Mesoporous carbon/silica nanocomposite through multi-component assembly†

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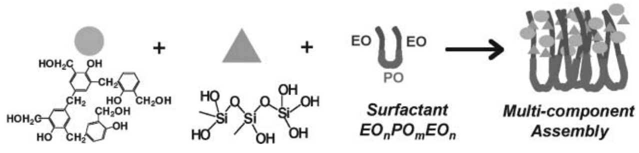
Ordered mesoporous carbon/silica nanocomposites were synthesized through a novel multi-component molecular assembly and show promising potential as corrosion-resisted electrocatalyst supports.

Ordered mesoporous silica has been extensively studied due to its unique properties, such as high surface area, controllable pore size and pore structure. These materials are typically synthesized by assembling surfactant with silicate building clusters into nanocomposites that contain ordered lyotropic liquid crystalline mesostructure followed by surfactant removal.[1,2] Soon after its inception, the field of mesoporous material research has expanded far beyond the original silica materials by replacing silicate clusters with other inorganic or organic building blocks.[3] Multi-component assembly, a process that simultaneously assembles surfactant with two or more kinds of building blocks, is of particular interest for the synthesis of mesoporous nanocomposites. To date, such nanocomposites are limited to mesoporous organosilica and hierarchically mesoporous silica from mixtures of hybrid silicate building blocks or silicates with other building blocks such as polymer, surfactant, and inorganic salt.[4]

Here we report a simple and efficient synthesis of ordered mesoporous polymer/silica and carbon/silica nanocomposites through multi-component assembly using silicate and phenolic oligomer as building blocks (see Scheme 1). Similar to silicate clusters that contain silanol groups, the oligomers contain a large number of hydroxyl groups allowing strong hydrogen bonding with the EO blocks of Pluronic surfactant ($EO_nPO_mEO_n$, where EO and PO are ethylene oxide and propylene oxide, respectively). Furthermore, similar to the silicate condensation reaction, the oligomers undergo polymerization at similar temperature forming cross-linked polymer. Driven by hydrogen bonding, these building blocks cooperatively assemble with surfactant resulting in ordered nanocomposites after silicate condensation and oligomer polymerization. Surfactant removal and subsequent carbonization creates ordered mesoporous polymer/silica and carbon/silica nanocomposites, respectively. Besides the mesoporous structure control by selecting appropriate surfactants and reaction conditions, this method can be used to synthesize various mesoporous nanocomposites with controlled composition through selecting respective building blocks and the ratio of building blocks used.



Scheme 1 Schematic of a multi-component assembly using silicate (▲) and phenolic oligomer (●) as building blocks.

Experimentally, the multi-component assembly was achieved through an aerosol process. Briefly, beginning with a multi-component precursor solution containing oligomers, silicate clusters and Pluronic surfactant F127 ($EO_{107}PO_{70}EO_{107}$), atomization process creates precursor droplets that undergo drying, assembling, and condensation reactions (Supplementary Fig. S1 and S2 and Experimental section†). During the process, solvent evaporation enriches surfactant, silicate, and oligomer, inducing their co-assembly into nanocomposite particles containing ordered mesophases.[2] Further silicate condensation reactions and polymerization of the oligomers at high temperature generate polymer/silica/surfactant nanocomposite particles. Subsequent surfactant removal at 350 °C and carbonization process at 900 °C under nitrogen create ordered mesoporous polymer/silica and carbon/silica nanocomposite particles, respectively. Besides the spherical morphology, it is worth noting that nanocomposites in the forms of thin films, fiber, or arrays can also be prepared through a simple coating, fiber extruding, or micro-writing technique.

Fig. 1 shows representative transmission electron micrographs (TEM) of mesoporous polymer/silica and carbon/silica nanocomposites synthesized using this approach. All particles are spherical in morphology. In our experiments, a commercial TSI (Model # 3076) atomizer was employed, which resulted in the formation of polydispersed particles with particle size centered at about 250 nm. The particle size distribution of these particles is similar to that in our early publication.[5] Fig. 1a and 1b show polymer/silica particles prepared with oligomer:silica weight ratios of 1 : 0.75 and 1 : 0.5, respectively. Ordered mesostructures, especially near the solid–air interface, were observed. Less ordered core region is a common phenomenon in the aerosol-assisted assembly due to associated kinetics of evaporation and mass transport.[2] The mesostructural

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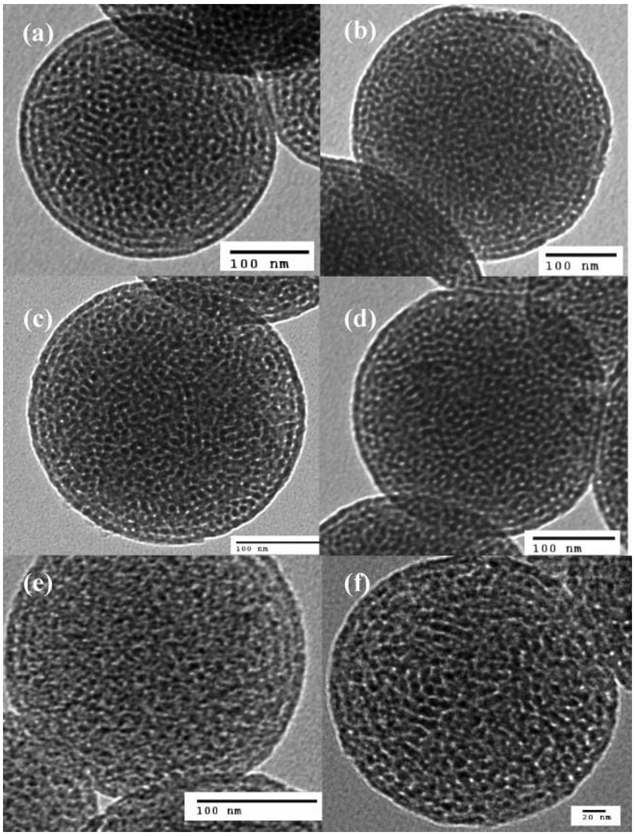

Fig. 1 Representative TEM images of mesoporous (a and b) polymer/silica, (c and d) carbon/silica and (e and f) pure carbon particles prepared from precursors containing oligomer : silica weight ratio of 1 : 0.75 and 1 : 0.5, respectively.

ordering was further confirmed by the low-angle X-ray diffraction peak (Supplementary Fig. S3†). We noticed that further increasing the oligomer content may gradually deteriorate the mesostructural ordering, which is probably due to the relatively slow oligomer polymerization compared with the short resident time of the aerosol apparatus used (~7 seconds). In fact, highly ordered mesoporous polymer/silica or carbon/silica materials with all composition ranges can be prepared through slower casting process (Supplementary Fig. S4†). Fig. 1c and 1d are TEM micrographs of carbon/silica nanocomposites converted from polymer/silica samples shown in Fig. 1a and 1b, respectively. Carbonization process has no obvious effect on pore size distribution and pore structure (also see Supplementary Table S1†).

The pore structure was quantized using nitrogen sorption techniques (Fig. 2 and Supplementary Table S1†). Typical type-IV nitrogen sorption isotherms with hysteresis loops and a narrow pore size distribution centered around 7 ~ 8 nm were observed for all polymer/silica nanocomposites (curve a). Increasing oligomer content leads to a broader pore size distribution and less surface area, which is consistent with the TEM and the X-ray diffraction results. The nitrogen sorption isotherms of the carbon/silica particles (curve b) exhibit similar features with increased surface area and pore volume. Pore diameter of the carbon/silica nanocomposites, however, is slightly decreased to 6 ~ 7 nm. The increased surface area and pore volume are due to the creation of microporosity during the conversion from polymer to carbon (see Supplementary Table S1†); while the decreased pore diameter may be attributed to the high temperature (900 °C) carbonization process that shrinks the pore structure.

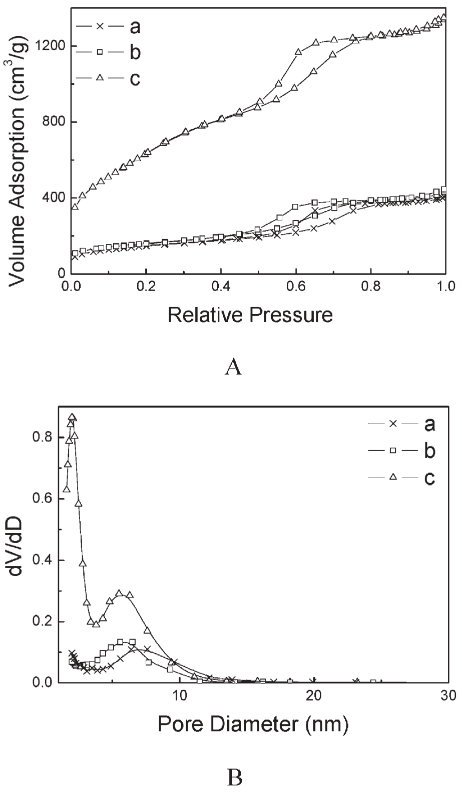

Fig. 2 (A) Nitrogen adsorption–desorption isotherms and (B) pore size distributions of (a) mesoporous polymer/silica, (b) carbon/silica prepared from precursors containing oligoemr:silica weight ratio of 1 : 0.75; and (c) pure carbon was prepared by removing silica from (b).

In order to further examine the nanocomposite structure and understand this multi-component assembly process, the silica component of the carbon/silica nanocomposite particles (Fig. 1c and 1d) was removed by HF etching, which created mesoporous carbon particles shown in Fig. 1e and 1f, respectively. Comparing with the carbon/silica particles, resulted mesoporous carbon particles show less ordered mesostructure. Yet, the overall spherical morphology and mesostructure remain intact, indicating the formation of homogenous and continuous carbon networks in the carbon/silica predecessor. Nitrogen uptake of the pure mesoporous carbon particles (Fig. 2A, curve c) is significantly increased, suggesting an increased pore volume and surface area. For example, for samples prepared from a precursor solution containing oligoemr:silica = 1 : 0.75 (weight ratio), the surface area and pore volume increased from 566 m^2 g^{-1} and 0.64 cm^3 g^{-1} to more than 2300 m^2 g^{-1} and 2.0 cm^3 g^{-1} after silica removal. The dramatic increase in surface area and pore volume is due to the pore formation upon silica removal. The pore size distribution was calculated from the BJH model (Fig. 2B, cure c), showing a bimodal pore size distribution centered at 2 and 6 nm, respectively. Note that the pore size distributions of the large and small pore systems are fairly narrow. The 6 nm pores are originated from the surfactant template, matching well with those of carbon/silica sample; while the 2 nm pores are created after silica removal.[6] Combination of the TEM and nitrogen sorption results indicates that the silicate and oligomeric building clusters are homogenously mixed and organized around the surfactant liquid crystalline template (Scheme 1). Condensation reactions of the silicate building clusters form small silica aggregates within the carbon/silica frameworks with an average domain size of 2 nm. Polymerization of the oligomers forms continuous polymer networks or carbon networks after carbonization process if the oligomer content is high enough.

Carbon black is the most commonly used catalyst support for electrocatalysis applications (*e.g.*, fuel cell electrode). It is made up of amorphous carbon particles and possesses high porosity, surface area and adequate conductivity (>1 S cm^{-1}) for sufficient reactant transport, catalyst deposition and electron transport. However, these materials are exposed to a highly oxidative environment, which often leads to significant carbon corrosion. This durability issue is one of the main barriers preventing commercialization of automotive-scale fuel cells.[7] The ordered mesoporous carbon/silica nanocomposites might be a potential candidate for corrosion-resisted catalyst support. Continuous carbon network can provide excellent electron conductivity while inorganic silica component may improve chemical stability. In our preliminary study, catalyst Pt nanoparticles were deposited onto the mesoporous carbon/silica nanocomposite (silica molar ratio 10%) to fabricate electrode (See Supplementary Experimental details†). Commonly used commercial carbon Vulcan XC-72 was also used as a control. The carbon/silica nanocomposite showed an electrical conductivity of 2.3 S cm^{-1}, which is lower than Vulcan XC-72 (20 S cm^{-1}); nevertheless, such an electrical conductivity is adequate for current fuel cell device application. Further optimization is underway to improve the electrical conductivity. Standard accelerated thermal sintering experiments were conducted as oxidation test to evaluate the durability. Promising corrosion resistance was obtained from the carbon/silica nanocomposites. For example, the weight loss of carbon/silica nanocomposite was only 3% after one sintering test compared with Vulcan XC-72 that showed a much higher weight lost of 40%. With only 10% silica addition, the weight loss under oxidative environment is reduced over ten times while the nanocomposites still retain high enough electrical conductivity. Detailed analysis and systemic studies for catalyst support applications will be published elsewhere soon.

In summary, we have demonstrated an efficient one-step approach to synthesize ordered, homogenous spherical mesoporous polymer/silica and carbon/silica nanocomposite particles through aerosol-assisted multi-component self-assembly. Mesostructure control is similar to those of well-established silicate-surfactant assembling systems. Composition of the nanocomposites can be easily controlled by adjusting ratio of silicate to oligomer used. This simple method provides a new family of mesoporous nanocomposites for many potential applications, such as adsorbents, catalyst supports and hydrogen storage.[8] Increased corrosion resistance to oxidative environment has been illustrated and is worth of further study. More importantly, the concept of multi-component assembly opens up a new way to synthesize mesoporous nanocomposites with both composition and mesostructure controlled.

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