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Synthesis of hybrid graphene–porphyrin micro/nanofiber structures by ionic self-assembly

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ABSTRACT

Cationic mesa-tetra(4-pyridyl) porphine (TPyP)-graphene oxide (GO) hybrid structures have been synthesized by ionic self-assembly. The different aggregated structures shape were obtained through electrostatic and π–π stacking interactions, as indicated by redshift of porphyrin Soret band throughout the pH range of 1.5–9.1, fluorescence quenching, Raman spectra and Energy dispersive X-ray spectroscopy. A strong fluorescence quenching of the cationic porphyrin in the presence of graphene indicated that efficient electron or energy transfer occurred from the excited state of the cationic porphyrin to graphene. The investigation revealed a three-dimensional fiber structures formation under the acid conditions and leaf-like structures of the TPyP/GO assemblies under the alkaline conditions of the solution. The fibers morphology and cross-section was determined quantitatively by Scanning force microscopy; this revealed a diameter of the fibers up to hundreds of nanometers and the lengh up to hundreds of micrometers. The electrical properties of the fibers were investigated by spreading resistance and current–voltage characteristics measurements using Atomic Force Microscopy (AFM) with conductive cantilevers. The current–voltage characteristics fit to the Poole–Frenkel emission mechanism in the case of TPyP/GO sheets and Schottky emission dominate in the nanofibers case. This new graphene material shows a potential for energy, sensing and photonic applications.

1. Introduction

Producing arrays of novel materials with ordered structures as device building blocks represents an important approach to many nanomaterials applications [1–4]. Functional self-assembled materials created from small molecules with well-defined shapes and dimensions often show a unique and/or enhanced properties and are of great current interest especially for applications in electronics, photonics, light-energy conversion and catalysis. Carbon-based materials are presently considered as potential candidates for the development of new nanoelectronic devices, due to their exceptional electronic properties [5–7]. Patterned graphene, carbon nanotubes (CNT) and graphene ribbons have been proposed as ingredients in nanocarbon circuits [8–10]. In these low-dimensional structures, the presence of defects dramatically modifies their electronic properties. It is highly desirable to assemble graphene at specific locations and into desired patterns, for rational design of functional devices at a large scale [11].

An effective method to improve graphene oxide (GO) process ability is through the covalent or noncovalent functionalization of graphene based materials with various molecules and nanomaterials both in water and organic solvents [12]. On the other hand, porphyrins and metalloporphyrins provide an extremely versatile nanometer-sized building block for the control of materials properties [13]. The different routes have been used to functionalize the graphene and graphene oxide with porphyrins [12,14]. Graphene based materials morphology, structure and devices performance relationship have been investigated by several authors [15–17]. The physical properties of graphene nanoribbons are highly dependent on their width and the topology of the edge structures. Depending on the edge-shape of the graphene structure, different band gaps for similarly sized systems can be generated since its electronic structure is greatly influenced by disorder. Therefore, tailoring the graphene based nanomaterials boundaries using different technologies will lead to the exploration of numerous applications such as transistors, chemical and biosensors, energy storage devices, nanoelectromechanical systems and others, just as the research community has done with carbon nanotubes previously. The functionalized graphene oxide based conductive or semiconductive nanofibers can open a promising way to build a simple and cheap conductive type molecular sensing devices with selected sensitivity.

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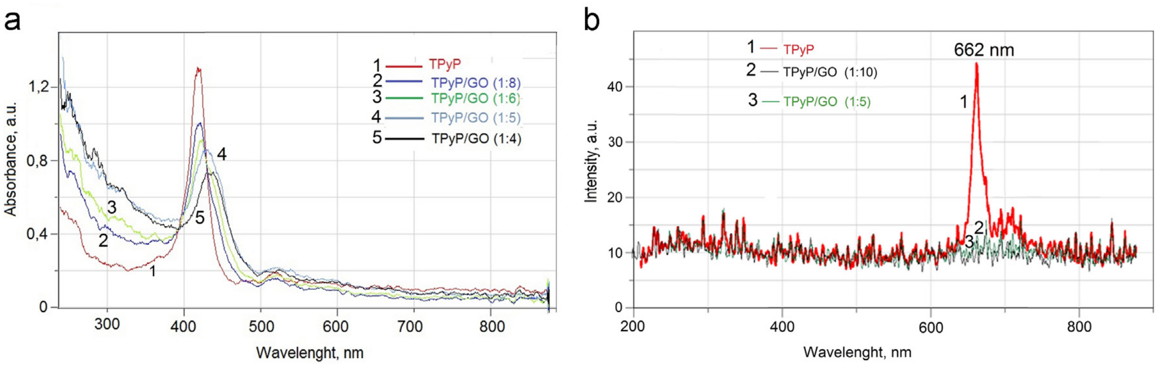

Fig. 1. The influence of GO concentration on the absorption (a) and fluorescence (b) spectra of the TPyP/GO hybrids.

The motivation of this work was to design a route to synthesize a functionalized graphene oxide based micro/nanofiber type structures for possible application in sensing, energy storage devices. In this study, the ionic self-assembly [18] between a negatively charged GO and a cationic meso-tetra (4-pyridyl) porphine (TPyP) was used to produce a novel hybrid GO/ TPyP nanofibres structures. In the presence of cationic TPyP, superstructures with controlled lengths are generated in an ionic self-assembly process, primarily through electrostatic interactions between charged GO sheets and oppositely charged TPyP molecules. Hydrophobic and π–π interactions act as the secondary driving forces to promote self-organization and formation of nanofibers. The hybrid graphene/porphyrin nanofiber-like structures represent a new class of carbon material, for which the molecular building units can be altered to control their structural and functional properties and the method opens a new strategy toward the extraction of micro and nanofibers without destruction of the π-conjugated system.

2. Experimental

2.1. Chemicals and materials

Meso-Tetra(4-pyridyl) porphine was purchased from Frontier Scientific, USA, graphene oxide from Graphene Supermarket, USA and the rest of the chemicals were all purchased from Sigma-Aldrich.

2.2. The Synthesis of TPyP/GO

TPyP was dissolved in deionized (DI) water at room temperature under acidic aqueous medium (HCl was added to reach pH 2 at the concentration $5*10^{-4}$ M), obtaining a greenish colloid. GO solution as purchased with a concentration of 500 mg/L was diluted with deionized water. In a typical experiment, GO solution was suspended in anionic Meso-tetra (4-sulfonatophenyl) porphine dihydrochloride aqueous solution. The influence of pH on TPyP (concentration $5*10^{-4}$ M) and GO (concentration-50 mg/l) ionic self-assembly in solution, the pH was adjusted using HCl solution to reach pH 1.5–2.3 and 1% CaCO3 solution to reach pH 5.4–9.1. Measurements of the absorption and fluorescence spectra were carried out after mixing $5*10^{4}$ M porphyrin solution with different concentrations ratio of graphene oxide solution at room temperature within 1 min. Atomic Force Microscopy (AFM), Scanning electron microscopy (SEM) measurements were carried out on dried solution drop on glass substrate and electrical measurements on gold coated substrate.

2.3. Characterizations

The morphology and composition of the TPyP/GO aggregates were examined using a SEM/Focused Ion Beam (FIB) workstation Helios Nanolab 650 with an energy dispersive X-ray (EDX) spectrometer INCA Energy 350 X-Max 20 and by AFM (SMENA, NT-MDT Inc.). Conductivity measurements were made using AFM spread resistanse and current-voltage(I–V) measurement modes (Smena NT-MDT) with conductive CSG10 TiN coated cantilevers (NT-MDT Inc.). Raman spectra were collected using spectrometer (Spectra, NT-MDT Inc.), exited with 532 nm wavelenght laser. The UV–vis and fluorescence spectra were recorded on Ocean Optics USB-4000spectrometer.

3. Results and discussion

3.1. UV–vis characterization of TPyP/GO aggregates

As shown in Fig. 1, the ground state absorption spectrum of TPyP exhibited a very intense Soret band (Q_{max}=419 nm) corresponding to the S2 transition, while the weaker Q bands between 500 and 700 were assigned to a pair of vibronic progressions corresponding to S1 transition [19]. With increase of the GO concentration, the position, width and intensity of the absorption spectra of TPyP/GO solution were changed. The most obvious change occurred in the Soret band region of the absorption spectrum: the intensity of the original Soret band at 419 nm decreased gradually and a new Soret band appeared at 435 nm. This red shift of 16 nm indicates that interactions took place between GO and TPyP. The results indicate that the functional groups on the surface and edge of graphene sheets played an important role in interactions between various molecules through supermolecular interactions such as π–π stacking, electrostatic interaction and hydrogen bonding [20].

Since TPyP is positively charged owing to the presence of pyridyl groups, the GO sheets has a negative ζ-potentials in both DI water and ionic salt solutions. GO has functional groups: hydroxyl (–OH), carboxyl groups (–COOH), epoxy (C–O–C). The oxygen amount in the GO affects the surface charge and its dispersion in aqueous solutions. Although ζ-potential plays a key role in colloidal stability, it does not show the true particulate state in various environments. Here, GO samples showed an excellent colloidal dispersion and stability in D.I. water even after 24 h at room temperature. It is because of their high negative surface charge (electrostatic stabilization). However, even though the surface charge of GO was negative in D.I. water, in the presence of TPyP, GO formed observable aggregates and came completely out of suspension after 1 h incubation at room temperature. Hydrophobic and π–π interactions acted as the driving forces to promote