



# Pore size control of porous carbons using novel silica-based copolymer template and their application in supercapacitor



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## ABSTRACT

A brand new silica-based copolymer template is developed by co-condensation of tetraethyl orthosilicate (TEOS) and (3-methacryloxypropyl)-trimethoxysilane (MPS). The framework morphology and size of this template can be tailored by tuning the MPS concentration. Thus, unimodal mesoporous, bimodal mesoporous and macroporous carbon can be easily obtained by varying the preparation techniques. Meanwhile, the pore size and BET surface area of this carbon can be tuned from 4.3 to 55.0 nm, and 779–1649 m<sup>2</sup>/g, respectively. The as-prepared carbon materials with well-controlled pore size distribution are then used as model to investigate the ion transport inside the nanopores. The electrochemical results reveal that the capacitances of carbon materials are positively related to the surface area and the large mesopore or macropore can accelerate ion transport and then lead to enhanced rate performance.

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## 1. Introduction

Porous carbons have been one of the most attractive materials in energy, environment, catalyst and adsorption [1–7]. Precise pore structure control is extremely significant for the application of porous carbons. In the past decades, silica templates have been widely employed to design and prepare porous carbon materials due to their superior pore size tunability [1,8]. However, in most cases, the framework of silica templates is either worm-like or particle-like in the absence of surfactant, which is limited by the current sol–gel theory of silica gels. Normally, silica templates are prepared by using tetraethyl orthosilicate (TEOS) or tetramethyl orthosilicate (TMOS) as single silica source, and acids (HCl, H<sub>2</sub>SO<sub>4</sub>, etc.) or bases (NH<sub>3</sub>·H<sub>2</sub>O, etc.) as catalysts. When acid catalysts are adopted, the reaction rate is low and the final silica gels are always transparent monoliths with worm-like framework [9–11]. Once the condensation of silica source is catalyzed by NH<sub>3</sub>·H<sub>2</sub>O, spherical silica particles precipitate in several minutes, which is so called Stöber method [12–14]. As a result, the corresponding silica templated carbons are generally single-sized with low pore size controllability. Up to now, to the best of our knowledge, there is still no method can fill the gap between worm-like and particle-like nanoporous carbon. Sometimes, to get carbon with bimodal or multi-modal nanopores, two or more different type of silica

templates are used together, which are relatively complicated and time-consuming [15].

In the present work, a novel silica-based copolymer template is constructed by co-condensation of (3-methacryloxypropyl)-trimethoxysilane (MPS) and TEOS in the presence of NH<sub>3</sub>·H<sub>2</sub>O. Unlike traditional method in which silica spheres precipitate quickly, herein, the relatively strong steric hindrance of long chains in MPS decrease the reaction rate of TEOS and create silica gel monolith. The silica gel framework morphology and size are well-controlled by tuning MPS concentration. As a result, the nanopore of carbon replica can be tailored from worm-like to particle-like with varying MPS concentration (Fig. 1). Meanwhile, the pore size and BET surface area of this carbon can be tuned from 4.3 to 55.0 nm, and 779–1649 m<sup>2</sup>/g, respectively. Furthermore, this carbon also can be used as model to investigate the ion transport inside nanopores.

## 2. Experimental

Sucrose (1.5 g) was dissolved in a vial containing 2 ml water and 2 ml NH<sub>3</sub>·H<sub>2</sub>O. Then a solution of 10 ml ethanol containing predetermined amount of MPS was poured into. After the mixture turned to homogenous, 3 ml TEOS was added quickly under vigorous stirring. Subsequently, the vial was kept at 60 °C for 12 h and 100 °C for another 12 h. The obtained solid gel monolith was then carbonized at 900 °C for 3 h with a heating rate of 5 °C/min. After etching the silica template using superfluous 40 wt% HF and drying at 100 °C for 8 h, the ultimate carbon materials were harvested.

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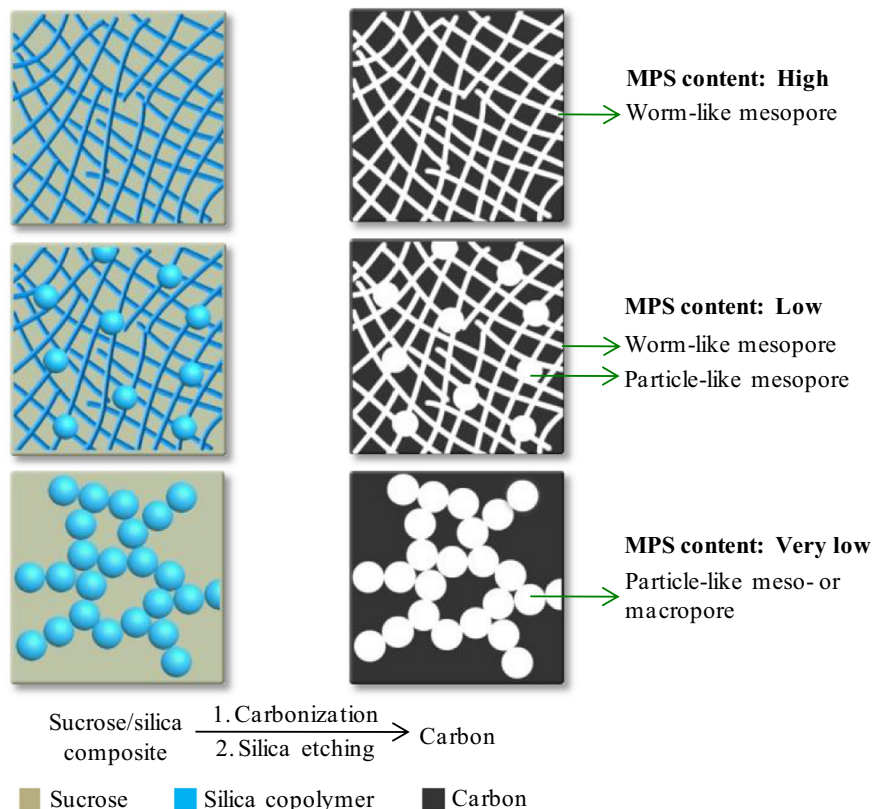


Fig. 1. Schematic illustration for the effect of MPS content on the nanopore structure of as-prepared carbon materials.

The carbon samples were denoted as TMC-xx (TEOS and MPS co-gelation templated carbons), where xx is varying with the MPS amount. More specifically, the MPS contents of TMC-1, TMC-2, TMC-3, TMC-4 and TMC-5 are 1.2, 0.8, 0.2, 0.1 and 0.05 mL, respectively.

### 3. Results and discussion

Fig. 2 gives TEM images of TMCs, which vividly presents their nanostructure development. When the MPS content is relatively high, e.g., greater than or equal to 0.2 mL (TMC-1, TMC-2 (not shown) and TMC-3), the obtained carbon are of worm-like mesoporous structure (Fig. 2A and B), which is similar to that of some previous reports [9,16]. Meanwhile, the worm-like mesopore size exhibits a distinct increase with decreasing MPS content from 1.2 to 0.2 mL. When the MPS content decreases to 0.1 mL, the carbon material (TMC-4) presents a hierarchically bimodal mesoporous structure, in which some large particle-like mesopores are embedded into small worm-like mesoporous skeleton (Fig. 2C). While the MPS content is very low, such as 0.05 mL for TMC-5, particle-like meso- or macropores become much larger and the worm-like mesopores disappear (Fig. 2D).

$N_2$  adsorption characterization was used to evaluate the nanopore structure of TMCs. Fig. 3 show the adsorption-desorption isotherms and BJH pore size distributions of TMCs. It can be found that TMC-1, TMC-2 and TMC-3 show uniform mesopore size distribution at 4.3, 4.5 and 5.7 nm, respectively. From TMC-1 to TMC-3, the worm-like pore size increases due to the decrease of MPS concentration. When the MPS content was reduced to 0.1 mL, the small worm-like mesopore shift to 7.4 nm, and meanwhile, large mesopore with peak pore size at 30.3 nm shows up, which is corresponding to the particle-like pores in TEM image (Fig. 2C).

Finally, when MPS amount was further reduced to 0.05 mL, the diameter of particle-like pores increases to 55.0 nm and small worm-like mesopores disappear. According to BET equation, the surface areas of TMC-1, TMC-2, TMC-3, TMC-4 and TMC-5 are 1649, 1256, 1082, 1016 and 779  $m^2/g$ , respectively, presenting a distinct decrease with the increase of pore size.

TEOS is generally used to prepared silica nanospheres catalyzed by  $NH_3 \cdot H_2O$  in Stöber method [12]. It's unexpected here the addition of MPS results in the formation of silica gel. The control experiment reveals that no gelation or precipitation was created in two days when TEOS was not added, and without MPS, silica precipitated in several minutes. This implies that the reaction rate of MPS is much lower than that of TEOS due to its less reaction sites and relatively strong steric hindrance. Then, when the two monomers are mixed, the reaction of TEOS is slowdown, resulting in the formation of silica-based copolymer gels but not silica precipitation. Decreasing MPS content, gelation is accelerated and the gel framework turns to thicker, leading to an increase of worm-like mesopore size. Furthermore, if MPS amount is relatively low, e.g. 0.1 mL, TEOS has a very strong trend to self-condensation and generates spherical silica nanoparticles quickly. At the same time, silica gel network forms, and then the silica nanoparticles are froze in silica gel network *in situ*. As a result, the obtained carbon possesses hierarchically small worm-like mesopores and large particle-like mesopores. Finally, when the MPS content is very low (0.05 mL), in a very short time, silica particles form and expend most of the monomers, then there is no enough time and monomers to create silica gel framework. Meanwhile, higher reaction rate leads to larger silica particle size, and thus, particle-like macroporous carbon is prepared.

TMCs show precise pore size controllability, which are good model to investigate the ion transport inside the nanopores. Taking this into consideration, supercapacitive performance of TMCs

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