



# SYNTHESIS AND CHARACTERIZATION OF ELECTROCHEMICALLY EXFOLIATED GRAPHENE-MOLYBDOPHOSPHATE HYBRID MATERIALS FOR CHARGE STORAGE DEVICES



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## ABSTRACT

A novel electrochemically exfoliated graphene-molybdophosphoric acid nanohybride (EG-MoPA) was prepared via a simple method. Both scanning electron (SEM) and atomic force microscopy (AFM) results show that MoPA clusters are attached to the surfaces of graphene sheets. By changing the mass ratio of EG-MoPA, the morphology of nanohybride itself can be significantly modulated, from mostly flat graphene like structure at low amount of MoPA to very uneven, wavy surfaces when MoPA is present in higher concentration. The Raman and Fourier transform infra red (FTIR) spectra in conjunction with electrochemical results indicate that strong interaction exists between the components of nanohybride based on charge transfer and electrostatic interaction of graphene sheets and MoPA. The electrochemical performances are improved by synergetic effect of reversible redox properties of MoPA and the double layer capacitance of a high-surface area of the obtained nanohybrides. The higher current capability of EG was achieved by anchoring the small MoPA concentration on the graphene support. The strong bonding of EG with the MoPA prevents acid to dissolve in the electrolyte upon cycling, enabling the stable capacitance behaviour of the low-doped EG sample. The capacitance for the EG doped with the high amount of MoPA was found to be much larger than for EG. However, the obtained capacitance decreases at the beginning of cycling due to the dissolution of excessive amount of surface MoPA, weakly bonded to the graphene support.

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## 1. Introduction

Polyoxometalates (POMs) are a large class of nanosized metal-oxygen clusters known for more than one century. One of the most important and investigated classes of POMs are heteropoly acids and their salts (HPAs). There are different structures of HPAs, but the most interesting are HPAs with Keggin structure, where a tetrahedron, with heteroatom (P or Si) in the center, is surrounded by a cage of  $\text{MO}_6$  octahedron of transition metals (Mo, W) [1–3]. The existence of a number of protonic species in HPAs in

equilibrium at room temperature, such as:  $\text{OH}^-$ ,  $\text{H}^+$ ,  $\text{H}_5\text{O}_2^+$ ,  $\text{H}_3\text{O}^+$  and  $\text{H}_2\text{O}$  was shown by Fourier transform infrared (FTIR) and Raman spectroscopy, and confirmed by dielectric and incoherent inelastic neutron scattering (IINS) measurements as well [4–6]. The unique structure of HPAs enables extremely high proton mobility manifested as a high proton conductivity, comparable to the strongest inorganic acids [1,2].

The use of POMs is very wide due to their high structural, chemical and electronic versatility. They found application in catalysis (redox, acid-base properties), material science (magnetic, optical and electrical properties), medicine (antitumor, antiviral, antibacterial activities), environmental protection, energy storage, analytical chemistry etc. [1–3,7–11]. Thanks to their excellent electronic properties, they display high stability of their oxidation and reduction states and can participate in a multi-electron

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transfer without changing geometry. However, a main difficulty in the utilizing of POMs, as functional materials for many applications, comes from their low specific surface and high solubility in water and other oxygen containing solvents. These drawbacks can be overcome by supporting of POMs on insoluble mesoporous and microporous substrates such as  $\text{TiO}_2$ ,  $\text{SiO}_2$ , zeolites etc. Recently, various nanosized carbon materials such as activated carbon [12,13], carbon nanotubes (CN) [14–18], highly oriented pyrolytic graphite (HOPG) [19] and graphene [17,20–23] have been used as a support for POMs. The capability of 12-molybdophosphoric acid (MoPA) to anchor into the carbon matrix gives the opportunity to use these hybrid materials in various fields of application including supercapacitors.

In this study as a matrix we used an electrochemically exfoliated graphene. Graphene is a monolayer of  $\text{sp}^2$ -hybridized carbon atoms hexagonally arranged. As a two-dimensional (2D) building material, graphene represents a basic structure for carbon materials with different dimensionality such as buckyballs, carbon nanotubes and graphite. Its one atom thickness and large two dimensional planes provide it large specific surface area, which makes this material convenient support for various compounds.

In the last decade, graphene has attracted an enormous attention from scientific community due to unique electrical, mechanical, thermal and optical properties [24–26]. Up today, a great number of synthetic approaches have been developed [27,28]. All these approaches can be divided into bottom up and top down synthesis. Recently, electrochemical exfoliation of graphite rods has been developed as a new top down approach [29]. The exfoliation is based on the intercalation of ions electrolyte between graphene layers. This process can occur in both anodic and cathodic conditions. The major advantages of electrochemical exfoliation of graphite over other synthetic approaches are production of graphene in a large scale amount, easy processing and high-quality of obtained material [30]. Employing the electrochemical exfoliation, graphene samples were fabricated and used in our experiments. Beside exfoliation itself, this method can create functionalization of graphene with oxygen containing groups located on the basal plane or at the sheet edges. In our case, we used this as an advantage to make sure that components of a nanohybride can interact with each other.

Raman spectroscopy plays a vital role in the characterization of both carbon nanomaterials and HPAs due to its sensitivity to highly symmetric covalent bonds that possess little or no dipole moment, the orientation of the bonds and type of the atoms at either end of the bond. Therefore, micro Raman and infrared spectroscopy were combined with atomic force microscopy (AFM) and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) methods to investigate structure, morphology and composition of exfoliated graphene-MoPA samples. The charge storage behaviour of exfoliated graphene-MoPA samples was examined and analysed taking into account the applicability of these materials as electrodes in supercapacitors.

## 2. Experimental details

### 2.1. Materials and methods

MoPA was purchased from Merck, Darmstadt, Germany. In order to obtain stable hexahydrate form of acid, MoPA was heated up to  $60^\circ\text{C}$ .

Electrochemically exfoliated graphene was obtained in a two-electrode system using graphite rods of 99.999% purity (Ringsdorf Werke GmbH, Bonn, Germany) as the working electrodes. Before electrochemical exfoliation, electrodes were rinsed thoroughly with MiliQ water and ethanol (98%) and allowed to dry. Electrolyte solution was prepared by dissolving ammonium persulfate

$((\text{NH}_4)_2\text{S}_2\text{O}_8)$  in Milli-Q water (in concentration of 0.1 M). A direct current voltage of +12 V was applied until complete exfoliation of graphite occurred, or no further exfoliation could be observed. The exfoliated graphene (EG) was separated and cleaned from ammonium persulfate by filtration with MiliQ water. Then EG was dried at  $80^\circ\text{C}$  in air and the resulting powder was obtained.

Samples with different mass ratio of EG to MoPA were synthesized as follows. EG (387 mg) was mixed with 387 mg of MoPA in 2 mL of water-methanol mixture (1:1) with 1% v/v of ethylene glycol as dispersing agent. The pH of the mixture was about 1, which is important for MoPA stability [31]. Samples were stirred for 24 h at the room temperature, and then centrifuged. The precipitate was separated from supernatant and washed with 3 ml of water-methanol solution and dried at  $50^\circ\text{C}$  in the air. The obtained sample was named EG-MoPA (1:1). The samples labelled as EG-MoPA (2:1) and EG-MoPA (1:10) were prepared by applying the same procedure but with masses of EG and MoPA in ratios of 2:1 and 1:10, respectively. The samples labelled as MoPA (2:1) and EG-MoPA (1:10) are considered as high level MoPA doped. As mentioned, HPAs are soluble in water and oxygen containing solvents. Therefore, in order to investigate the influence of rinsing of MoPA from nanohybride, the precipitate obtained during EG-MoPA (1:1) sample preparation was washed with excess of deionized water, dried at  $50^\circ\text{C}$  in the air, named as EG-MoPA (1:1)<sub>r</sub> and considered as low level MoPA doping.

Raman spectra of synthesized nanohybrides were obtained by DXR Raman microscope (Thermo Scientific) using a diode pumped solid state high-brightness 532 nm laser as excitation source. The instrument was equipped with an Olympus optical microscope with infinity corrected confocal optics,  $50\ \mu\text{m}$  slit aperture, standard distance objective 50x and a CCD detector. The laser power at the sample surface was kept at 2 mW. The scattered light was analyzed by spectrograph with a grating with 1800 lines/mm. Acquisition time was 10 s with 10 scans repetitions. The laser spot diameter on the sample was  $1\ \mu\text{m}$ . Thermo Scientific OMNIC software was used for spectra collection and manipulation.

Raman mapping images were generated by measuring Raman spectra from areas of about  $80 \times 80\ \mu\text{m}^2$  in step sizes of  $10\ \mu\text{m}$  ( $9 \times 9$  probe spots). The sample was mounted on an automated XY translation stage controlled by a computer. The mapping was obtained by focusing the laser beam with 50x magnification. At each point, the Raman spectrum was recorded with exposed time of 5 s, number of exposures 6 and power of 5 mW at sample. The size of the laser spot on the sample was  $0.7\ \mu\text{m}$ .

FT-IR spectra of the powdered samples, dispersed in potassium bromide and compressed into pellets, were recorded in the range of  $1600\text{--}400\ \text{cm}^{-1}$  at 64 scans per spectrum at  $2\ \text{cm}^{-1}$  resolution using an Avatar 370 FT-IR Spectrometer (Thermo Scientific).

X-ray diffraction was measured on the Rigaku Smart Lab diffractometer at room temperature. Diffraction data were recorded in a  $2\theta$  range of  $5$  to  $60^\circ$  with the step size of  $0.05^\circ$  and counting time of 0.7 per min in 0.02 steps.

The morphology of the samples was characterized by scanning electron microscopy (SEM JEOL JSM-6390LV) in vacuum at room temperature with 15 kV acceleration voltage. Elementary analysis of samples was obtained with energy dispersive spectroscopy (EDS, Oxford Aztec X-max). The samples dispersions were drop-casted ( $20\ \mu\text{L}$ ) on Si wafers. Scanned surface area was  $1 \times 1\ \text{mm}^2$ .

Surface morphology of samples was also analyzed with atomic force microscopy (Quesant, Ambios Technology, USA) operating in tapping mode in air, at room temperature. All images were obtained at 1 Hz, with  $512 \times 512$  pixels image definition over different square areas. We used AFM Q-WM300 probe, rotated, monolithic silicon probe for non-contact high frequency applications. Water dispersions of EG and EG-MoPA samples were deposited on mica substrate by spin coating and imaged after

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