

Selective Polymerization of Polypyrrole in Silica Mesopores Using an In-Situ Generated Oxidizing Agent on a Silica Surface

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Electronic Supplementary Information

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Experimental Section

Synthesis An optimum condition used to prepare MSU-H/ppy involves dispersing 200 mg silica in 100 mL distilled water by stirring for two hours and adding 0.7 mL pyrrole solution. (The final concentration of pyrrole in the 100 mL solution was 0.1 M). For the maximum adsorption of ppy in the mesopores, stirring was continued for several hours. Polymerization was initiated upon addition of 0.69 g of NaNO₂. After one day of stirring, the composites were collected by filtering the solution using a membrane filter with 0.2 micron pore size and washing with deionized water. The resulting MSU-H/ppy composite powders show uniform black color. For purification, the composites were re-dispersed in 100 mL deionized water for filtering and washing twice more. The products were dried under vacuum at 50 °C for 72 hours before further characterization.

Characterization The presence of ppy in the composite sample was confirmed by the UV-vis spectroscopy (SCINCO S-3100) after eluting ppy from the composite sample using acetone (Figure S2). Thermal gravimetric analysis (TGA) of the samples was carried out with a heating rate of 10 °C/min (TA Instruments-SDT 2960). XRD patterns were recorded using a Rigaku D/Max 2500 diffractometer using Cu K_α radiation. TEM studies were performed using a JEOL JEM 2100F microscope operated at 200 kV (Figure S3). The nitrogen adsorption-desorption isotherms were obtained using a Micromeritics TriStar 3000 at liquid N₂ temperature (Table S1). In order to measure conductivity, pellets of MSU-H/ppy composite were pressed in a 7.00 mm diameter round steel cell under 4,000 lbs (equivalent to *ca.* 460 MPa). The thickness of the pellets was measured using a digital micrometer with an accuracy of ±0.004 mm (0.47 mm for the pellet used for the measurement shown in Figure 3(c)). Pellets were mounted on an ITO substrate (surface resistivity, 8-12 Ω) with colloidal Ag paste. Ag paste contacts were then placed on the pellet and ITO surface. I-V measurements were obtained using Au-placed leads connected to a source meter (Keithley 2400).

Table S1. Structural parameters of the MSU-H and MSU-H/ppy composite.

Material	a^a / nm	S_{BET}^b / m ² g ⁻¹	D_{BJH}^c / nm	V_{tot}^d / cm ³ g ⁻¹	$W_{\text{framework}}^e$ / nm
MSU-H	12.5	579	9.27	1.29	3.23
MSU-H/ppy	12.5	527	9.06	1.16	3.44

^a Unit cell parameter of a 2D hexagonal structure calculated from XRD patterns ($a = 2 d_{100}/\sqrt{3}$).

^b BET surface area calculated in the range of relative pressure (p/p_0) = 0.05–0.20.

^c Mesopore diameter calculated from the N₂ adsorption branches using the BJH method.

^d Total pore volume measured at $p/p_0 = 0.99$.

^e Framework thickness calculated from the lattice parameters and pore sizes.

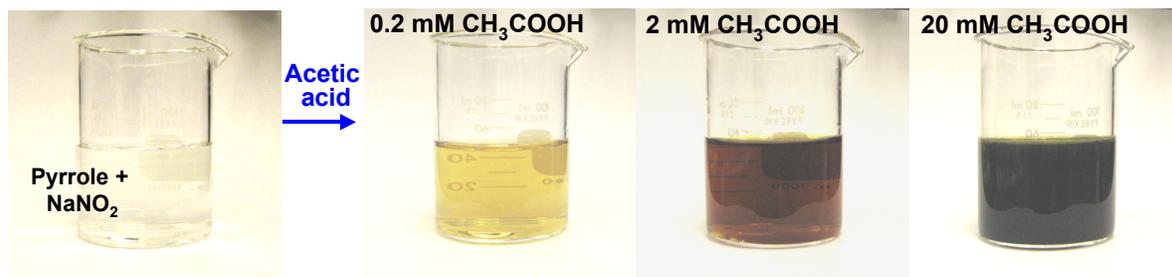


Figure S1. Photographs demonstrating polymerization of ppy in a solution containing 0.1 M pyrrole, 0.1 M NaNO₂ and varying concentrations of acetic acid proceeded for 5 min. The pH of the solutions containing 0.2 mM, 2 mM, and 20 mM, were 5.8, 5.6, and 4.8, respectively.

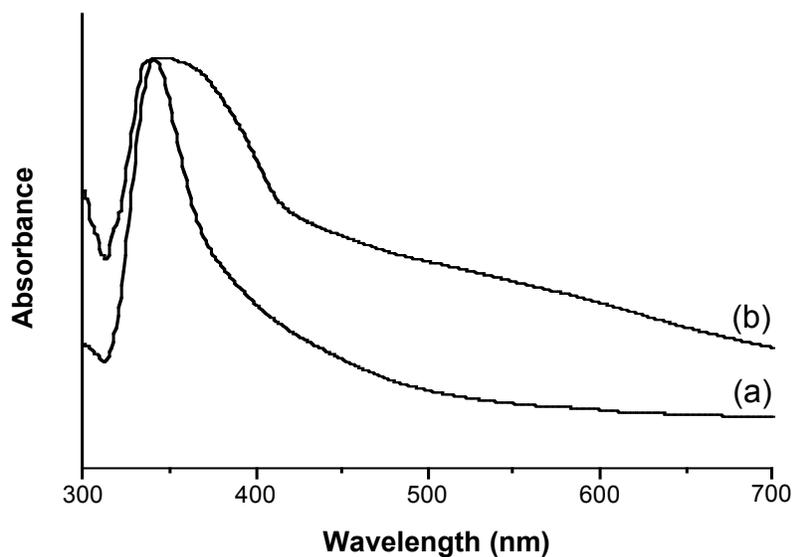


Figure S2. UV-Vis spectra of (a) pyrrole in acetone and (b) ppy oligomers eluted from the MSU-H/ppy composite using acetone showing an absorption peak due to the π - π^* transition of pyrrole and ppy, respectively.^{1,2}

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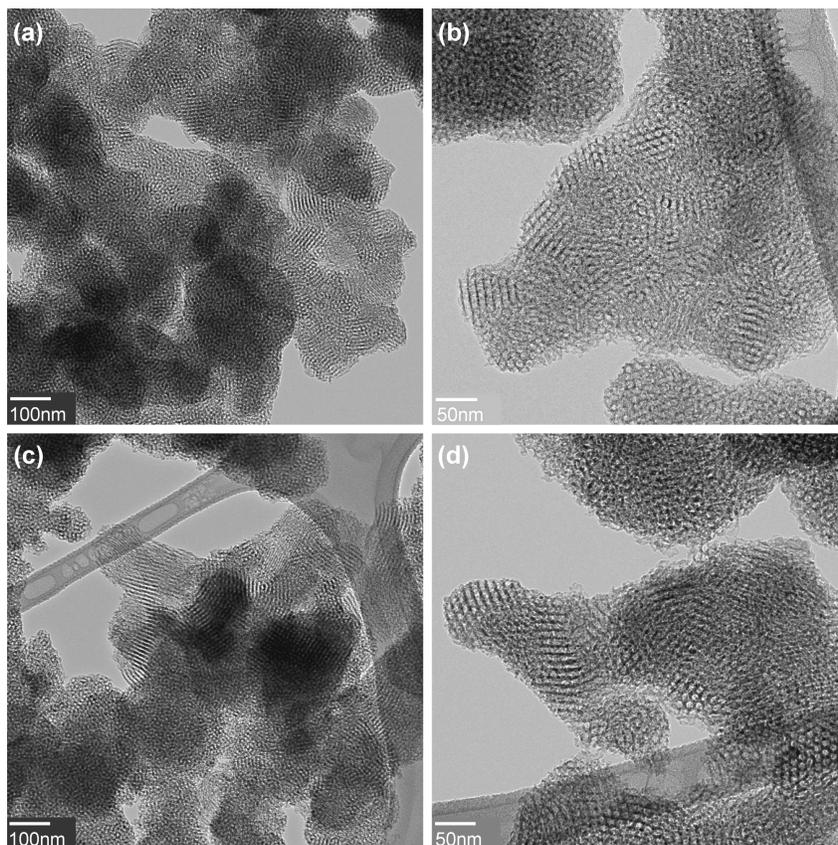


Figure S3. TEM images of (a-b) MSU-H and (c-d) MSU-H/ppy composite particles. TEM study could not be used to directly visualize the presence of ppy layer in the MSU-H/ppy composite sample because the contrast of this polymer layer against the background was too low and ppy is present as an extremely thin coating layer. However, TEM studies on multiple specimens confirmed that ppy agglomerates were not present on the outer surface of composite particles.