

TiO₂ Nanocrystals Decorated CVD Graphene for Electroanalytical Sensing

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Abstract— In this work, the manufacturing and characterization of an optically transparent and UV-light photoactive anode, formed of monolayer graphene grown by chemical vapor deposition (CVD) and decorated with a close packed multilayered nanostructured layout of colloidal TiO₂ nanocrystals (NCs), are reported. The hybrid material has been prepared by a facile solution-based procedure, which relies on soaking the CVD graphene in a solution of 1-pyrene butyric acid (PBA) surface coated TiO₂ NCs, achieved upon implementation of a capping exchange process for displacing the pristine organic ligand deriving from the colloidal synthesis. Pyrene undergoes π - π stacking interactions, anchoring the NCs to the platform with retention of the NC geometry and composition. The NCs immobilize onto the graphene platform with preservation of its aromatic structure and the resulting hybrid has been found optically transparent in the visible spectral range. (Photo)electrochemical investigation shows that the composite material has a promising sensitivity for selectively detecting dopamine and norepinephrine and, concomitantly, exhibits a (photo)electric activity higher than that of bare graphene. Thus, the achieved hybrid material results interesting for the manufacturing of photo-active components to integrate in photo-renewable sensor elements along with photodetectors and solar cells.

Keywords—colloidal TiO₂ nanocrystals, CVD graphene, pyrene linker, hybrid material, cyclovoltammetry, photocurrents

I.

INTRODUCTION

Since its first isolation, graphene has attracted the scientific community for its unique structural properties, as light transparency from visible to infrared, excellent thermal and electrical conductivity, high specific surface area, good biocompatibility, impermeability to gases, high strength, elasticity, stiffness and environmental stability [1]. Such functionalities are typically fully exploited in devices and

systems, e.g. field-effect transistors (FETs), sensors, supercapacitors, touch panels, lithium-ion batteries, conductive inks, field emitters and solar cells [2]. The surface chemical reactivity of graphene allows the implementation of chemical decoration approaches for fully exploiting the outstanding functionalities of the aromatic compound and for further improving its properties (e.g. mechanical, electrical and thermal properties). Colloidal nanocrystals (NCs) or nanoparticles (NPs), prepared by means of solution-based colloidal chemistry routes, are optimal candidates for functionalizing graphene, as their unique size- and shape-dependent optoelectronic properties [3] can be effectively conveyed to graphene, resulting in hybrid materials with outstanding novel or improved functionalities, promising for advanced technological applications [4]. In this work, monolayer graphene, grown by chemical vapor deposition (CVD), has been surface modified with pyrene-1-butyric acid (PBA)-coated TiO₂ NCs. CVD grown graphene is a scalable material, suited for large scale applications [5]. Conversely, NC TiO₂ is widely used in electrochemical sensors, solar cells and photocatalytic systems for its UV-light photo-activity, low toxicity, optical transparency and photostability [6].

The merging of properties of the TiO₂ NCs with those of the carbon based nanostructures has been demonstrated to yield to hybrid materials with enhanced electrical conductivity, photoelectrical conversion efficiency, photocatalytic properties and environmental stability [7].

The interphase at the junction of two hybrid components is expected to play an essential role in determining their electron coupling. Here, the hybrid material has been fabricated by exposing the graphene film to a dispersion of the PBA surface coated TiO₂ NCs. Such a ligand, coordinating the NC surface by means of the carboxylic functionality and chemically

binding them to the aromatic graphene platform by means of π - π stacking interactions, is able to electrically interconnect them, each other and with graphene, leading to a p-doping of graphene [4].

The morphology, structure, sensitivity and the spectroscopic, as well as, the (photo)electrical properties of the hybrid material have been investigated. The composite has been found optically transparent, concomitantly exhibiting a promising selectivity in detecting biologically relevant molecules, as dopamine and norepinephrine. In addition, the decoration of graphene with the PBA-coated TiO₂ NCs has demonstrated effective in combining the electron acceptor and ballistic charge transport capability of graphene, with the UV-light photo-activity of the TiO₂ NCs, showing a photo-electric responsivity higher than that of bare graphene. Thus, such a material has a great potential as photoactive component, suited for manufacturing optically transparent electrodes to integrate in photo-renewable sensors and in solar cells, photodetectors and FETs.

II. EXPERIMENTAL

Oleic acid (OLEA)-capped TiO₂ NCs were synthesized as reported in [8], under N₂ atmosphere and at low temperature, by hydrolysis of the tetraisopropoxide (TTIP) precursor in OLEA surfactant and in presence of ethylene glycol and of trimethylamino-N-oxide dihydrate (TMAO) base which catalyzes polycondensation reaction of TTIP. The as synthesized TiO₂ NCs were repeatedly washed with methanol to remove the excess of the OLEA ligand coordinating the NC surface. Then, the NCs were exposed to a chloroform solution of BPA in a 1:5 TiO₂/PBA molar ratio. The mixture was left to stir at room temperature and then, the NCs were washed with methanol to remove the aromatic ligand in excess and re-dispersed in chloroform.

Monolayer graphene was grown by CVD on 25 μ m thick copper foils (Alfa Aesar, item No. 13382) in a typical quartz tube CVD reactor at 1000°C using CH₄/H₂ as precursors. The prepared graphene was then transferred onto SiO₂/Si or ITO/glass substrates by using a thermal release tape and a water solution of ammonium persulfate (0.1 M) as a copper etchant. Before graphene transfer, the SiO₂/Si substrates were treated with O₂ plasma for improving adhesion. All graphene samples were dipped in a toluene/ethanol/anisole (1/1/1) solution, for removing any organic impurities of thermal tape traces.

The monolayer graphene film transferred on SiO₂/Si or ITO was incubated in a 10⁻³ M chloroform solution of PBA-capped TiO₂ NCs and finally rinsed with chloroform to remove NCs not specifically adsorbed.

Steady state UV-Vis absorption spectra were recorded with a Cary 5000 (Varian) UV/Vis/NIR spectrophotometer on PBA-coated TiO₂ NCs. Raman spectra of graphene were collected by using a LabRAM HR Horiba-Jobin Yvon spectrometer with a 532 nm excitation laser source. The Raman measurements were carried out under ambient conditions at a low laser power (1 mW) to avoid laser-induced damage. The

Raman band recorded from a silicon wafer at 520 cm⁻¹ was used to calibrate the spectrometer, and accuracy of the spectral measurement was estimated to be 1 cm⁻¹.

TEM analyses were performed by using a Jeol Jem-1011 microscope, operated at 100 kV. TEM images were acquired by a Quemesa Olympus CCD 11 Mp Camera. TEM images of PBA-coated TiO₂ NCs were collected by dipping the 300 mesh amorphous carbon-coated Cu grid in chloroform solution of the NCs and leaving the solvent to dry. Size statistical analyses (NP average size and size distribution) of the samples were performed by the freeware ImageJ analysis program. Field emission scanning electron microscopy (FE-SEM) was performed by a Zeiss Sigma microscope, operating in the range 0-10 keV and equipped with an in-lens secondary electron detector and an INCA Energy Dispersive Spectroscopy (EDS) detector. Samples were mounted onto stainless-steel sample holders by double-sided carbon tape and grounded by silver paste.

Topography and phase mode AFM measurements were performed in air and at room temperature, by means of a PSIA XE-100 SPM system operating in tapping mode. A silicon SPM sensor for noncontact AFM (Park Systems), having a spring constant of 42 N m⁻¹ and a resonance frequency of 330 kHz, was used.

Electrochemical cyclic voltammetric features of dopamine (Dopamine hydrochloride, pharmaceutical secondary standard, traceable to USP) and norepinephrine (L-norepinephrine hydrochloride, Sigma, \geq 98.0%) were registered using the method optimized in [9] at a scan rate of 0.1 V s⁻¹, in a three electrode cell, by using an Autolab PG-Stat 30 (EcoChemie B.V., The Netherlands) potentiostat/galvanostat, equipped by Nova 2.0 software for the result analysis. In each electrochemical experiment, a 0.1 M NaClO₄ aqueous solution (Aldrich, ACS reagent, \geq 98.0%) was used as a supporting electrolyte. A platinum wire, a saturated calomel electrode and a surface modified ITO glass substrate were used as a counter, reference and working electrode, respectively. Electrochemical photocurrent transient density measurements were performed at the bias voltage of 1V by using the same equipment of the cyclic voltammetric measurements. The working electrode was illuminated at definite times with an UV Jelosil HG500 iron halogenide lamp (λ = 356 nm). All the measurements have been carried out in N₂ atmosphere after degassing the cell with nitrogen flow for at least 10 min.

III. RESULTS AND DISCUSSION

Here, a facile method has been used to chemically functionalize graphene, grown by chemical vapor deposition (CVD), with 1-pyrene butyric acid (PBA)-coated TiO₂ NCs. Pre-synthesized oleic acid (OLEA)-coated TiO₂ NCs [8] have been surface functionalized with PBA, upon capping exchange for displacing the insulating pristine OLEA ligand. The prepared PBA-coated TiO₂ NC modified graphene has been characterized by means of microscopy, Raman spectroscopy, and (photo)electrochemical analysis in order to investigate morphology, structure and (photo)electrochemical properties of the nanocomposite. PBA molecules have been found to

coordinate the NC surface by its carboxyl group, while the pyrene moiety is effective in anchoring the NCs by means of π - π stacking interactions onto graphene, without any significant modification of its structure, ensuring electrical interconnection with the NCs [4]. Panel A of Fig. 1 shows the TEM image and the UV-vis absorption spectrum of the achieved PBA-coated TiO₂ NCs. Such nano-objects show the typical unstructured absorption line-shape of a high band gap TiO₂ NC semiconductor [8] pointing out the optical transparency of the solution, explained by the lack of aggregation phenomena among the PBA-treated NCs. Monolayer CVD graphene films transferred on SiO₂/Si have been functionalized with a stable dispersion of the PBA-coated TiO₂ NCs. CVD graphene film morphology significantly changes after treatment with the PBA-coated TiO₂ NCs. Namely, the AFM topography image, reported in panel B of Fig. 1 shows that the morphology of the hybrid is mainly characterized by a dense and closely interconnected layered nanostructures. The comparison between the NC size, estimated by the TEM image reported in panel A, and the dimension of the features imaged in panel B, suggests that the PBA-coated TiO₂ NCs are arranged in a random close packed nanoporous multilayered structure. Secondary electron microscopy micrograph provides an overview of the large area, highly interconnected arrangement of the NCs, and EDS analysis further prove the deposition of the TiO₂ NCs on graphene. The films of CVD graphene have been analyzed also by Raman spectroscopy before and after decoration with the PBA-capped TiO₂ NCs.

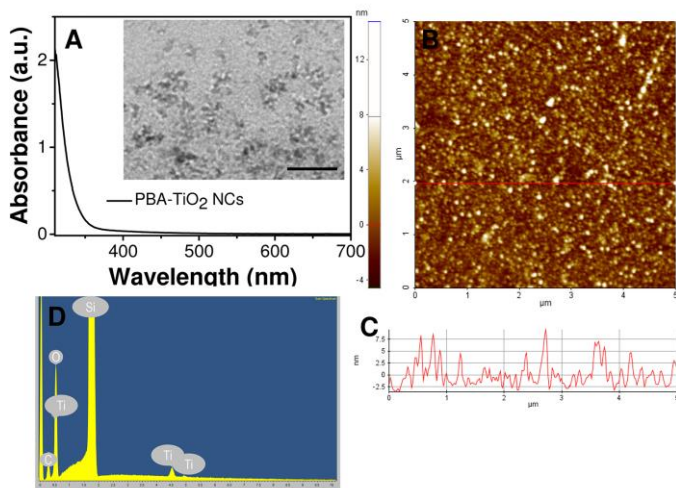


Fig. 1. (A) UV-vis absorption spectrum and (in the inset) TEM micrograph of PBA-coated TiO₂ NCs. (B) 2D topography AFM image and (C) EDS spectrum in the range of 0-10 keV of CVD monolayer graphene (G) functionalized with PBA-capped TiO₂ NCs. (D) Cross sectional line profile taken along the red line of panel B.

Panel A of Fig. 2 reports the Raman spectra of the monolayer CVD-graphene transferred on SiO₂/Si substrate, as bare (black line) and functionalized with the PBA-capped TiO₂ NCs (red line). The Raman spectrum shows the typical G and 2D peaks of graphene, at 1583 cm⁻¹ and 2678 cm⁻¹, respectively. After decoration by the PBA-coated TiO₂ NCs, the G and 2D peak

positions, as well as the ratio between their intensities drastically change, indicating the occurrence of a change of the graphene electronic properties due to the increase of the hole carrier concentration in the organic platform [10]. Finally, two new peaks (*), namely at 1240 cm⁻¹ and 1620 cm⁻¹, are accounted for the typical Raman signals of pyrene [4]. Panel B of Fig. 2 reports the UV-vis spectrum of the CVD graphene modified with the PBA-coated TiO₂ NCs, showing the optical transparency of the hybrid material.

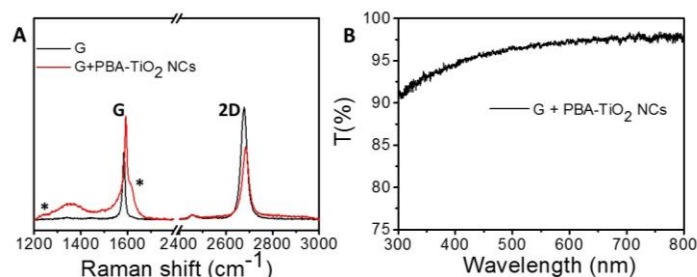


Fig.2. (A) Raman spectra of CVD monolayer graphene (G) transferred on SiO₂/Si as bare and functionalized with PBA-capped TiO₂ NCs. (B) UV-vis absorption spectra of CVD graphene (G) modified by PBA-coated TiO₂ NCs.

The graphene-based electrodes have been tested for the detection of two important analytes: dopamine and norepinephrine. Figure 3 shows the voltammetric patterns of the two species at 1 mM concentration in aqueous 0.1 M NaClO₄ on the two modified electrodes, in dark conditions.

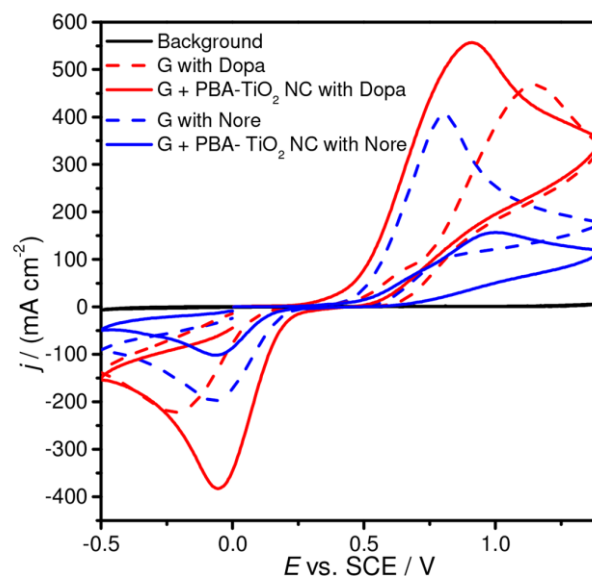


Fig. 3 Cyclic voltammetric measurements of 1 mM dopamine (Dopa) and norepinephrine (Nore) registered at 0.1 V s⁻¹ in 0.1 M aqueous NaClO₄ on ITO electrodes modified with monolayer graphene (G) and with PBA-TiO₂ NC functionalized monolayer.

The CV patterns on graphene monolayer (dashed lines) present two intense peaks, well-spaced (about 300 mV) to allow the simultaneous determination of the two analytes. The presence of PBA-TiO₂ NCs shifts the voltammetric signal of dopamine towards less positive potential, due to the electrocatalytic effect of TiO₂ NCs, provided by the p-doping

effect of the nano-oxide on graphene, which also enhances the signal in terms of current density, thus allowing an increase in sensitivity. Conversely, an opposite trend is observed in case of norepinephrine, which instead presents an up-shift of the potential.

The photoelectric properties of the PBA-coated TiO₂ NC modified graphene have been investigated by photoelectrochemical measurements. Fig. 4 reports the photocurrent density of the manufactured working electrodes formed of bare and of PBA-coated TiO₂ NCs functionalized graphene, under illumination with an UV-lamp. All the *I-t* curves are anodic, attesting for the occurrence of oxidation of the medium, with concomitant transfer of photogenerated electrons from the photoanode hybrid material to ITO. The bare graphene based working electrodes show a photocurrent signal of 0.15 μA cm⁻², originated from the π-π* transition of the graphene -C=C- bond^[30] that takes place under UV-irradiation. Upon immobilization of the PBA-coated TiO₂ NCs on graphene, the photocurrent density is higher than that detected for bare graphene, increasing up to ca. 0.18 μA cm⁻². This result is ascribed to the intrinsic UV-light activity of the TiO₂ NC film, which generates and separates electron-hole pairs, then transferred to graphene through pyrene. Indeed, pyrene stabilizes the photoelectrons by its π ring system [4], facilitating separation of the photoexcited electron-hole pairs and transferring them from the NCs to graphene.

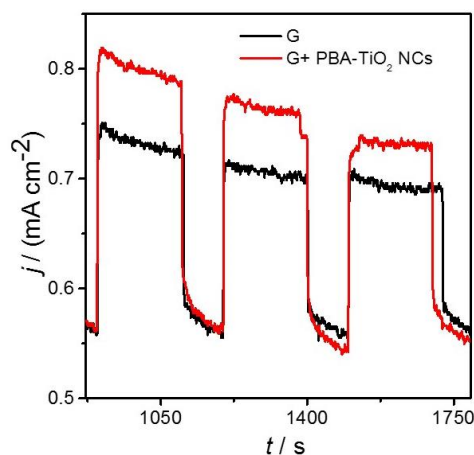


Fig. 4. Photocurrent density transient measurements collected under UV-light ($\lambda=365$ nm) irradiation of ITO electrodes modified with monolayer graphene (G) and with PBA-TiO₂ NC functionalized monolayer G.

IV CONCLUSION

An optically transparent and UV-light photoactive hybrid material based on a large area CVD grown monolayer graphene film, chemically functionalized with colloidal TiO₂ NCs has been manufactured. The TiO₂ NC film acts as a p-doping layer of graphene, resulting in an improved electrocatalytic and photoelectric activity, exhibiting concomitantly promising results in terms of selectivity and sensitivity for dopamine and norepinephrine. The achieved hybrid material can result promising for the detection of biomolecules of pharmaceutical and medical interest. These

preliminary results will pave the way towards the use of more accurate and sensitive voltammetric techniques, capable of decreasing the limits of detection and quantification, enhancing also the selectivity. Moreover, the decoration of graphene with UV-light active and hence self-cleaning TiO₂ NCs can be exploited in view of the manufacturing of photo-renewable electroanalytical sensors [11], allowing to overcome the well-known problem of electrode fouling and passivation, typically encountered in detecting such analytes. In addition, components made of the achieved composite materials can result interesting for photodetectors and solar cells.

Finally, the solution-based approach here implemented for the preparation of the G/TiO₂ NC hybrid can be extended to other nanoparticles having diverse composition (metal, oxide, chalcogenides) and coordinated by aromatic ligands having different structure, for manufacturing nanocomposites possessing a range of diverse interesting functionalities, with a relevant potential for advanced technological applications.

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