Electrochemistry Communications 83 (2017) 36–40

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Effect of thermal treatment on the charge storage properties of graphene oxide/12-tungstophosphoric acid nanocomposite

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ARTICLE INFO

Keywords:
Graphene oxide
12-tungstophosphoric acid
Nanocomposite
Supercapacitor

ABSTRACT

The influence of thermal treatment in an inert atmosphere on the charge storage properties of graphene oxide (GO)/12-tungstophosphoric acid (WPA) nanocomposite was examined. The transmission electron microscopy analysis revealed high dispersion of WPA on GO matrix, while the surface analysis showed thermal activation of structural changes of WPA and desorption of oxygen functional groups from GO and GO/WPA nanocomposite. Initial GO/WPA nanocomposite had approximately two times higher capacitance compared to initial GO. The thermal treatment of initial GO and GO/WPA to 500 °C induced twofold increase of capacitance of GO and 40% increase of GO/WPA, accompanied with significant increase of operating voltage compared to GO (for 300 mV). Above 500 °C, a decrease of capacitance of both GO and GO/WPA was observed. The results suggest that understanding of structural changes of components and their interaction is crucial for improvement of electrochemical properties of considered composite.

1. Introduction

The composites of nanocarbons (NCs) and polyoxometalates (POMs) have shown great prospect for electrochemical charge storage [1–4]. However, to exert composite's full potential the POMs should be firmly anchored to a carbon matrix [5], with high dispersion and sub-monolayer coverage [5–8].

As the nature of POMs' bonding to carbon matrix is still under debate, both theoretical [9,10] and experimental [6,11], the aim of the present work is to contribute to the understanding of this interaction. The common feature of approaches used for preparation of POM/NC composites was structural integrity i.e. without significant structural modification of either NCs or POMs [5–7,12,13]. In this work, we promote the thermal treatment as a simple method for simultaneous integration and surface/structural modification of both graphene oxide (GO) and 12-tungstophosphoric acid (WPA).

2. Materials and methods

The GO (TIMREX PP44 graphite precursor, Imerys Graphite & Carbon Switzerland Ltd.) and WPA were synthesized as described previously [14,15]. The nanocomposite (GO:WPA = 5:1, mass ratio) has been prepared by 2 h ultrasonication of components in ultrapure water, followed by overnight drying at 100 °C in air. The obtained solid was powdered, sieved through 150 μm mesh and annealed up to 800 °C in argon.

The nanocomposite was characterized by transmission electron microscopy (TEM, JEM-2100, JEOL), thermogravimetric analysis (TG/DTA, Setsys, SETARAM Instrumentation), Fourier transform infrared spectroscopy (FTIR, Avatar System 370, Thermo Nicolet), temperature-programmed desorption (TPD, Extorr XT 300). The cyclic voltammetry (CV) was realized in 1 M H_2SO_4 in a three-electrode configuration by using Gamry PCI4/300 Potentiostat/Galvanostat (Pt as a counter electrode, saturated calomel electrode (SCE) as the reference one). The preparation of working electrodes and calculation of capacitance was performed as described in Ref. [16].

3. Results and discussion

The TEM analysis of the as-prepared nanocomposite shows that WPA particles, mostly 2 nm in size, are agglomerated on the edges of GO sheets, which highlights the oxygen complexes as probable anchoring sites to carbon matrix (Fig. 1a).

The stable CVs of GO and GO/WPA samples, annealed in argon, display characteristic redox peaks (Fig. 1b,c). The overlapping of CVs of

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http://dx.doi.org/10.1016/j.elecom.2017.08.017
Received 19 July 2017; Received in revised form 15 August 2017; Accepted 21 August 2017
Available online 24 August 2017

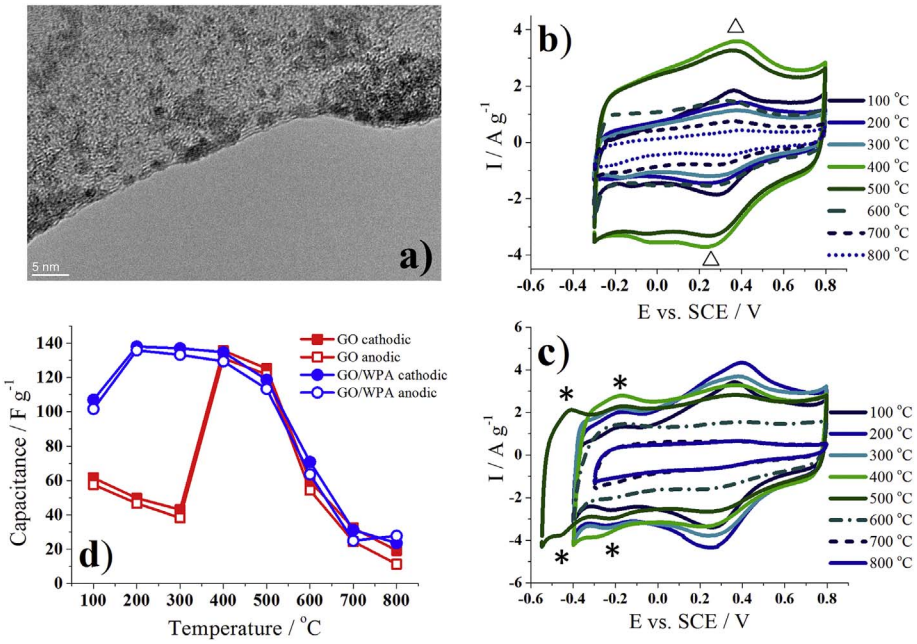

Fig. 1. a) The TEM micrograph of the initial GO/WPA nanocomposite prior to thermal treatment. The stable CVs measured in 1 M H_2SO_4 at 20 mV s^{-1} of b) GO and c) GO/WPA reduced in argon up to 800 °C and d) corresponding capacitance values (after 50 cycles). The triangles in b) and asterisks in c) denote peaks of quinone/hydroquinone and Keggin anion redox reactions, respectively.

GO/WPA composite measured during 50 repetitive cycles confirms anchoring of WPA to GO sheets.

The Fig. 1d shows that the capacitance of initial GO/WPA is almost two times higher than the capacitance of initial GO. Also, the treatment up to 300 °C increases the capacitance of nanocomposite for almost three times compared to GO; above 300 °C the capacitance of GO and GO/WPA is similar and follows the same trend, with notable decrease above 500 °C. The capacitance obtained at various scan rates show that initial GO and GO/WPA samples exert stable capacitance retention (Fig. 2c), while in the case of treatment at 500 °C, the GO/WPA nanocomposite exerted better capacitance retention (Fig. 2d).

Beside the temperature evolution of the capacitance, an interesting change of the onset potential vs. SCE for the water reduction was observed (Fig. 1b,c). Two characteristic cases of samples treated at 100 and 500 °C are shown in Fig. 2a,b. In the case of initial GO and GO/WPA the onset potential was observed at ~ − 0.3 V (Fig. 2a). However, the nanocomposite treated at 500 °C has shown substantial increase of the overpotential of water reduction (for 300 mV) compared to GO treated at the same temperature (Fig. 2b). In fact, the CVs of GO show improved water reduction kinetics as the temperature increases (Fig. 1b). In the case of nanocomposite, the active sites of GO, formed by desorption of oxygen functional groups, interact with the Keggin's anion (KA), thus preventing the reduction of water at the corresponding potential.

To explain the evolution of capacitance and the change of the operating voltage with temperature, a surface and structural analysis of samples was performed. The FTIR spectra of GO, WPA and GO/WPA, thermally treated in argon up to 800 °C, are shown in Fig. 3. The vibration bands of GO at 1720, 1586, 1394, 1235, 1063 and 800 cm^{-1} are broadened, shifted and/or absent/less prominent as annealing

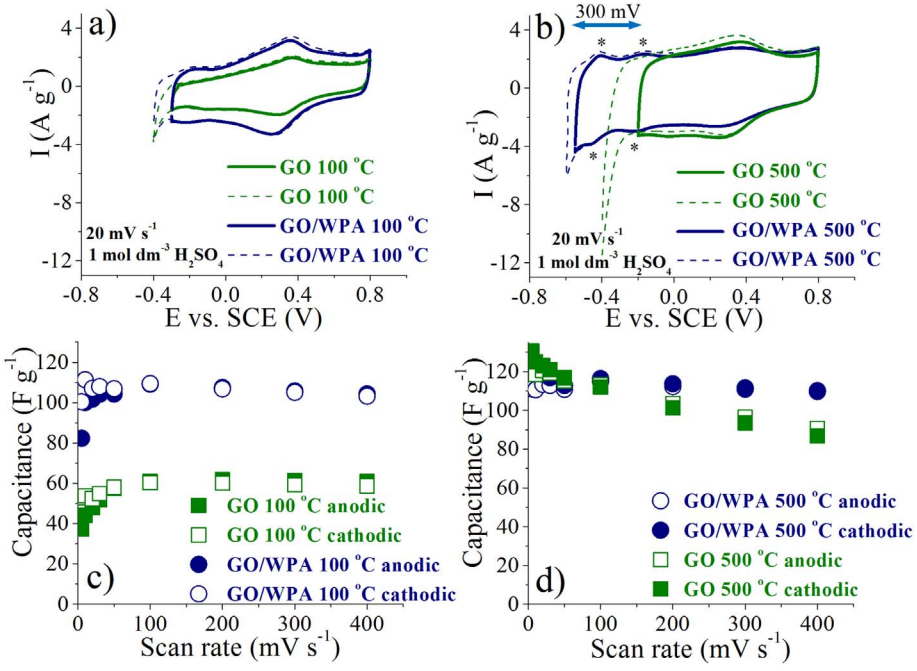

Fig. 2. Stable CVs of GO and GO/WPA treated in argon at a) 100 °C and b) 500 °C (after 50 cycles). The specific capacitance vs. the scan rate for GO and GO/WPA treated in argon at c) 100 °C and d) 500 °C. The dashed line CVs show the onset potential of water reduction. The asterisk marks WPA redox peaks.