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TiO_2 Nanocrystals Decorated CVD Graphene based Hybrid for UV-light Active Photoanodes

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Abstract

In this work, the manufacturing and characterization of an optically transparent and UV-light photoactive anode, formed of graphene grown by chemical vapor deposition (CVD) decorated with a close packed multilayer nanostructured layout of colloidal TiO_2 nanocrystals (NCs), has been reported. The hybrid material was prepared by a facile solution-based procedure, which relays on incubating the CVD graphene in a solution of 1-pyrene butyric acid (PBA)-surface coated TiO_2 NCs. Pyrene undergoes π-π stacking interactions, anchoring the NCs to the graphene platform with retention of the NC geometry and composition. Concomitantly, the NCs immobilize onto graphene preserving the structure of the aromatic platform. Photoelectrochemical investigation shows that the composite material exhibits a photoelectric response 50% higher than that of bare graphene based electrodes.

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Keywords: colloidal nanocrystals, CVD graphene, hybrid material, UV active photoanode

1. Introduction

Since its first isolation, graphene has attracted scientific community for its unique structural properties, as optical transparency from visible to infrared, excellent thermal and electrical conductivity, high specific surface area, good biocompatibility, impermeability to gases and high strength, elasticity, stiffness and environmental stability [1]. Such functionalities are fully exploited in devices and systems, as field-effect transistors (FETs), sensors, supercapacitors,

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touch panels, litium-ion batteries, conductive inks, field emitters and solar cells [2]. In addition, the high reactivity of graphene offers the opportunity of implementing a large variety of chemical routes of functionalization with other nanostructured compounds. In the resulting nanocomposite materials, the synergic combination of properties of the single components provides materials exhibiting novel functionalities that graphene does not intrinsically possesses (i.e. light harvesting in the visible and infrared spectral range, selective molecular recognition capability) or improve its original properties, with enhanced electrical, mechanical and thermal properties and higher capabilities for light-matter interaction based mechanisms [3].

Colloidal nanocrystals (NCs) or nanoparticles (NPs), prepared by means of solution-based colloidal chemistry routes, are optimal candidates for graphene functionalization. Such nanostructured materials are tiny portion of inorganic matter, which exhibits unique size- and shape-dependent optoelectronic properties at the nanoscale [4], which can be conveyed to graphene, resulting in hybrid materials with outstanding functionalities, promising for advanced technological applications. In particular, NCs/NPs prepared by colloidal routes are surface coated by surfactant molecules that can be tuned according to the surface functionalization procedure in order to modulate their chemical interactions with surrounding structures.

Here, a facile method has been used to chemically functionalize graphene, grown by chemical vapor deposition (CVD), with 1-pyrene butyric acid (PBA)-coated TiO_2 NCs. CVD is the most suited method for preparing graphene for mass production and industrial purposes. Indeed, CVD graphene is a scalable material, which can be transferred onto several substrates (i.e. glass, silicon or polymer substrates) also in multilayers [5]. On the other hand, TiO_2 is a wide band gap semiconductor, widely used in (photo)electrochemical sensors, solar cells and photocatalytic systems for its low toxicity, optical transparency, low cost, biocompatibility, photostability and for its photocatalytic and photoelectrochemical activity [6]. Therefore, the synergic combination between the ballistic charge transport and electron sink properties of graphene with the UV-light light harvesting ability of the TiO_2 NCs has been found to provide hybrid materials with enhanced electrical conductivity, photoelectrical conversion efficiency, photocatalytic properties and environmental stability [7].

Here, pre-synthesized oleic acid (OLEA)-coated TiO_2 NCs have been surface functionalized with 1-pyrene butyric acid (PBA), upon a capping exchange procedure aiming to displace the insulating pristine OLEA ligand. The PBA molecule, coordinating the surface of the nano-objects by carboxyl group, is expected to provide the immobilization of the NCs onto the surface of graphene by π-π stacking interactions [8]. The prepared PBA-coated TiO_2 NC modified graphene has been characterized by means of TEM, AFM, Raman spectroscopy and (photo)electrochemical analysis in order to investigate morphology, structure and (photo)electrochemical properties of the nanocomposite. The results indicate that PBA is effective in anchoring the NCs onto graphene, without any significant modification of its structure, ensuring electrically interconnection among the nano-objects by π-π interactions. In addition, PBA plays a crucial role in the electronical coupling, acting as a channel for the charge transfer between the two hybrid components [8]. Indeed, the hybrid material exhibits photoelectrochemical light-energy conversion improved with respect to that of neat graphene, thus resulting suited as UV-light photoactive component of optically transparent electrodes for solar cells, photodetectors, FETs and sensors.

2. Experimental Section

Oleic acid (OLEA)-capped spherical TiO_2 NCs, were synthesized with a diameter of 6 nm under N_2 atmosphere by using a standard air free technique [9]. After the synthesis, the TiO_2 NCs were repeatedly washed with methanol by centrifugation cycles and exposed to a solution of 1-pyrene-butyric acid (BPA) in 1:5 TiO_2/PBA molar ratio, to displace the OLEA ligand with PBA and then finally dispersed in chloroform.

Monolayer graphene with 50-110 μm^2 grain sizes was grown by CVD on 25 μm thick copper foils (Alfa Aesar, item No. 13382) in a typical quartz tube CVD reactor at 1000°C using CH_4/H_2 as precursors. The prepared graphene was then transferred onto 300 nm SiO_2/Si or ITO/glass substrates by using a thermal release tape and a water solution of ammonium persulfate (0.1 M) as copper etchant. Before graphene transfer, the SiO_2/Si substrates were treated with O_2 plasma for improving adhesion. Bilayer graphene was fabricated by transferring of additional graphene layers onto ITO/glass substrates. All graphene samples were dipped in toluene/ethanol/anisole (1/1/1) solution for removing any