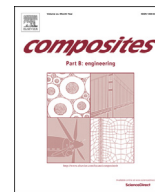




Contents lists available at ScienceDirect

## Composites Part B

journal homepage: [www.elsevier.com/locate/compositesb](http://www.elsevier.com/locate/compositesb)

## Polyoxometalate-enabled photoreduction of graphene oxide to bioinspired nacre-like composite films for supercapacitor electrodes

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## ARTICLE INFO

## Article history:

Received 23 November 2016

Received in revised form

9 February 2017

Accepted 17 February 2017

Available online xxx

## Keywords:

Graphene

Polyoxometalates

Bioinspired electrodes

Supercapacitors

## ABSTRACT

A bioinspired nacre-like composite film was successfully fabricated by a polyoxometalate of  $H_3PW_{12}O_{40}$  (HPW) assisted reduction of graphene oxide to graphene under an ultraviolet irradiation at room temperature. It was found that nanosized HPW clusters were uniformly attached onto the graphene surface and hence sandwiched between graphene sheets within the composite film. The self-supported composite film electrode shows high specific capacitance of 337.5 F/g at a scan rate of 5 mV/s and 156.9 F/g at a current density of 0.5 A/g, respectively. The specific capacitance remains 98.5% after running 1000 cyclic voltammetry loops at 100 mV/s and retains 98.3% after 1000 galvanostatic charge-discharge cycles at 5 A/g, respectively. Furthermore, the retention of initial specific capacitance was calculated to be 86.4% with increasing the scan rate from 5 to 100 mV/s and up to 94% with increasing the current density to 10 A/g from 0.5 A/g, showing high rate capability. Such free-standing composite film electrodes exhibit excellent electrochemical performance due to the unique nacre-like layered architecture and synergistic effects between electric double-layer graphene and pseudo-capacitive HPW clusters.

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## 1. Introduction

Graphene has been considered as an extraordinary candidate for electrode materials due to its large specific surface area, great electronic conductivity, high theoretical specific capacitance (550 F/g) and capacity (744 mAh/g) as well as excellent electrochemical stability [1,2]. However, the bulk performance of graphene-based materials is strongly dependent on the arranged way of individual sheets [3]. As with other nanomaterials, the aggregation or restacking of graphene inevitably occurs due to the inter-sheet van der Waals interactions. Many outstanding intrinsic properties for individual sheets are significantly compromised and even

unavailable. For instance, the supercapacitor based on the vacuum-filtrated graphene film electrode only shows a moderate capacitance (140 F/g at 0.1 A/g) due to the inhibition of ion diffusion because of substantial restacking of graphene sheets [4]. To mitigate the above setbacks, many alternative methods have been achieved by hybridizing graphene with metals [5], metal oxides [6,7], conducting polymers [8–10], and carbonaceous materials [11] through the *in-situ* growth and *ex-situ* recombination ways [12].

Till now, the most widely used methodology is the post-reduction of graphene oxide (GO) in the presence of pre-synthesized materials or their precursors [2]. For instance, Du et al. [13] fabricated binary polyaniline (PANI)/graphene composites by *in-situ* oxidative polymerization of aniline in the presence of phenylenediamine-grafted reduced GO (RGO) sheets. Recently, Ma et al. [1] reported ternary PANI/TiO<sub>2</sub>/graphene composites produced by *in-situ* polymerization of aniline with TiO<sub>2</sub> and subsequent mixing with GO sheets followed by chemical reduction of GO and re-doping of PANI. We also developed poly(ionic liquid)/graphene composites through solvothermal reduction of GO in the

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presence of imidazolium-based poly(ionic liquid)s [14]. More recently, Gryglewicz et al. [15] prepared polypyrrole/Fe<sub>2</sub>O<sub>3</sub>/graphene nanocomposites by *in-situ* oxidative polymerization of pyrrole in the presence of hydrothermally-synthesized Fe<sub>2</sub>O<sub>3</sub>/RGO hybrids. In these graphene-based nanocomposites, the presence of additional components is capable of preventing the agglomeration and stacking of graphene sheets and vice versa, thereby offering a large accessible surface/interface for electrolyte ions and high electrochemical utilization of the composite electrodes. RGO sheets bridge a conductive pathway for rapid charge transport and also preserve the structural integrity of the overall electrode during the cycling process. Such synergistic effects thus endow the composite electrodes with improved specific capacitance, rate capability, and cycling stability. However, the fabrication methods of graphene-based composites are generally complicated and unsuitable for practical purposes. The electrochemical performance has also been limited to some certain extent by the presence of less and non-capacitive components such as poly(ionic liquid)s [14] and TiO<sub>2</sub> [1].

In this work, we report a facile ultraviolet (UV) irradiation method to reduce GO with the assistance of a Keggin-type polyoxometalate (phosphotungstic acid, H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, HPW), yielding a composite consisting of graphene sheets from reduced GO (RGO) and HPW. HPW serves as an effective photocatalyst to facilitate the reduction of GO to graphene under UV irradiation [16–18]. Compared to the conventional chemical reduction and thermal annealing, the photoreduction of GO is environmentally friendly and easy to control via the irradiation [19,20]. Of note, polyoxometalates such as HPW are generally composed of metal ions and oxo ligands to form clusters with dimensions of approximately 1–6 nm [21]. These nanosized HPW clusters were uniformly absorbed on the surface of RGO sheets. This enlarges the interlayer spacing and prevents the restacking of RGO sheets, thus providing abundant interior spaces for charge transport and storage. Polyoxometalates also enable reversible electrochemical reactions and provide the additional pseudocapacitance to the composite electrode [22].

Furthermore, HPW-assisted photoreduction of GO nanosheets yielded bioinspired nacre-like composite films with a layer-by-layer self-assembled structure. The bioinspired nanostructured electrodes have been reported to possess excellent electrochemical performance [23,24]. Herein the as-fabricated bioinspired nacre-like HPW/RGO composite electrodes exhibit the specific capacitance of 337.5 F/g at 5 mV/s and the retention of initial capacitance is up to 86.4% at 100 mV/s. The specific capacitance remains more than 98% after 1000 cycles. Such large specific capacitance, high rate capability and excellent cycling stability for graphene-based nacre-like electrodes thus allow for the development of high-performance supercapacitors for practical applications.

## 2. Experimental

### 2.1. Materials

GO was synthesized by the modified Hummers method [25,26]. Ethanol, sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), and phosphotungstic acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>·xH<sub>2</sub>O) were purchased from Sinopharm Chemical Reagent Ltd. Co. All chemicals were used without further purification. The ultraviolet light (SDJG8W, λ = 365 nm) was purchased from Zhongshan XiaoLan Town Jia Zhan Electric Appliance Factory.

### 2.2. Photoreduction of GO

First, 10 mL of an as-prepared 10.0 mg/mL GO aqueous solution and 500 mg of HPW were mixed in 80 mL of ethanol with the

assistance of sonication and stirring to form a homogeneous suspension. The dispersion was poured into a glass dish followed by placing under the UV light. After irradiation for about 1.5 h, the HPW/RGO composite films were gradually formed on the solution surface and then isolated for the use of supercapacitor electrode.

### 2.3. Characterization

Transmission electron microscopy (TEM) measurements were conducted on a Tecnai G20 electron microscope at 200 kV. Scanning electron microscopy (SEM) measurements were carried out on a JSM7100F system at 15.0 kV. Fourier transform infrared (FT-IR) spectra were performed over a wavelength range of 500–4000 cm<sup>-1</sup> using a PE-100 system with KBr pellets as the background. Raman spectra were obtained by using a Renishaw 2000 system over 100–3200 cm<sup>-1</sup> with an excitation wavelength of 514 nm. X-ray diffraction (XRD) was conducted using a D/MAX-IIIIC system with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) spectra were measured on an AXIS-ULTRA DLD-600 W XPS system.

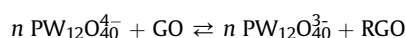
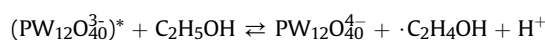
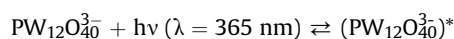
### 2.4. Electrochemical measurements

Electrochemical characteristics were evaluated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) using a CHI760E electrochemical workstation (Shanghai CH Instruments Inc.). All measurements were carried out using a conventional three-electrode system at room temperature. The counter and reference electrodes were a platinum plate and a saturated calomel electrode (SCE), respectively. The working electrode was a glassy carbon electrode (3 mm in diameter dropped with 5 μL of 1 mg/mL samples). A 5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution was used as the electrolyte. CV measurements were carried out with voltage sweep rates from 5 to 100 mV/s in a voltage range of 0–0.8 V. GCD tests were carried out at current densities ranging from 0.5 to 10 A/g. EIS tests were conducted from 10 mHz to 100 kHz with an amplitude of 5 mV referring to the open-circuit potential. The cycling measurements were performed by GCD under a current density of 5 A/g and by CV at a scan rate of 100 mV/s.

## 3. Results and discussion

### 3.1. Fabrication of bioinspired nacre-like composite films

Fig. 1 shows the photograph of the HPW/RGO composite films recorded with a digital camera. Under UV irradiation, the reduction reaction took place that converted GO to RGO in the presence of photocatalytic active HPW clusters [16,27]. With increasing the UV irradiation time, the light yellow homogeneous solution of GO (Fig. 1a) gradually turned isabelline with tiny flakes (Fig. 1b) to many brown sheets (Fig. 1c) until big black films were generated on the surface of liquid phase (Fig. 1d). The formation of films comes from the self-assembly of RGO sheets with increasing the reduction degree of GO and hence the hydrophobicity under UV irradiation. The possible photoreduction mechanism is proposed by the following equations [17,28–30]:



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