltaics. We report on photoelectrochemical functionality of the multilayer system consisting of carbon nanofibers (CNFs)/photoactive anatase TiO_2/conductive ZnO thin films. The CNFs' layers were obtained by annealing the polyacrylonitrile (PAN) web deposited by the electrospinning method. Titanium dioxide and zinc oxide layers were deposited by means of a hollow cathode cold plasma deposition system. Raman spectra confirmed carbon nanofibers, crystalline TiO_2 and ZnO forming individual layers as well as the final multilayer assembly. A mixture of various $Zn_xTi_yO_z$ phases was also observed. These structures were produced due to the reactions between the highly energetic zinc ions generated in the plasma environment and the TiO_2 layer. The same phenomenon is probably responsible for the doping of TiO_2 by carbon atoms originating from CNFs and leading to a significant decrease of the photocatalytic activity.

1. Introduction

There have been significant advances in the development of heterogeneous photocatalysts based on metal oxide semiconductor thin films, mostly of anatase TiO_2 [1–7]. Also ZnO possesses high photocatalytic efficiency but it holds the drawback of photocorrosion [8]. Particularly ZnO nanostructures have been extensively studied as important wide-bandgap semiconductors (3.37 eV) [e.g. 9]. Carbon nanofibers (CNFs) possess unique physical and chemical properties and are widely used in nanoelectronics, sensing applications and in catalysis [10,11]. Recently, carbon nanofibers have been used as templates or scaffolds for assembly of various nanoparticles, such as Au–TiO_2, SiO_2–TiO_2, Ag, Pd or Ir–V, because of their hardness preserved even at high nanoparticle loadings [12–16]. The interest in using CNFs as catalytic support material arises due to their large surface area, high aspect ratio and their ability to disperse catalytically active particles [17]. Various techniques have been applied to obtain carbon nanofibers, such as chemical vapor deposition [18] or carbonizing electrospun precursors [19]. Electrospun precursors are usually obtained by the use of the PAN nanofibers [20]. Only a few works have employed TiO_2 or ZnO photocatalysts individually assembled on CNFs [21,22], and even less using their combinations. Several attempts have been made to reduce the recombination of photoinduced hole/electron pairs during the photocatalytic reactions by conjugation of the photocatalysts with electron scavenging agents such as metals, organic molecules or carbon nanofibers. Teng et al. introduced a novel $TiO_{2-x}N_x$/CNFs heterostructured photocatalyst [23]. In this work the authors proposed that owing to the synergistic effect of rather high adsorption capacity of CNFs and excellent vis-photocatalytic activity of $TiO_{2-x}N_x$ nanoparticles, the arrangement of the $TiO_{2-x}N_x$/CNFs showed higher photocatalytic efficiency than appropriate references of the TiO_2/CNFs and $TiO_{2-x}N_x$ [23].

The present work is a continuation of our recent studies on preparation, characterization and photocatalytic activity of different types of thin films [24–27].

2. Experimental

2.1. Preparation of layers

The films were initially prepared individually. All samples were deposited onto silicon wafers coated by a 100 nm thick titanium layer. The preparation of the CNFs was based on thermal calcinations of a polymer (polyacrylonitrile – PAN, Aldrich, average Mw 150,000) nanofibers web fabricated by the electrospinning proce-

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dure. The homogenous clear solution was prepared by dissolving PAN and N,N-dimethylformamide at laboratory temperature. The polymer concentration was 15% (w/v). Conductivity of the solution was modified to 140 μS/cm by adding tetraethylammonium bromide. The prepared solution was placed into SPUR® noncommercial laboratory equipment working on the basis of needle electrospinning method. The flow rate was 2 ml/h, applied high voltage was 50 kV, electrode distance was 180 mm, temperature was 22 °C and relative air humidity was approximately 30%. The transformation of the as-deposited polymer web to the form of the CNFs was carried out under inert nitrogen atmosphere and using a thermal ramp. The temperature initially increased in the rate 5 °C/min up to 250 °C. At this temperature level the samples were stabilized for 30 min. Finally the temperature was increased with the same rate to 950 °C and left here for another two hours during which the carbonization was provided.

TiO_2 and ZnO thin layers were produced by means of a hollow cathode plasma jet system. The main advantage of this method lies in its capability to produce highly crystalline thin layers during the deposition procedure under certain precisely adjusted deposition conditions. It means that the temperature of substrates does not exceed 423 K when being coated and thus even thermally sensitive substrates (polymers) can be used. The system of two simultaneously working hollow cathode plasma jets was applied in the case of titanium dioxide thin films. The hollow cathodes are cooled titanium nozzles (purity 99.99%), which are connected to the DC pulsed supplier and also to the RF power supplier. The hollow cathodes were placed in the UHV chamber with marginal pressure of 10^{-6} Pa maintained by a turbomolecular pump. The real pressure level depends on the gases' flow rates and varies in the range of 2.5–5 Pa. Argon, flowing in each nozzle with the rate of 40 sccm ($cm^3\ s^{-1}$), serves as the working gas. The oxygen, fed to the chamber by a lateral entrance at a rate of 20 sccm, acts as the reacting gas. The first hollow cathode was placed perpendicular to the substrate and the angle between the nozzles was 30°. Between the supports positioned on a movable bench, and the hollow cathodes, a mask was situated in order to achieve thin films with high thickness homogeneity. The jets were connected to the supply of the DC pulse current with a frequency of 2.5 kHz and with an active discharge during 25% of the modulation period. Additionally, a low RF voltage with the power of 7 W was also used to increase the degree of ionization of the plasma. Grounded poles of static electromagnets were situated close to the nozzle outlet in order to provide a higher intensity and superior stability of the plasma stream in the reactor. DC pulsed hollow cathode discharge was broken down in the nozzle being sputtered due to ion bombardment. Argon gas flow was present in the sputtering nozzle. The sputtered particles were blown out of the nozzle into the reactor under the collateral oxidation and carried by this created plasma jet towards the substrate.

The ZnO layers were deposited using only one hollow cathode. The coating conditions were as follows: argon flow rate of 100 sccm, oxygen feeding of 10 sccm, RF power of 30 W and time of deposition of 2 h.

Characteristic photoelectrochemical features were evaluated and compared among a set of layers deposited by described methods. The individual tested layers and their compositions in hierarchical structures are coded in the text as: L1 – TiO_2 single thin films, L2 – TiO_2/CNFs, L3 – TiO_2/CNFs/ZnO and L4 – TiO_2/ZnO.

2.2. Characterization of layers

The crystallographic phases of the layers were determined with help of Raman spectroscopy. Unpolarized Raman spectra were recorded in a back-scattering configuration using Renishaw Raman Microscope RM 1000. The spectra were excited by the 514 nm Ar^+ line at a power <1 mW focused down to a spot of 2–3 μm in diameter. The spectral range was 150–4000 cm^{-1} and the resolution was ~1.5 cm^{-1}. The layers' morphologies and the formation of CNFs were studied by SEM Hitachi S-520 or Quanta 200. 3D surface pictures were also taken on the AFM microscope (Thericroscopes) and these were then analyzed to estimate the parameter of the relative surface roughness.

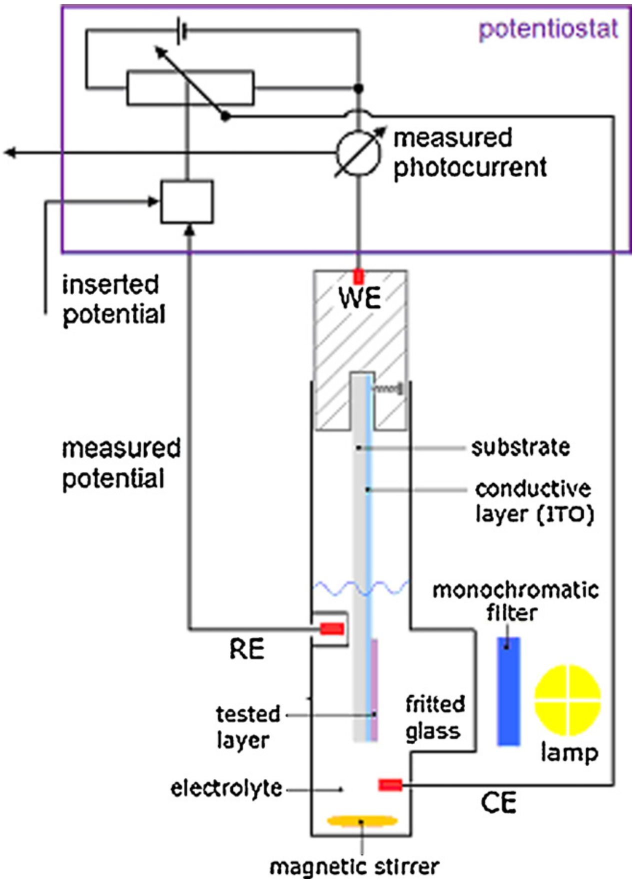

Fig. 1. Standard three-electrode photoelectrochemical arrangement. WE denotes working electrode, CE counter electrode and RE referential electrode.

2.3. Photoelectrochemical investigation of layers

The electrochemistry experiments were carried out using a three compartment electrochemical cell with three electrodes in the system (Fig. 1). The particular layer or the multilayer structure formed the working electrode (WE). As the referential electrode (RE), the Ag/AgCl electrode (environment of 3 M KCl) was employed and a platinum sheet introduced the counter electrode (CE). All these electrodes were immersed in the electrolyte solution (0.1 M Na_2SO_4). The layers were, during the experiments, illuminated by the polychromatic light from DC Arc polychromatic high pressure mercury lamp (LOT, LSH201/2 Hg, Xe) [28].

Three different kinds of measurements were performed. The dependency of current density on the applied potential to the tested layers – the polarization curves of the linear voltammetry were recorded in the periodic cycles of 5 s illumination (UV) of the layers and 5 s dark intervals. The experiments were run from the inserted potential of −400 mV to 1000 mV with the rate of the potential increase of 10 mV s^{-1} with help of Voltalab PGZ-100 all-in-one potentiostat.

Such measurements expressing dependency of the current density on time with constant applied potential (600 mV – our