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Preliminary study towards photoactivity enhancement using a biocompatible titanium dioxide/carbon nanotubes composite

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ABSTRACT

Recent research is focused on the enhancement in photoactivity of titanium dioxide/carbon nanotubes through formation of novel nanocomposites that exhibit a high specific surface area, remarkable electron transfer and biocompatibility. Here, we explore a new synthesis route in the system composed of nanocrystalline titanium dioxide supported on external walls and inner space of multiwalled carbon nanotubes (MWCNT). The advantages of this method are: its simplicity, direct fusion of titanium dioxide particles on the carbon material, and formation of chemical bond Ti–O–C between TiO_2 and MWCNT. Photocatalytic performance of this system has been compared to a commercial catalyst (Degussa P25) in a model reaction of phenol decomposition in/under UV light. The efficiency of the process increased by the factor of 2.5 when the TiO_2–MWCNT photocatalyst was utilized. Further, the photoactive nanocomposite was analysed towards its biocompatibility in order to establish a safe dose of the catalyst. Its influence on the cells viability was studied on mouse fibroblasts and human liver tissue cells, in the range from 0 to 100 μg/mL. This has revealed that the composite in concentrations up to 25 μg/mL exerted low toxicity, which allowed for finding a compromise between the highest safe dose and acceptable photoactivity of the catalyst.

1. Introduction

For industrial application, one of the most exciting sub-fields of nanotechnology is nanocatalysis focused on photocatalysis. Its main goal is to control photocatalytic reactions by changing the size, dimensionality, chemical composition and morphology of catalytic particles. Among photocatalysts, three types of molecular nanostructers have been widely studied: titania/carbon nanotubes and nanofibres [1], titania nanospheres and particles [2] and core–shell structures composed of titania with silica or carbon materials [3].

Titanium dioxide has been intensively investigated as a semiconductor for photocatalysis since Fujishima and Honda discovered the ability of photocatalytic water splitting on TiO_2 electrodes in 1972 [4]. Recently, the use of TiO_2 has been mainly concentrated on the decomposition of toxic and hazardous organic pollutants in contaminated water/air, which is of great importance for both health and environmental protection [5,6]. Many scientists studied different applications of titania as a nanocatalyst or as an additive for lithium-ion batteries. Great interest has been concentrated on the enhancement of photocatalytic activity of TiO_2 particles by modification with carbon nanostructures e.g. graphene [7,8]. The size, shape, form and method of titania doping and their relation with the surface are still widely discussed [9].

In this contribution, we explore a novel method of multi-walled carbon nanotubes/titanium dioxide nanocomposite formation where both counterparts are chemically bonded via Ti–O–C formation. The designed molecular hybrid is composed of carbon nanotubes as a core template with titanium dioxide placed inside and outside the nanotubes.

2. Experimental

2.1. Supporting titania on carbon nanotubes (TiO_2–MWCNTs)

A concentrated solution of titanium (IV) butoxide (TBT) was used as a source of titanium dioxide. 1 ml of TBT was added to 20 mg of MWCNT being previously functionalized with carboxyl groups (purchase – Shenzhen Nanotech Port Co.,

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Shenzhen, China). Next, the mixture was sonicated for 3 h at the temperature of 50 °C. Then, the material was diluted with propanol and centrifuged (8000 rpm for 20 min) to get rid of free titanium dioxide precursor. In order to remove the excess of TBT, the sample was washed several times with propanol. After the purification step, the nanotubes with TBT were treated with a mixture of water–ethanol (96%) to proceed the hydrolysis of the precursor to titanium dioxide. Finally, the sample was heated in air flow at 400 °C for 2 h.

2.2. Determination of photocatalytic activity of TiO_2–MWCNTs

The activity of TiO_2–MWCNTs was examined via photocatalytic decomposition of phenol. The reaction was carried out in an inner-irradiation-type quartz reactor. A mercury lamp of 150 W was used as the light source. The process involved 600 cm^3 of phenol solution (initial concentration: 50 mg/dm^3) and an appropriate mass of the catalyst (TiO_2–MWCNTs or TiO_2-Degussa P25). After 30 min of adsorption in darkness, the reaction mixture was placed in the photoreactor and irradiated. Phenol concentration was measured using a UV–Vis spectrophotometer (Jasco, Japan) at the wavelength of 270 nm.

2.3. The in vitro cytotoxicity test

The mouse fibroblast cell line (L929) and human liver tissue cell line (Hep G2) was plated in 96-well culture plates (PAA) at an initial density of 1×10^4 cells/well, and incubated (at 37 °C in humidified 5% CO_2 atmosphere) in 100 μl of culture medium [Dulbecco's Modified Eagle Medium, High Glucose (DMEM, PAA, Austria) supplemented with 10% heat-inactivated fetal bovine serum (FBS, Thermo Scientific), 0.4% penicillin–streptomycin (Sigma) and L-glutamine (2 mM, Sigma)]. Following a 24-h incubation period, the culture medium was removed and suspensions of TiO_2-MWCNTs were added at concentrations: 100 μg/mL, 50 μg/mL, 25 μg/mL, 12.5 μg/mL, 6.25 μg/mL, 3.125 μg/mL. After a 24-h incubation period with the studied nanostructures, WST-1 reagent was added for 2 h, and the absorbance was measured at 450 nm wavelength using a micro plate spectrophotometer. The absorbance values were hence analyzed (calculating the average value from three wells per each experimental point in the case of the studied nanomaterials and from nine wells in the case of free medium PBS) to determine cell proliferation compared to control wells.

2.4. Characterization

For qualitative characterization, the materials were investigated by transmission electron microscopy (Fei Tecnai G2 F20 S Twin with energy dispersive X-ray spectroscopy), to verify the formation of the TiO_2–MWCNTs nanocomposites. The crystalline structure of the samples was studied by X-ray diffraction method. The XRD measurements were performed with a PRO X-ray diffractometer (X,Pert PRO philips diffractometer, Co Kα radiation). To analyse the vibronic properties, the samples were measured using a Renishaw In Via Raman spectroscope (excitation = 785 nm). Thermogravimetric analysis was performed via SDT Q600 Simultaneous TGA/DSC under an air flow of 100 mL min^{-1} and at a heating rate of 10 °C min^{-1}. The specific surface area was analysed through nitrogen adsorption using the Brunauer, Emmett and Teller (BET) isotherm, performed with a Quadrosorb SI (Quantachrome Instruments). In order to investigate the optical properties of the materials, a FT-IR Spectrometer (Nicolet 6700) was applied, as well as a diffuse reflectance (DR) UV–Vis spectrophotometer-Jasco V-650 (Japan).

3. Results

3.1. Physical characteristic

Fig. 1a shows morphology of pristine material, while Fig. 1b and c indicate changes in the structure of nanomaterials after the functionalization procedure. One can clearly see that the inner space of nanotubes is filled with guest molecules. However, a thin layer of TiO_2 is deposited on the external wall of the tubes. The EDX spectrum, shown in Fig. 1d, clearly demonstrates the presence of carbon, oxygen and titanium. Copper comes from a standard TEM grid. The thickness of the structure was not significantly changed, which means the most of titania was placed inside the hollow space of the tube. Surface area of the nanocomposites, measured with the BET method, was 25 g/m^2 (pristine MWCNT-140 g/m^2). The reproducibility of the TiO_2–MWCNT nanocomposites was estimated by comparison of three different samples.

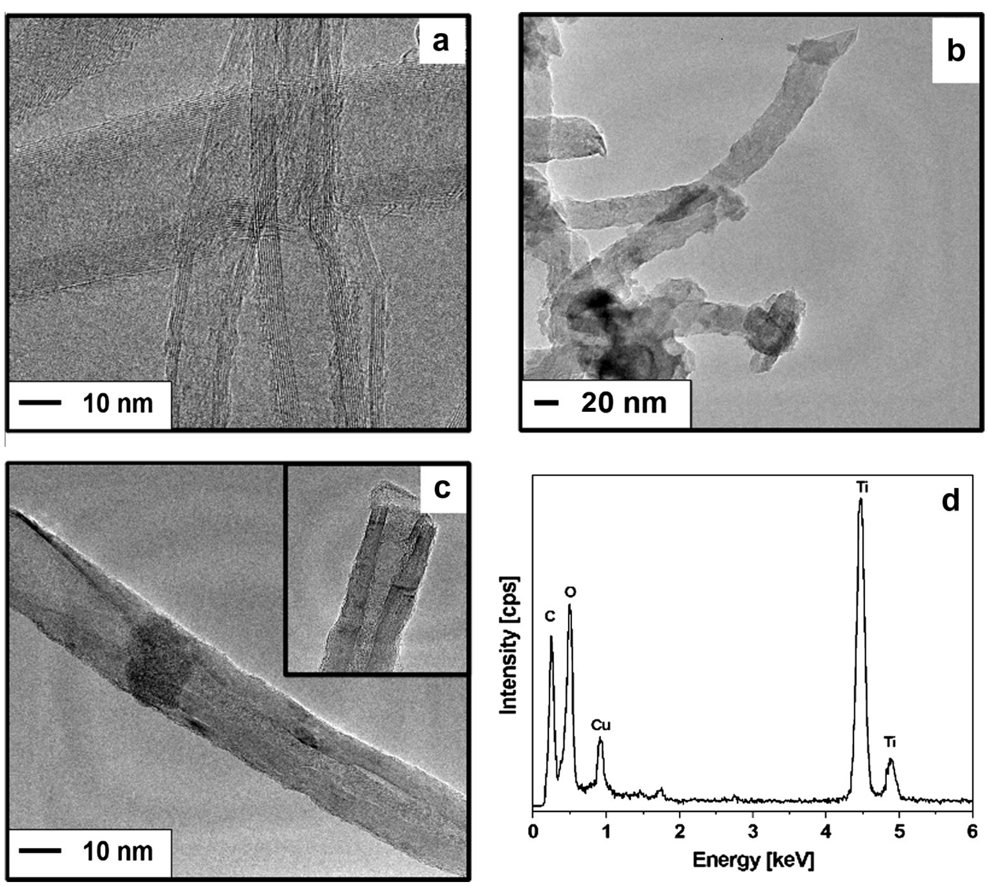

Fig. 1. TEM images of pristine MWCNTs (a) and titania–MWCNTs (b and c). EDX of TiO_2–MWCNTs (d).