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Talanta

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Graphene oxide vs. reduced graphene oxide as carbon support in porphyrin peroxidase biomimetic nanomaterials



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ARTICLE INFO

Article history:

Received 6 August 2015

Received in revised form

3 November 2015

Accepted 6 November 2015

Available online 10 November 2015

Keywords:

Thermally reduced graphene oxide

Graphene oxide nanocomposites

Supramolecular assemblies

Tetrapyrrolylporphyrin

Peroxidase-like activity

Vitamin E

ABSTRACT

The paper describes the preparation of supramolecular assemblies of tetrapyrrolylporphyrin (TPyP) and its metallic complexes with graphene oxide (GO) and thermally reduced graphene oxide (TRGO). The two carbon supports are introducing different characteristics in the absorption spectra of the investigated nanocomposites. Raman spectroscopy shows that the absorption of iron-tetrapyrrolylporphyrin is more efficient on GO than TRGO, suggesting that oxygen functionalities are involved in the non-covalent interaction between the iron-porphyrin and graphene. The biomimetic peroxidase activity is investigated and the two iron-containing composites exhibit a better catalytic activity than each component of the assembly, and their cobalt and manganese homologues, respectively. The main advantages of this work include the demonstration of graphene oxide as a very good support for graphene-based nanomaterials with peroxidase-like activity ($K_M=0.292$ mM), the catalytic activity being observed even with very small amounts of porphyrins (the TPyP:graphene ratio=1:50). Its potential application in the detection of lipophilic antioxidants (vitamin E can be measured in the 10^{-5} – 10^{-4} M range) is also shown.

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1. Introduction

Graphene is a two-dimensional nanomaterial which received an increased attention over the last decade. Nowadays, graphene-based nanocomposites have grown as a well-defined and continuously expanding domain in the large field of materials science. Their properties can be tailored by the choice of the synthesis method, from the clean carbon honeycomb surfaces obtained by chemical vapor deposition to the large quantities that can be achieved by the oxidation of graphite. Further tuning of the targeted property was accomplished by decorating the carbon surface with metallic nanoparticles, doping with heteroatoms or by covalent and non-covalent functionalization with organic molecules [1].

The organic-based supramolecular assemblies of porphyrins as biomimetic systems became extensively studied due to their potential applications, from biology to energy field [2]. It is well known that heme (an iron-containing porphyrin) is the catalytically active building-block in a variety of proteins, including peroxidases [3]. Replacement of iron with other metals, like

manganese or cobalt, has been used to model the naturally P450 cytochrome [4,5] and for the synthesis of artificial hemoglobins. Manganese porphyrins have also been investigated for their superoxide dismutase-like activity [6] while cobalt-containing nanomaterials were recently studied for their peroxidase-like catalytic activity [7,8].

Given our recent interest in exploring the peroxidase-like activity of different graphene-based nanomaterials [9], we decided to investigate the potential of (metallo)porphyrin conjugates with graphene-based nanomaterials, to be efficiently used as peroxidase mimetic. Most of the molecularly modified graphene nanocomposites that mimic the catalytic behavior of peroxidase are decorated with inorganic nanoparticles [10,11]. Among the porphyrin-conjugates, a hemin-chemically reduced graphene nanomaterial has been investigated for its biomimetic catalytic activity in the oxidation of pyrogallol by hydrogen peroxide and also compared with an iron porphyrin-graphene conjugate [12]. Two other papers report on the ability of hemin-chemically reduced graphene nanocomposites to decompose hydrogen peroxide, by using large amounts of the organic modifier [13,14]. The peroxidase-like activity of porphyrin-based nanomaterials has been proven also in case of carbon nanoparticles as support [15].

Because the intrinsic catalytic activity of graphene is dependent on the surface modifications of the carbon lattice, we considered important to study both graphene oxide (GO) and thermally

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reduced graphene oxide (TRGO), as supports of the (metallo)porphyrin conjugates. Besides measuring the influence of graphene on the catalytic behavior of an iron-containing porphyrin, we also synthesized the cobalt(III) and manganese(III) complexes of the porphyrin and observed their peroxidase-like activity when assembled on carbon nanostructures.

The peroxidase-like activity of carbon nanomaterials found applications in the detection of different analytes [16,17,18]. The presence of functional groups at the surface of graphene oxide enables surfactant properties [19], which should also render the spectrophotometric detection of lipophilic compounds. α -Tocopherol (the main component of the vitamin E family) has a key role in our metabolism and was determined both in blood components and in foods [20,21]. The continuous interest in developing methods for the determination of this antioxidant [22,23] is justified by the difficulties related to its lipophilic nature, air and light sensitivity. Therefore, we have investigated the application of graphene oxide-iron porphyrin composite for the detection of α -tocopherol.

2. Experimental

2.1. Materials and methods

All the reagents were of analytical grade and used without further purification. 3,3'-dimethylbenzidine (ortho-tolidine) and 5,10,15,20-tetra(4-pyridyl)porphyrin (TPyP) were purchased from Sigma-Aldrich. Cobalt(II)chloride, manganese(II)chloride, iron(III)chloride, ethanol, dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were purchased from Merck. Graphene oxide and thermally reduced graphene oxide were prepared according to a previously described synthesis [9,24].

The morphology of graphene nanocomposites were observed by transmission electron microscopy (TEM) (H-7650 120 kV Automatic TEM, Hitachi, Japan) and scanning electron microscopy (SEM) (SU-8230 STEM – Hitachi, Japan). For TEM images, the samples diluted in ethanol were dropped on a copper grid. The ultraviolet–visible (UV–vis) absorption spectra of enzyme mimic and the time-dependent absorbance spectra were measured with a V-570, JASCO Spectrophotometer.

The Raman spectra were collected at room temperature by using a JASCO type NRS3300 spectrophotometer arranged in a backscattering geometry, coupled to a CCD ($-69\text{ }^{\circ}\text{C}$) detector with a 1200 l/mm grid and a spectral resolution of 7.5 cm^{-1} . The incident laser beam with a diameter of $1\text{ }\mu\text{m}^2$ was focused through an Olympus microscope ($100\times$ objective), and the calibration was made by using the Si peak at 521 cm^{-1} . The excitation was done by using an Ar-ion laser with a wavelength of 514 nm and a power at the sample surface of 1.1 mW.

2.2. Preparation of graphene-(metallo)porphyrin nanocomposites

Graphene oxide has the molecular weight larger than TRGO so, in order to ensure the use of the same porphyrin:graphene ratio, the following reaction procedure was applied: a solution of GO (50 mg) or TRGO (25 mg) in 20 mL ethanol was sonicated for 30 min. In each solution, a volume of 350 μL of TPyP or M(III)TPyP (5 mM in DMF) was added and the final mixture was stirred at room temperature, overnight. The dispersion was then centrifuged (3000 rpm for 25 min) and the supernatant discarded. The solid was washed three more times with the same volume of ethanol, followed by centrifugation. Finally, the solid was dried at $35\text{ }^{\circ}\text{C}$. The resulting nanocomposites were following denoted GO-(M)TPyP or TRGO-(M)TPyP.

The M(III)TPyP were synthesized by refluxing a solution of

TPyP (30.9 mg, 0.05 mmol, 10 mL DMF) with the appropriate metal chloride (0.06 mmol) for six hours (Scheme S1).

2.3. Peroxidase catalytic activity experiments

The catalytic activity study of all graphene-based nanomaterials was performed as follows: 230 μL of graphene suspension (2.5 mg in 5 mL of 0.5% HCl) was added in a reaction volume of 3 mL acetate buffer solution (ABS, 0.2 M, pH 4.2) with H_2O_2 (1 mM) and ortho-tolidine (1 mM).

The kinetic analysis were carried out with 230 μL of graphene suspension (2.5 mg of GO-FeTPyP or TRGO-FeTPyP in 5 mL of 0.5% HCl) in a reaction volume of 3 mL ABS (0.2 M, pH 4.2) with ortho-tolidine (0.8 mM final concentration) and variable H_2O_2 concentration. The reactions were carried out in a quartz cuvette with an optical path length of 1 cm and the time course measurement set at 630 nm.

2.4. Experiments for vitamin E detection

A stock solution of well sonicated α -tocopherol (7.55 mM in ABS:DMSO-7:1) was used to prepare three other solutions ($3\times 10^{-3}\text{ M}$, $3\times 10^{-4}\text{ M}$ and $3\times 10^{-5}\text{ M}$) in ABS (0.2 M; pH 4.2) which were next employed to dilute α -tocopherol, down to 10^{-7} M . The analysis was carried out with 230 μL of graphene suspension (2.5 mg of GO-FeTPyP in 5 mL of 0.5% HCl) in a reaction volume of 3 mL ABS (0.2 M, pH 4.2) with ortho-tolidine (0.8 mM final concentration) and variable α -tocopherol concentration. The reactions were carried out in a quartz cuvette with an optical path length of 1 cm and the UV absorption spectra were measured after 10 min reaction.

3. Results and discussion

3.1. Synthesis and characterization of nanocomposites

The formation of the non-covalent assemblies of graphenes with (metallo)tetrapyrrolylporphyrins is depicted in Scheme S2. The iron(III), manganese(III) and cobalt(III)tetrapyrrolylporphyrin were synthesized by the reaction of free porphyrin with MnCl_2 , CoCl_2 or FeCl_3 [25]. The insertion of Mn(II) and Co(II) metallic ions into the macrocyclic structure change their oxidation state, from $2+$ to $3+$. The metals oxidation was ensured by the non-anhydrous reaction conditions [26]. The formation of the more stable Mn(III)porphyrin complexes starting from Mn(II) salts has been long described [27,28] and the measured UV–vis spectra of the MnTPyP graphene nanomaterials (Fig. S1b and S4) correspond to a Mn(III)-porphyrin complex, both in shape and Soret band position [29]. Further, cobalt(II) oxidation in the presence of oxygen [30] and the blue-shift of Soret band [31] has been also previously mentioned and fit well with our data. The nanocomposites were synthesized by overnight stirring of a well-dispersed solution of GO or TRGO with a small amount of the corresponding (metallo)tetrapyrrolylporphyrin, the mass ratio being 50:1 and 25:1, respectively. At the end of the reaction, the careful washing of the unbound porphyrin was performed, followed by centrifugation.

In our previous study, the structural characterization of the starting GO and TRGO revealed that graphene oxide was bearing the typical oxygen functionalities, the major ones being hydroxyl groups, epoxy and carboxyl groups that caused a large space between the 2D carbon sheets. After the thermal reduction of lyophilized graphene oxide, some carboxylic groups were still present at the surface, while the aromatic carbon structure was partially restored and the interlayer distance dropped from 7.7 to 3.4 nm [24]. After the formation of the supramolecular assemblies with

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