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# Three-Dimensional Macroporous Graphitic Carbon for Supercapacitor Application

## Abstract

Two-dimensional (2D) graphene materials have attracted great interest as promising electrode materials in supercapacitors due to their high electrical conductivity derived from sp<sup>2</sup>-carbon network. These 2D layered materials, however, tend to stack with each other, which largely decreases the surface area. Here we report the design of highly graphitic macroporous carbon with large surface area suitable for supercapacitor applications. When benchmarked with other carbon materials, such as amorphous macroporous carbon, activated carbon, graphite or exfoliated graphene oxides, our graphitic macroporous carbon show superior capacitance.

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# Three-Dimensional Macroporous Graphitic Carbon for Supercapacitor Application

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## **Abstract**

Two-dimensional (2D) graphene materials have attracted great interest as promising electrode materials in supercapacitors due to their high electrical conductivity derived from  $sp^2$ -carbon network. These 2D layered materials, however, tend to stack with each other, which largely decreases the surface area. Here we report the design of highly graphitic macroporous carbon with large surface area suitable for supercapacitor applications. When benchmarked with other carbon materials, such as amorphous macroporous carbon, activated carbon, graphite or exfoliated graphene oxides, our graphitic macroporous carbon show superior capacitance.

**Keywords:** Macroporous carbon; Graphitic carbon; Graphene; Electrochemical energy storage; Supercapacitors

## Introduction

Lithium-ion batteries have been widely used for consumer electronics.<sup>1</sup> However, their tendency to volume expansion poses safety concerns and limit their implementation for commercial use. On the other hand, supercapacitors have risen as safe and maintenance-free devices, with high power density and long cycle life.<sup>2-3</sup> The major drawback with the present generation of supercapacitors is that they can only store a limited amount of charges compare to battery materials. Thus, research efforts have focused on developing highly conductive carbon materials with optimized pore sizes to improve their charge capacity and provide a fast charge-discharge rate by utilizing a suitably designed 3D architecture.<sup>4-5</sup>

Research on 2D graphene has rapidly boomed and yielded high-quality graphene synthesized through simple and low-cost routes.<sup>6</sup> Furthermore, the properties of graphene can be tuned by controlling its multiaxial dimensions, leading to suitable industrial applications.<sup>7</sup> Many reports focus on coating graphene with other carbons, metal oxides, or polymers, to synergetically enhance charge storage.<sup>8-10</sup> Fabricating such 3D carbon material with high electronic conductivity through a simple approach, however, remains challenging and very few efforts have led to directly synthesize multi-dimensional graphene materials.

Nanostructured carbon materials are of great interest because of properties such as high conductivity, high surface area, thermal stability, resistance to corrosion, pore-size tunability, *etc.*<sup>11-12</sup> Several structures, such as 1D (carbon nanotubes),<sup>13</sup> 2D (graphene),<sup>14</sup> 3D (activated carbons,<sup>15</sup> MOF-derived carbons<sup>16</sup>), have been reported for energy storage applications. In order to achieve high supercapacitor performance, 3D porous materials represent an attractive alternative as they do not tend to stack, unlike their 1D and 2D counterparts. Under optimal conditions, they are also prone to form  $sp^2$ -bonded carbons, thus promoting high electrical conductivity. Considering the aforementioned aspects, recently we proposed the simple synthesis of 3D graphitic macroporous carbon (G-MC).<sup>17</sup> In the present paper, we showcase the superior performance of G-MC as electrode in supercapacitor applications compared to other carbon materials such as amorphous macroporous carbon, activated carbon, graphite or exfoliated graphene oxides.

## Results and Discussion

The main synthetic steps involved in the fabrication of G-MC are illustrated in **Scheme 1**. Monodisperse silica nanospheres, with an average size of 250 nm, were prepared *via* the Stöber method (**Figure S1**) and assembled to form silica opal microballs (SOMs) in an emulsion system. Typically, an aqueous suspension of silica nanoparticles (20 wt.%, 0.4 mL) was added to 20 mL of silicone oil and stirred at room temperature for 10 min to form the water-in-oil emulsion. The emulsion was heated at 90 °C for 8 h, causing the water to diffuse/evaporate and driving the colloids to assemble into spherical SOMs. The silicon oil was removed by washing the reaction solution with hexane and separating through centrifugation. The washing procedure was repeated several times before collecting the final SOM product. The SOMs were calcined at 900 °C for 6 h in air to form the hard-template (**Figure 1a-b**). Low-molecular-weight phenolic resol (L-PR) was used as the carbon source, filling the voids between the SOMs with an iron source by repeated vacuum-assisted infiltration. The L-PR structure was cross-linked by heating the L-PR/SOMs composite at 120 °C, and then calcined at 600 °C for 8 h under argon atmosphere. For graphitization, the sample was then added to a ferric nitrate solution heated at 50 °C for 20 min under vacuum, prior to calcination at 800 °C for 3 h under argon atmosphere. Finally, the SOM template was removed by etching with hydrofluoric acid (4.8 wt%), yielding a graphitized macroporous carbon (*i.e.*, G-MC). Poorly graphitized carbon (amorphous macroporous carbon, A-MC) is obtained when the process is carried out without iron precursor. The morphology and pore size of A-MC and G-MC were observed by SEM (**Figure 1c-d**). The uniform spherical morphology can be clearly observed for both samples. The hexagonal arrangement of uniformly sized macropores (*ca.* 250 nm) are an accurate negative replica of the parent SOM.

The wide-angle X-ray diffraction (XRD) patterns of the A-MC and G-MC are shown in **Figure 2a**. The sharp peak observed at 26° is consistent with previously reported (002) diffractions pattern from graphite-type carbon layers. The absence of such peak in the A-MC sample is an evidence of a negligible graphitic degree. **Figure 2b** shows the representative Raman spectra of the A-MC and G-MC. For both samples, the characteristic peaks of carbon-based material could be measured at ~1350 cm<sup>-1</sup> (D band) and ~1580 cm<sup>-1</sup> (G band).<sup>19</sup> Since the D band is correlated to disordered network and the G band to *sp*<sup>2</sup>-carbon lattice, the higher  $I_G/I_D$  characteristic ratio observed for the G-MC sample confirms a stronger graphitic

degree. Besides supporting the formation of macropores by TEM analysis (**Figure 3**), high resolution TEM image and electron diffraction patterns (**Figure S2**) suggests the presence some graphitic layers.

N<sub>2</sub> adsorption-desorption isotherms were measured to investigate the surface area of our samples (**Figure S3a**). Here, four different samples were tested: Vulcan XC72 carbon (activated carbon), commercial graphite, A-MC, and G-MC. The Brunauer-Emmett-Teller (BET) surface area of each carbon materials was determined to be 225, 8.25, 967 and 504 m<sup>2</sup>·g<sup>-1</sup>, respectively. The G-MC, with a smaller surface area, shows less N<sub>2</sub> gas uptake in the low-pressure region ( $P/P_0 < 0.1$ ) than the A-MC, indicating that the amount of micropores (smaller than 2 nm) decreased during graphitization of the carbon framework. This can be expected since the formation of micropores necessitate abundant *sp*<sup>3</sup>-bonded carbons, which are mostly replaced by *sp*<sup>2</sup>-bonds during the graphitization process.<sup>20-21</sup> The presence of monodisperse mesopores of around 4 nm in diameter, connecting neighboring macropores, can be confirmed in both samples from their respective pore size distribution curves (**Figure S3b**).

As an alternative to batteries, supercapacitors (SCs) are devices with longer cycle life (> 500,000 times), high power density (500~10,000 W·kg<sup>-1</sup>) and can be operated safely as energy storage devices. The prepared materials were tested for their potential as electrode in SCs. We carried out standard three-electrode cyclic voltammograms (CV) measurements with Ag/AgCl as reference electrode, platinum as counter electrode, and Vulcan XC72 carbon, commercial graphite, A-MC, or G-MC as working electrode. The latter was prepared by dispersing the active electrode material (80%) with poly(vinylidene difluoride) (20%) in N-methyl 2-pyrrolidinone solvent. The slurry was then coated on graphite substrates and dried at 60 °C for 12 h. The electrode loading density was fixed at 0.5 mg·cm<sup>-1</sup>. The CV were collected using an electrochemical workstation (CHI 660E, CH Instruments, USA). The gravimetric capacitance C<sub>g</sub> (F g<sup>-1</sup>) was measured according to our previous report using the following equation:

$$C_g = \frac{1}{ms (V_f - V_i)} \int_{V_i}^{V_f} I(V) dV$$

where *s* is the voltage sweep rate, *V* is the potential window (0.0 - 0.8 V), the integration  $I(V)dV$  corresponds to the discharging part of the cyclic voltammograms, and *m* is the mass of the active material (in g). Because

of its mesoporous structure and graphitic nature, the integration window for the G-MC could be extended up to 0.0 - 1.0 V (vs. Ag/AgCl), while it is limited to 0.0 - 0.8 V (vs. Ag/AgCl) for the other samples.

The CV measurements are shown in **Figure 4**. The capacitance at 5 mV·s<sup>-1</sup> are 23.7, 58.64, 175 and 229 F·g<sup>-1</sup> for the Vulcan XC72 carbon, graphite, A-MC, and G-MC, respectively. As expected, the G-MC shows a higher capacitance than the A-MC, because of the high conductivity derived from graphitic carbon<sup>20-21</sup> which leads to a better utilization of the porous structure. The oxidation/reduction peaks derived from the redox reactions on the CV measured on the commercial graphite are due to the presence of inherent impurities (**Figure 4c**).<sup>22</sup> The capacitance values for the G-MC 5, 20, 40, 60, 80, 100, 150, and 200 mV·s<sup>-1</sup> are measured to be 229, 185, 165, 151, 140, 131, 116 and 105 F·g<sup>-1</sup>, respectively. The dependence of the capacitance on the scan rates is also shown in **Figure 4**. The G-MC retains high capacitance value at high scan rates, even higher than that of exfoliated graphene oxide (GO) nanosheets<sup>10</sup> (**Figures S4 and S5**).



## **Conclusion**

In this study, we have demonstrated a simple synthetic approach for the fabrication of 3D macroporous graphitic carbon. This material showcases several advantages, such as high surface area and high graphitic content. As shown in this work, the capacitance resulting from the 3D graphitic carbon structure has the potential to achieve high energy density. Such 3D materials are promising for microelectronic applications by means of surface functionalization or in form of composites with metal oxide and polymers to achieve high capacitance and stability. Apart from charge storage, such type of graphitic carbon can also be implemented for drug delivery, fuel cell and solar cell applications.

**Materials Characterization.** The structure of carbon sample was examined with X-ray diffraction analysis (Cu K $\alpha$  radiation: 40 kV, 40 mA). The Raman analysis (Horiba-Jobin-Yvon) was carried out to highlight the graphitic to disordered carbon ratio in the sample. The scanning electron microscopy (SEM, Nova NanoSEM 230) and transmission electron microscopy (TEM, JEOL JEM-1200EX II, operated at 100 kV) were carried out to determine the size, shape and surface structure of the carbon particles. The surface area measurements (Micromeritics ASAP2010) were carried out using nitrogen adsorption-desorption isotherms. The surface areas and the pore size distribution curves were obtained by the BET and the BJH methods using the adsorption isotherms, respectively.

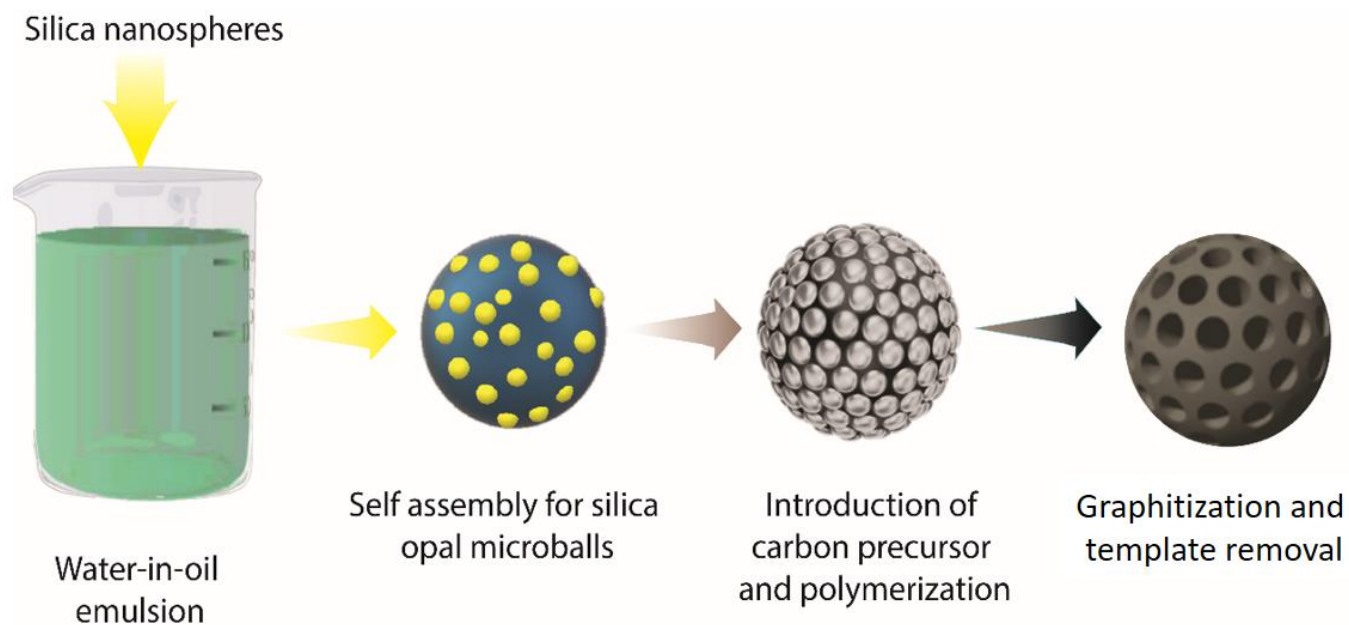
## **Acknowledgement**

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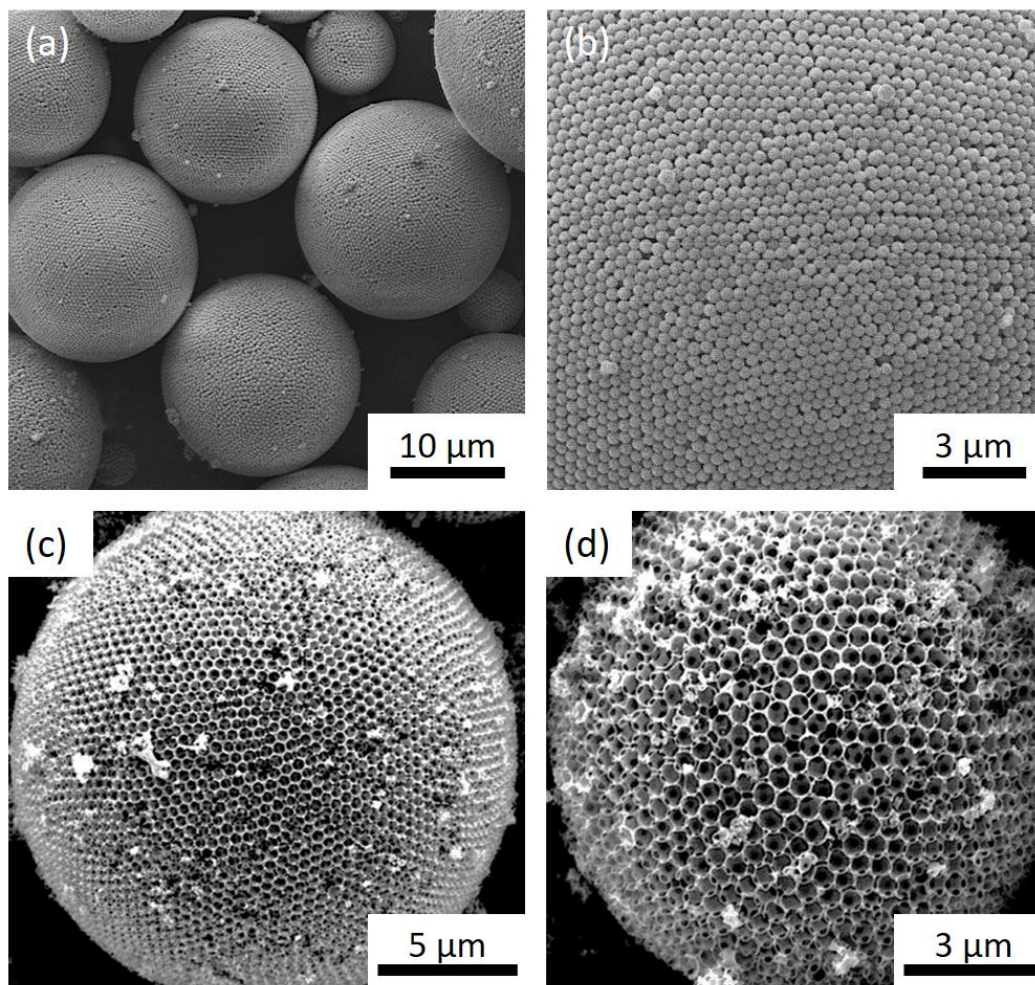
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## Scheme 1



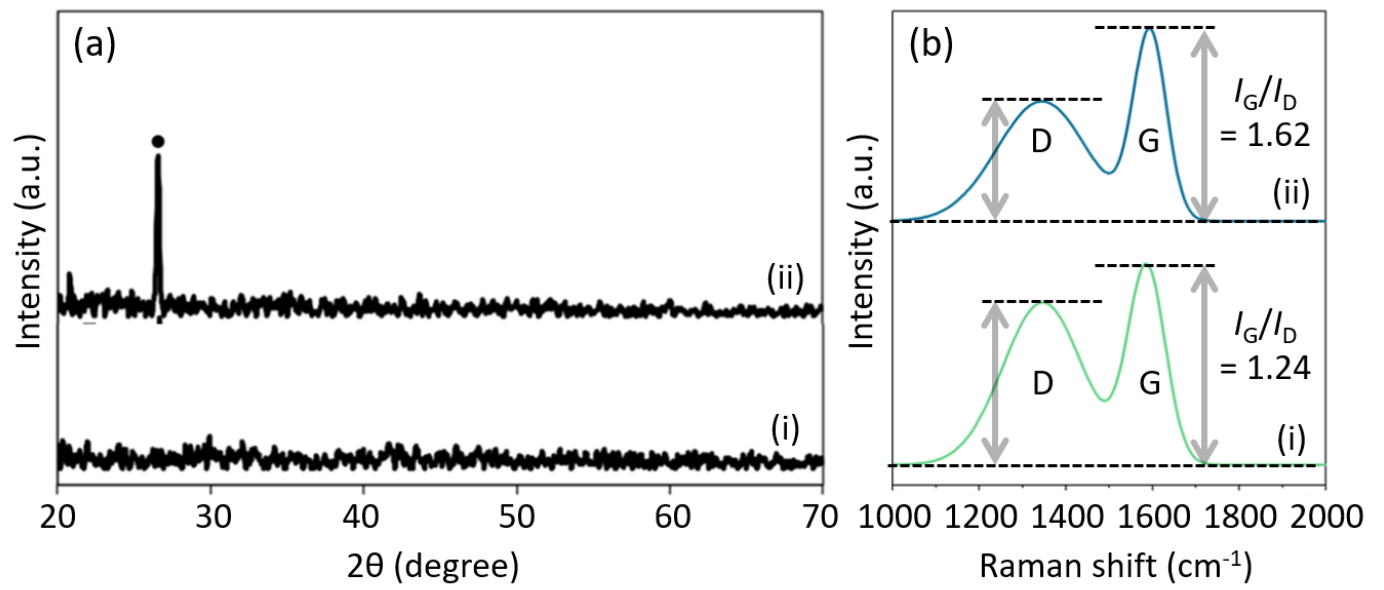
**Scheme 1** Schematic illustration of the synthesis of 3D graphitic macroporous carbon (G-MC) starting with silica nanospheres as template. The self-assembly of silica nanoparticles leads for the formation of silica opal microballs (SOMs). The introduction of carbon precursor (resol) and iron precursor leads to the formation of G-MC.

**Figure 1**



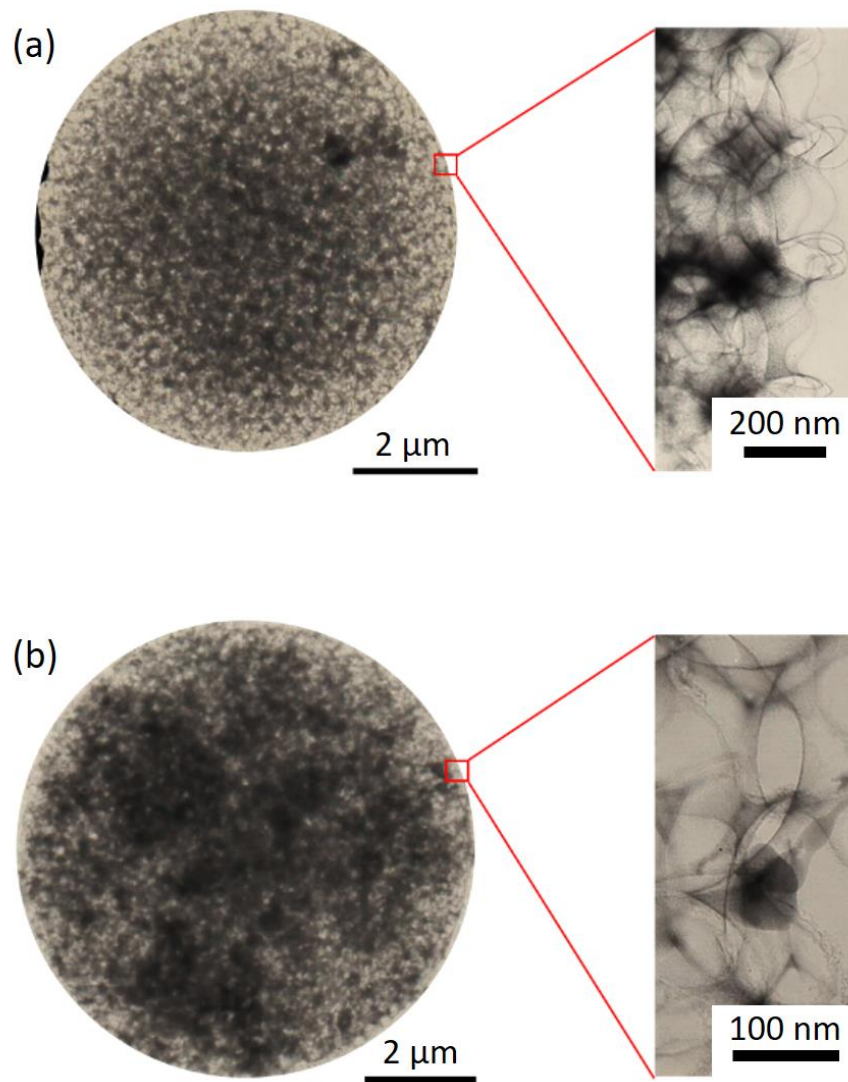
**Figure 1** SEM images of (a, b) the SOMs, (c) A-MC, and (d) G-MC samples.

**Figure 2**



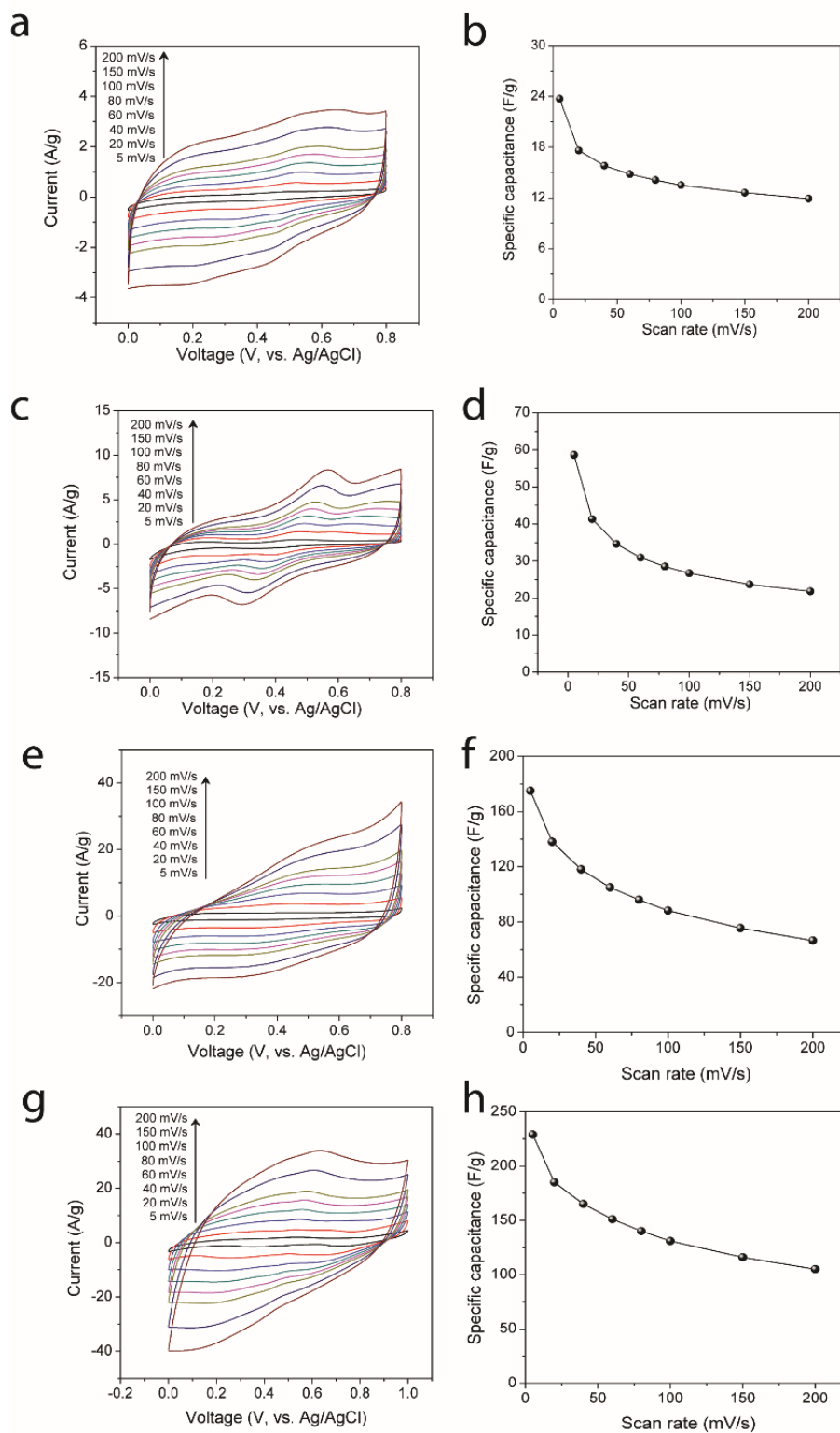
**Figure 2** (a) Wide-angle XRD patterns and (b) Raman spectra of the (i) A-MC and (ii) G-MC samples.

**Figure 3**



**Figure 3** TEM images (left side) and high resolution TEM images (right side) of the (a) A-MC and (b) G-MC samples.

**Figure 4**



**Figure 4.** Cyclic voltammograms (a, c, e, g) and dependence of the capacitance upon scan rate (b, d, f, h) of the (a, b) activated carbon, (c, d) commercial graphite, (e, f) A-MC and (g, h) G-MC.