

Electronic Supplementary Information (ESI) for

Enhanced electrochemical performance of polyaniline/sulfonated polyhedral oligosilsesquioxane nanocomposites with porous and ordered hierarchical nanostructure

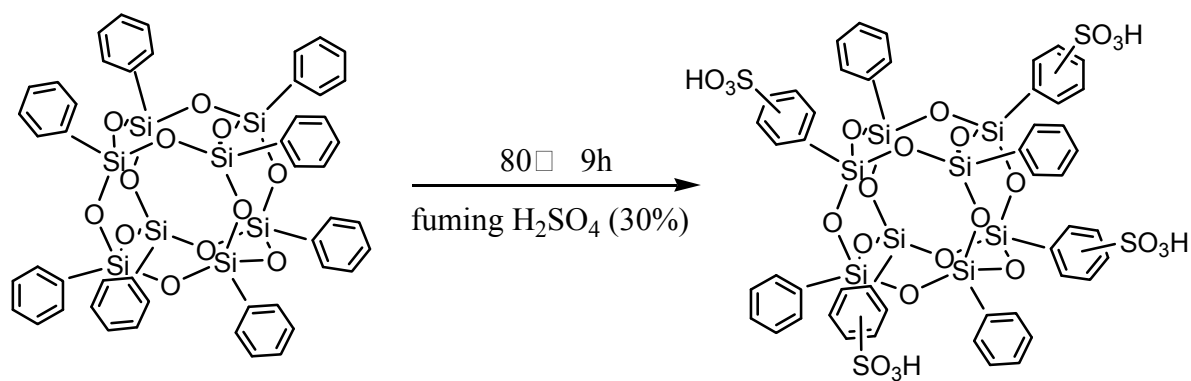
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S1. Sulfonation of octaphenyl polyhedral oligomeric silsesquioxane.

The sulfonic acid functionalized POSS was synthesized using sulfonation of POSS by fuming sulfuric acid (20% SO₃), as illustrated in Scheme S1. ¹³C NMR experiments were carried out at room temperature using a Bruker 350 MHz NMR Spectrometer operating at resonance frequencies of 100.47 MHz. ¹³C solid state NMR: δC (ppm) 142.2 (C-SO₃H), 136.0 (C-Si), 129.6 (Ar-C) due to sulfonated phenyl rings. In order to determine the sulfonation level of POSS, the protons in the SOPS suspension was titrated with NaOH solution. The number of sulfonic groups on a SOPS is nearly 4.3.



Scheme S1. Synthesis of SOPS.

S2. FTIR spectra of POSS and SOPS.

FTIR spectra were recorded on a Nicolet 8700 FTIR spectrometer. The spectra in the range of 4000 to 400 cm^{-1} were collected by the averaging of 32 scans at a resolution of 4 cm^{-1} . Figure S2 shows the FTIR spectra of the POSS particles before and after sulfonation reaction. The characteristic peak at 1135 cm^{-1} corresponds to the asymmetric stretch of the Si-O-Si groups of silica. The peaks of 740 and 691 cm^{-1} are due to out-of-plane bending for a mono-substituted aromatic ring. After sulfonation reaction, the peaks at 1623 and 1084 cm^{-1} are due to SO_3 asymmetric and symmetric stretching, respectively^{S1}, and the peaks at 951 and 804 cm^{-1} corresponds to out-of-plane bending for a meta-substituted aromatic ring.^{S2} In addition, there is a peak at 142.2 ppm of SOPS ^{13}C NMR due to the carbon attached to the sulfonic acid functionality, with an upfield shift on the carbon atoms of the sulfonated phenyl rings.^{S3} The spectra of FTIR and ^{13}C solid state NMR indicate that the POSS nanoparticles are successfully sulfonated.

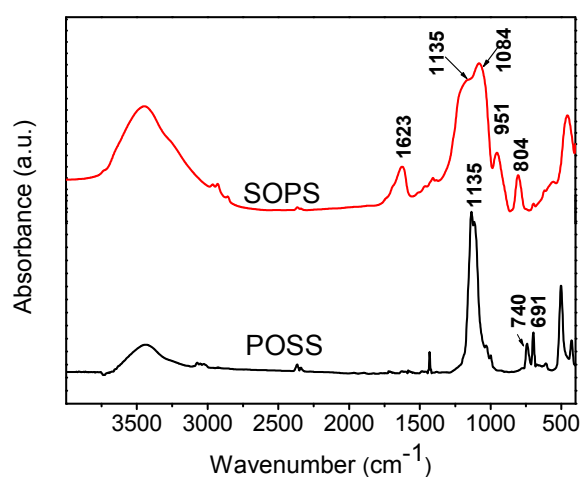


Figure S2. FTIR spectra of POSS and SOPS.

S3. Zeta potential measurement

Zeta Potential measurements were conducted on a Malvern Zetasizer NanoZS system with irradiation from a 632.8 nm He-Ne laser. The zeta potential is often used as an index of the magnitude of electrostatic interaction between colloidal particles and is thus a measure of the colloidal stability of the solution.^{S4} Particles with a zeta potential less than -15 mV or more than 15 mV are expected to be stable from electrostatic considerations. As clearly showed in Figure S4, the zeta potential value of SOPS is as low as -40.4 mV, indicating the good stability of SOPS suspension. The results are caused by the introduction of sulfonic groups on the surfaces of SOPS nanoparticles with numerous negative charges. The electrostatic interactions lead to the stable dispersion of SOPS nanoparticles in water over several months.

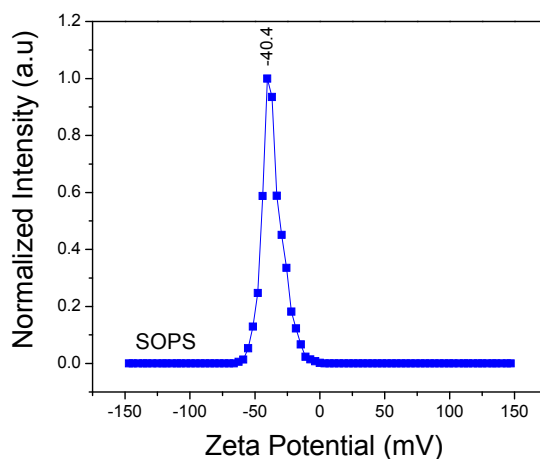


Figure S3. Zeta potential distribution of SOPS in aqueous solution.

S4. Formation mechanism of the rod-like and chrysanthemums-like PANI.

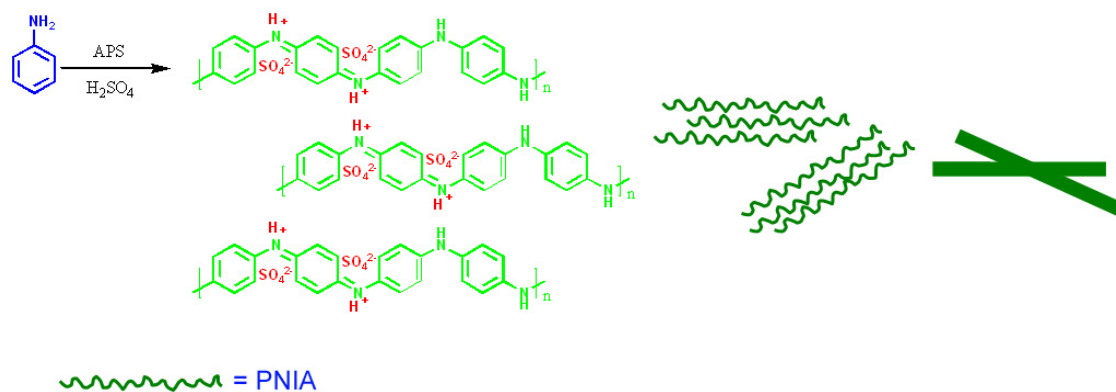


Figure S4. Schematic illustration for the growth mechanism of the PANI nanorods.

S5. Nitrogen adsorption/desorption

The textures of pure PANI and PANI/SOPS are measured by N_2 adsorption. The isotherms and pore size distribution curves of the samples are shown in Figure S5, and the BET surface areas and porosity data taken from adsorption–desorption isotherms are listed in Table 1. Figure S5a exhibits the isotherm curves with a sharp capillary condensation step at high relative pressures ($P/P_0 = 0.85–0.95$) and a H3-type hysteresis loop, indicating that pure PANI possesses a relatively large pore size and a relatively broad pore size distribution.^{S5} This loop does not exhibit any limiting adsorption at higher P/P_0 , demonstrating the existence of macropores. These results are in agreement with the pore size distribution presented in the inset of Figure S5a (3 – 100 nm, max. 66.7 nm). The isotherms of PANI/SOPS5% and PANI/SOPS2% composites are similar to that of pure PANI, but the capillary condensation step shifts to lower relative pressures ($P/P_0 = 0.5–0.93$). The samples containing 2% or 5% SOPS possess a broad pore size distribution, but the pore size becomes smaller and more regular. These mesoporous materials shorten the diffusion length and ensure the electrolyte transport, which are favorable in electrochemical energy storage.^{S6} PANI/SOPS25% and PANI/SOPS10% have H4-type hysteresis loops, which feature parallel and almost horizontal branches and their occurrence has been attributed to the adsorption-desorption in the narrow pores.^{S7,S8} The size distribution of the narrow pores is shown in the inset of Figure S5b and S5c (3 – 6 nm, max. ~3.9 nm).

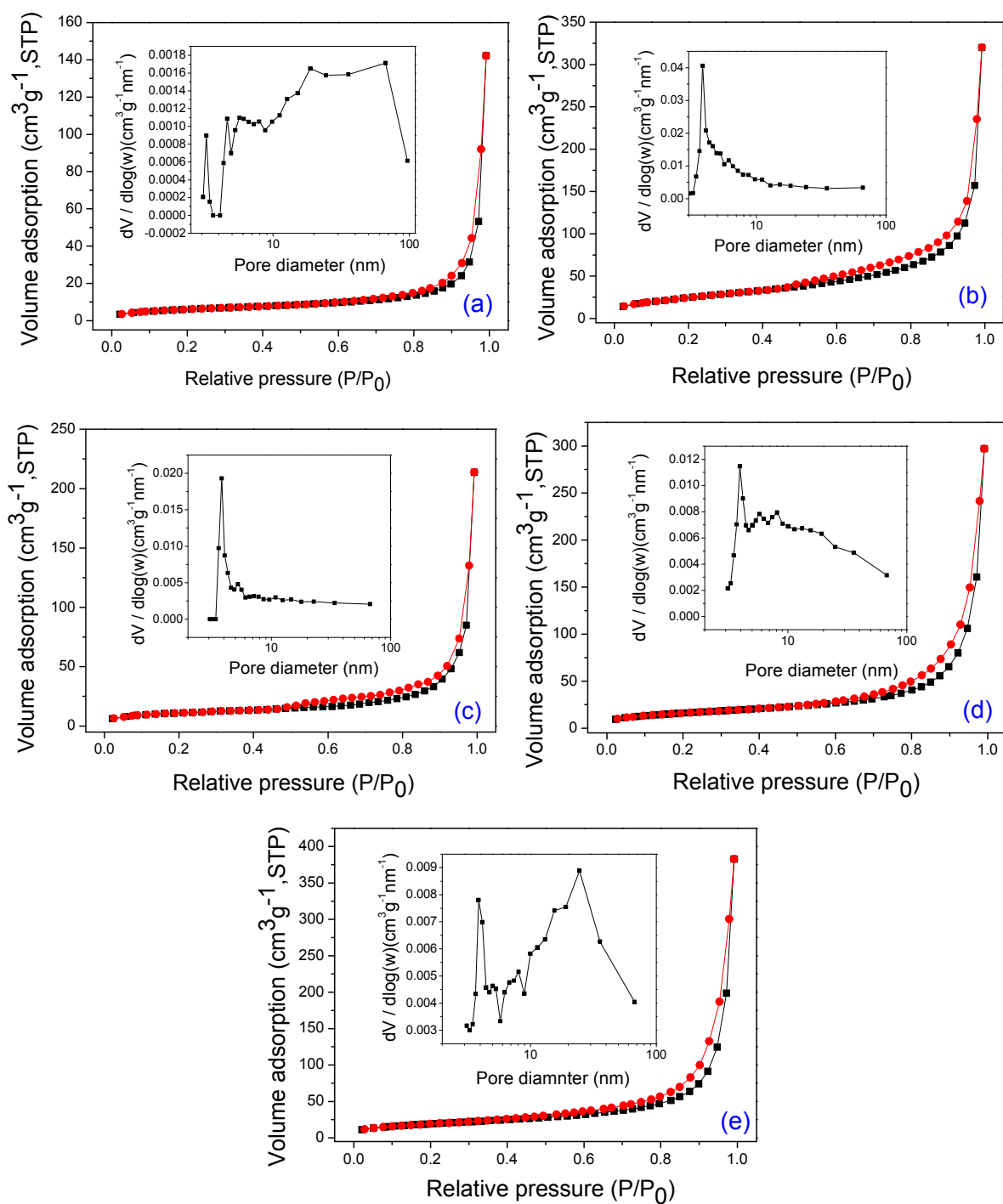


Figure S5. Nitrogen adsorption/desorption isotherms and the corresponding pore size distribution of (a) pure PANI, (b) PANI/SOPS25%, (c) PANI/SOPS10%, (d) PANI/SOPS5%, and (e) PANI/SOPS2%.

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