



Reduced graphene oxide/iron carbide nanocomposites for magnetic and supercapacitor applications



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ABSTRACT

Reduced graphene oxide/Fe₃C hybrids were prepared through Fe-based intercalation of graphite oxide (GtO). Altering pH (acidic to basic) of aqueous GtO dispersion, the immobilization of Fe-based intercalant bearing amino benzoate groups (IFe) was strongly affected following either the nucleophilic substitution (sample: IGO) or ion exchange path (sample: IGO/b). Subsequent pyrolysis of the intercalated materials provided magnetic hybrid materials (samples: r-IGO and r-IGO/b), differing in terms of BET surface area (87 and 163 m²/g), magnetization (70 and 43 J/T/kg), resistance (3 and 3.7 Ohm) and capacitance (5 and 17 F/g) correspondingly, displaying both magnetic and supercapacitor behavior. IFe triggered after thermal treatment in vacuum the formation of Fe₃C nanoparticles encapsulated in a graphite shell whose incorporation into the multi-layer reduced graphene oxide (GO) matrix provided multi-functional materials. In these materials, aggregation is prevented in two directions: (a) between adjacent Fe₃C nanoparticles, since the graphitic shell offers isolation, and (b) between bundles of neighboring multi-layer graphenes, due to Fe₃C nanoparticle interference. The graphitic shell assists cohesion of encapsulated Fe₃C nanoparticles with the graphene matrix as well as chemical stability, affording thus materials appropriate for a variety of applications.

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1. Introduction

Nanoparticles possessing magnetic properties embedded in a non-magnetic graphene matrix combine both the benefits of the unique properties of graphenes (e.g. high surface area, electrical conductivity [1], high flexibility [2], mechanical strength, light weight etc.) and magnetization. When these magnetic particles are encapsulated in a graphitic shell, the limits of application are extended since the carbon layers isolate the particles magnetically from each other, provide protection against oxidation and environmental degradation as well as stability in many organic and inorganic media [3,4]. These hybrid materials can open up new prospects in bio-engineering and biomedical applications, such as controlled drug delivery [5,6], magnetic recording media [7], magnetic toners, magnetic resonance imaging, ferrofluids [8], as well as in electrochemical energy storage and supply [9].

The energy applications including supercapacitor and lithium ion batteries require materials exhibiting reversible capacity, high cycle stability, electrical conductivity and active surface area [10].

Considerable efforts have been made towards this goal. Mainly, they include carbonaceous materials such as carbon nanotubes, graphenes and ordered mesoporous carbon [11] in composites with metal oxides (e.g. iron oxides [12,13]) in order to fully utilize the synergistic effects between these two components [14]. Drawbacks like low cycle stability is caused largely by the aggregation of metal or metal oxide particles and leads to the reduction of active surface area and subsequently lowers the efficiency of the active material. To overcome these problems carbon coating of metal oxide nanoparticles has been employed in several cases in order to enhance the electrical conductivity and electrochemical performance [10,15]. Especially, carbon encapsulated nanoparticles have been developed actively by various methods, including arc discharge techniques, chemical vapor depositions and pyrolysis of metal complexes [16].

In the present work the latter method of pyrolysis applied in an iron species-intercalated graphite oxide matrix resulted in a composite magnetic graphene-based material. By exploiting the chemistry of graphite oxide we have introduced functionality between graphene oxide layers. The modification of graphite oxide surfaces based either on grafting reactions or ion exchange has attracted considerable interest [17–20]. Trinuclear iron acetates have been

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used in the past for pillaring of graphite oxide, utilizing its ion exchange capacitance [21]. In our case instead of an acetate, an amino benzoate compound such as p-aminobenzoic acid was employed in a modified synthesis of Shova et al. [22] for the preparation of a trinuclear like iron compound that would allow, under appropriate conditions, the intercalation via grafting or ion exchange path. This parent material produces after thermal treatment in vacuum an exfoliated multi-layer graphene material bearing carbon coated magnetic nanoparticles. The major advantages of this route are in terms of: (a) blocking the aggregation between adjacent bundles of multi-layer graphenes, (b) isolation and environmental protection of encapsulated iron carbide nanoparticles and (c) improved cohesion between these two components which is of great importance if it is taken into consideration that a main drawback in the area of magnetic graphene hybrids is the weak interaction between magnetic nanoparticles and graphene.

Nyquist plots of the capacitor cells with graphene composite materials as well as cyclic voltammetry curves were investigated. In-series resistance and capacitance of the materials were determined, opening thus perspectives for their application as electrodes in supercapacitors. Mössbauer spectroscopy was performed in order to identify the iron species and their content in the sample and magnetization measurements revealed properties that can establish these hybrid materials as candidates appropriate for magnetic applications.

2. Experimental

2.1. Synthesis of graphite oxide (GtO)

GtO was synthesized according to a modified Staudenmeier method [23] where Graphite flakes (Natural, ~10 mesh 99.9%, metal basis) were used as pristine graphite. This procedure was applied twice.

2.2. Preparation of iron intercalant (IFe)

5 mmol p-aminobenzoic acid (99%, Alfa Aesar) were dispersed in 50 ml distilled water and 2.5 mmol K_2CO_3 (Riedel-deHaën) were added. The solution became transparent and then 2.5 mmol $FeCl_3 \cdot 6H_2O$ (Panreac) were added. The whole was left under stirring for 1 h.

2.3. Preparation of intercalated GtO samples (IGO, IGO/b)

50 mg GtO were dispersed in 50 ml distilled water under sonication for 1 h (pH~2.8). Then IFe solution was added and the whole was left under stirring for 48 h at room temperature. Washing, stirring and centrifugation followed several times (8–9) and finally drying in air (sample: IGO).

For the preparation of IGO/b sample 50 mg GtO were initially dispersed in 15 ml distilled water (sonication for 1 h) and 60 mg K_2CO_3 were added under stirring (pH ~ 9.8). Then it was mixed with IFe solution and an extra amount of 100 mg K_2CO_3 was added. The whole was left under stirring for 24 h at room temperature. Subsequently it was washed, stirred and centrifuged 3–4 times and finally dried in air (sample: IGO/b).

2.4. Synthesis of reduced graphene oxide/Fe₃C hybrids (samples: r-IGO, r-IGO/b)

Thermal annealing of samples IGO, IGO/b under vacuum (9.3×10^{-3} mbar) at 800 °C for 2 h (Samples: r-IGO, r-IGO/b correspondingly).

2.5. Characterization

Siemens D500 X-ray diffractometer was used for the XRD measurements. The nitrogen adsorption isotherms at -196 °C were obtained with the Quantachrome Autosorb-1 MP volumetric apparatus. SEM characterization was performed using a JEOL JSM-7401F field-emission gun scanning electron microscope. TEM analysis was carried out in FEI CM20 transmission electron microscope operating at 200 kV. Raman spectra were obtained using an inVia Reflex (Renishaw) micro-Raman spectrometer using a laser excitation of 514.5 nm. The IR transmittance spectra of the samples (KBr pellets) were measured on EQUINOX 55/5, Bruker instrument. The prepared materials mixed with 10 wt% carbon black and 5 wt% PVDF, used as binder, were deposited as an electrode layer on aluminium foil of 2 cm^2 square area used as current collector. Such electrodes were then used to fabricate an electrochemical double layer capacitor (EDLC) cell with 1 M TEABF₄/PC

electrolyte. The electrochemical properties of the materials were then investigated using impedance spectroscopy in the range 10 mHz–1 MHz and cyclic voltammetry (CV) in a voltage range 0–3 V. Mössbauer spectroscopy was carried out using a constant acceleration spectrometer with a Co^{57} (Rh) source calibrated using a metallic α -iron foil at RT. All isomer shifts are quoted with respect to α -iron at RT. Powdered samples were measured in an Oxford Instruments cryostat at temperatures in the range 78–300 K. Magnetization measurements were carried out in a Quantum Design SQUID magnetometer.

3. Results and discussion

The characteristic groups of IFe, its incorporation in GtO matrix (samples: IGO, IGO/b) and the effect of thermal annealing on the composite material (samples: r-IGO, r-IGO/b) were investigated through FTIR spectroscopy (Fig. 1). The FTIR spectrum of pristine GtO demonstrates the presence of C=O at 1732 cm^{-1} (carboxyl stretching vibration), C=C at 1629 cm^{-1} (in aromatic ring assigned to skeletal vibrations of unoxidized graphite domains), C–OH at 1387 cm^{-1} (stretching) and C–O–C at 1070 cm^{-1} (in epoxide). The peaks at 2928 and 2855 cm^{-1} result from the $-CH_2$ stretching (alkyl groups present in GtO). The wide peak appearing at 3000 – 3500 cm^{-1} is related to the presence of hydroxyl groups. By taking into consideration that IFe was prepared by a modified method of Shova et al. [22] describing the synthesis of trinuclear iron acetates and the fact that in the present work instead of sodium acetate, potassium p-aminobenzoate salt was employed, there are indications of a trinuclear like structure. The FTIR spectra of carboxylate complexes are usually dominated by two strong bands between 1350 and 1650 cm^{-1} arising from the carbon–oxygen stretching vibrations. The frequency difference ($\Delta\nu$) between the symmetric ($\nu_{\text{sym}}(\text{CO}_2)$, typically between 1400 and 1450 cm^{-1}) and asymmetric ($\nu_{\text{asym}}(\text{CO}_2)$, typically between 1550 and 1650 cm^{-1}) C–O vibrations are correlated with the coordination mode of a carboxylate ligand [24]. The observed vibrational frequencies $\nu_{\text{asym}}(\text{CO}_2)$ (1603 and 1558 cm^{-1}) and $\nu_{\text{sym}}(\text{CO}_2)$ (~ 1414) for the carboxylate ligands support the presence of bridging coordinated carboxylates in IFe [25]. The band at 624 cm^{-1} can be assigned to the O–C–O out-of-plane deformation mode ($\pi(\text{COO})$) [24]. In IFe spectrum the peak at 1019 cm^{-1} indicates the presence of C–N bond (due to amino group) while that of N–H ($\sim 1580 \text{ cm}^{-1}$) cannot be seen probably because is overlapped by $\nu_{\text{asym}}(\text{CO}_2)$ which is very intense, indicative of successful incorporation of p-aminoacid in IFe compound [26]. The peak at $\sim 2880 \text{ cm}^{-1}$ in IFe was assigned to CH groups of p-aminobenzoic acid, while the peaks between 3200 – 3500 cm^{-1} are attributed to amino groups and moisture. In

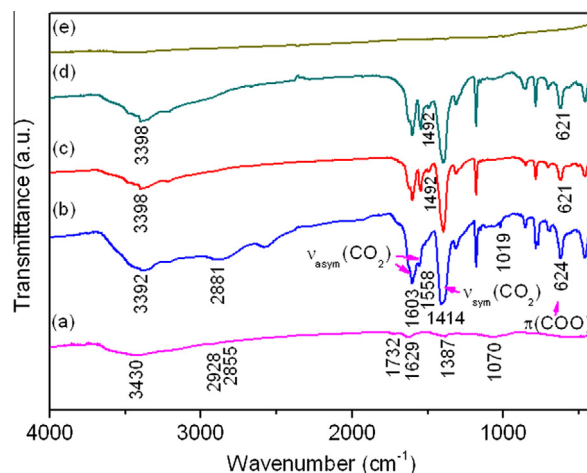


Fig. 1. FTIR spectra of (a) GtO, (b) IFe intercalant, (c) IGO, (d) IGO/b and (e) thermally annealed sample r-IGO, (FTIR spectrum of r-IGO/b is omitted due to similarity with r-IGO).

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