



# Hydrophilic modification of ordered mesoporous carbons for supercapacitor via electrochemically induced surface-initiated atom-transfer radical polymerization

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## ABSTRACT

Ordered mesoporous carbons (OMCs) grafted with poly(N-vinylpyrrolidone) (PVP) was prepared through electrochemically induced surface-initiated atom-transfer radical polymerization (SI-eATRP). The introduction of hydrophilic polymer PVP brushes on the surface of OMCs results in the improvement of wettability and a remarkable increase in the specific capacitance. The results of electrochemical performance of OMCs-PVP show good specific capacitance of  $253 \text{ F g}^{-1}$ , excellent rate performance and good cycling stability with capacitance retention of 89.6% over 5000 cycles. The PVP modification of OMCs via the SI-eATRP method demonstrates an effective way to improve the wettability and electrochemical properties.

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## 1. Introduction

Electric double-layer capacitors (EDLC) have attracted much attention as an electrical energy storage system [1]. The high capacitance of EDLC is produced by the quick formation of an electrical double layer at the electrode/electrolyte interface, which accumulates electrical charges on the electrode surface [2,3]. With this regard, ordered mesoporous carbons (OMCs) can deliver high specific capacitance for EDLC due to its well-ordered pore structure, narrow pore size distributions, high specific pore volumes and high specific surface areas [4,5]. Despite its attractive features, the low electrolyte accessibility and instability of OMCs leads to loss of electrochemical performance; therefore, OMCs cannot meet the requirements for enhancing both energy and power densities of EDLC.

In recent years, surface modification has become a widely used method for modulating physicochemical properties to improve the suitability of carbon materials in various applications. Several modification methods have been developed, such as thermal treatment [6], oxidation [7], irradiation [8], or chemical modification [9–12]. Covalent grafting of different organic moieties using chemical modification is becoming a popular approach for surface modification [13]. In 1992, Pinson and coworkers [14] first described the electrochemical reduction of diazonium salt leading to the grafting of aryl groups at a carbon surface. Haddon

and coworkers [15] reported that single-walled carbon nanotubes grafted by poly(aminobenzene sulfonic acid) (PABS) and polyethylene glycol (PEG) exhibit excellent water solubility and increased electrical conductivity. Pickup and coworkers [16] reported an anthraquinone modified carbon fabric electrode providing 40% higher average capacitance, 56–86% higher energy density, and improved power duration than that of unmodified electrodes for EDLC application. Recently, Assresahegn and Bélanger [17] prepared a hydrophilic polyacrylic acid (PAA) layer directly onto the surface of carbon black by atom-transfer radical polymerization (ATRP). The PAA-modified electrodes gave an increased capacitance, wide working potential window, good wettability, and excellent specific capacitance retention. Electrochemically induced surface-initiated ATRP (SI-eATRP), which was recently developed, is an effective way to prepare different types of polymer brushes on different initiator-decorated substrates [18]. This novel modification method has distinct characteristics in polymerization controllability and can be applied to synthesize polymers with well-defined structure under environment-friendly conditions [19,20]. Here, we would like to introduce a new procedure for the chemical grafting of organic layers at the surface of carbon materials via SI-eATRP.

In this paper, hydrophilic poly(vinylpyrrolidone) (PVP) brushes were grafted onto the surface of OMCs by using the SI-eATRP method. The capacitance performance of OMCs materials can be improved greatly due to the introduction of hydrophilic PVP brushes onto the OMCs surface. As the electrode material for EDLC, the OMCs-PVP electrode exhibits high capacity, superior rate capability and long-term stability.

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## 2. Experimental section

Tetrahydrofuran (THF), triethylamine (TEA), 2-bromoisobutryl bromide (BIBB), benzyltributylammonium chloride (BBAC), *N, N, N, N*-tetramethylethylenediamine (TMEDA), and *N, N*-dimethylformamide (DMF) were purchased from Sigma-Aldrich Co., Ltd. All other chemicals were of analytical grade and used without purification.

In our experiment, OMCs was synthesized according to a previous publication [21]. The modified OMCs was prepared in three major steps. Firstly, the introduction of hydroxyl groups on the surface of the OMCs was carried out by acid treatment and deoxidizing by KI according to a procedure reported previously [22]. The OMCs with hydroxyl groups (OMCs-OH) on the surface were obtained. Secondly, 0.3 g OMCs-OH dissolved in 30 mL THF with 1.5 mL TEA was placed into an ice bath. After cooling to 0 °C, a mixture of 3 mL of BIBB in 20 mL THF was added. The reaction was allowed proceed for 5 h at 0 °C and then transferred into a 60 °C water bath for another 24 h. The obtained initiator-functionalized material (OMCs-Br) was washed and then dried overnight under vacuum. Thirdly, a typical SI-eATRP polymerization reaction was conducted using an electrochemical working station (CHI760D, Shanghai, China) with a three electrode system by using a platinum foil counter electrode, a saturated calomel electrode (SCE) reference electrode and a working electrode. The polymerization process took place in a solution of CuCl<sub>2</sub> (0.09 g), TMEDA (0.09 g), NVP (4.7 g) and BBAC (0.7 g) supporting electrolyte in 45 mL solution of 2:1 (v/v) H<sub>2</sub>O/MeOH. During the polymerization process, the nickel foam coated with initiator-modified carbon was placed around the working electrode. SI-eATRP was initiated at -0.14 V and continued for 7.5 h at room temperature to obtain a OMCs-PVP electrode.

The obtained products were characterized using transmission electron microscopy (JEOL, JEM-2010, Japan), field emission scanning electron microscopy (JEOL, JSM-6701F, Japan), small-angle X-ray scattering (SAXS) (Rigaku, D/Max-2400, Japan), FTIR spectrometry (Nexus 670, USA) and nitrogen absorption and desorption (Micromeritics, ASAP 2020M, USA). The contact angles were obtained on a video contact angle instrument (Dataphysics, OCA15+, Germany).

The electrochemical measurements were performed in a three-electrode system in 2 M KOH aqueous solution at 25 °C with a platinum foil as counter electrode, an SCE as reference electrode, and working electrodes prepared according to a method reported in the literature

[23]. Each working electrode was obtained by pressing a mixture of mesoporous carbon material (8 mg, 80 wt.%), acetylene black (10 wt.%) and polytetrafluoroethylene (PTFE, 10 wt.%) onto 1 cm<sup>2</sup> nickel foam (110PPI, pore density: 420 g m<sup>-2</sup>) that served as a current collector.

## 3. Results and discussion

### 3.1. Structure characterization of OMCs

From Fig. 1a, the SAXS pattern of the OMCs exhibits three well-resolved peaks that can be assigned to (100), (110), and (200) peaks of the 2-D hexagonal p6 mm space group, which indicates the long-range ordering of the carbon materials [24]. Fig. 1b shows the TEM image for OMCs, viewed perpendicular to the [100] direction of hexagonal pore arrangement. The well-developed mesoporous structure provides smooth channels for rapid transport of the electrolyte ions, which has been determined previously [25–27]. As shown in Fig. 1c, the SEM image of the OMCs sample exhibits almost 100% monodispersed rod-like particles, 0.2–0.4 μm in diameter and 0.7–1.0 μm in length. After the grafting of PVP, it can be seen that the surface of OMCs has been completely covered by PVP in Fig. 1d.

The SI-eATRP process for grafting PVP is shown in Fig. 2a. After this treatment process, PVP brushes are created all over the surface of the OMCs. The polar group of >N-C=O existing in PVP can effectively increase interaction of the electrolyte ions with the OMCs surface, which can provide fast ion response and electrolyte accessibility. Prior to PVP brush growth, cyclic voltammograms (CV) of an initiator-modified electrode are carried out to identify the potential window for electrochemical reduction of Cu<sup>2+</sup> to Cu<sup>+</sup> [28,29]. As seen in Fig. 2b, the CVs of the CuCl<sub>2</sub>/TMEDA complex exhibit a reversible peak couple without any extra redox process, which might interfere with the catalyst reduction. According to the CV curves, we can determine that SI-eATRP should be carried out by using a reduction potential of -0.14 V.

The chemical composition changes on the channel surface of the OMCs before and after grafting are investigated by FTIR spectroscopy. Fig. 2c shows a wide absorption band at approximately 3422 cm<sup>-1</sup> that is associated mainly with the -OH stretching vibration of the adsorbed water molecules. In comparison with the original OMCs-OH,

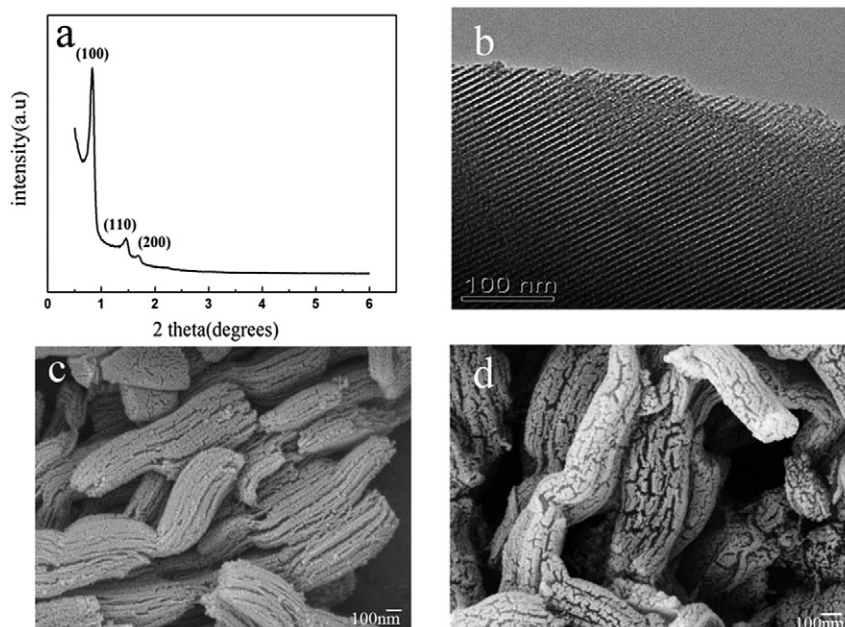


Fig. 1. Structure characterization of OMCs: (a) SAXS patterns; (b, c) TEM; (d) SEM.

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