### **Supplementary Information**

#### **Green-Nano Approach to Nanostructured Polypyrrole**

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#### Green Synthesis of Conductive Polypyrrole Nanofibers

In a typical synthesis, PPy nanofibers was obtained by adding catalytic amount (~2 mg) of  $V_2O_5$  seeds into 50 mL DI water, in which 0.5 mL pyrrole has been pre-dispersed. After the addition of 5 mL H<sub>2</sub>O<sub>2</sub>, the polymerization was initiated and lasted for 12 hrs. The dark precipitation of polypyrrole was filtered and washed with copious amounts of DI water (3 × 100 mL) and acetone (3 × 100 mL). The powder was then freeze-dried for 12 hrs, yielding ~100 mg of PPy nanofibers.

## Green Synthesis of Conductive Polypyrrole Nanospheres

In a typical experiment, polypyrrole nanospheres can be synthesized by first adding 0.1 g ferrous chloride (FeCl<sub>2</sub>) to 60 mL DI water, where 1 mL pyrrole has been pre-dispersed. After the addition of 5 mL  $H_2O_2$  to the pyrrole/FeCl<sub>2</sub>/H<sub>2</sub>O mixture, pyrrole polymerization was initiated and lasted for 12 hrs. The dark precipitated polypyrrole was filtered and washed with copious amounts of DI water (3 × 100 mL) and acetone (3 × 100 mL). The powder was then freeze-dried for 12 hrs, yielding ~100 mg of PPy nanospheres.

## Potential-time Profiling Characterization of in-situ Polymerization Process

The reaction mixture was setup for potential-time profiling using previously established procedure <sup>1,2</sup> (Pt wire electrode, saturated calomel electrode (SCE) reference). The potential was monitored continuously with time starting from the very beginning of the polymerization.

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- Mattoso, L. H. C.; Oliveira, O. N., Jr.; Faira, R. M.; Manohar, S. K.; Epstein, A. J.; MacDiarmid, A. G. Polym. Int. 1994, 35, 89.

# Particle Size measurement of the as-prepared polypyrrole nanospheres

The particle sizes of the as-prepared nanospheres were measured by a NICOMP 380 ZLS Particle Sizer in the dispersions of two different surfactants: dioctyl sulfosuccinate sodium (AOT) or Triton X-100 (TX-100). A typical testing process is described as follows: a certain amount of surfactant was added into 50 mL distilled water (0.10g for AOT, 0.50g for TX-100), which was stirred continuously at 80°C, until the surfactant was fully dissolved and the solution became transparent. Desired amount of polypyrrole nanospheres (e.g. 0.005g, 0.010g) were added into the as-prepared surfactant solution at 60°C and stirred for around 10 min. And then the dispersions were placed in water bath and ultrasonicated for 30 min. Finally, the obtained dispersions with known concentrations were added to the test cell of NICOMP 380 ZLS Particle Sizer and their particle sizes were measured subsequently.



*Figure S1.* (A, C) SEM image of PPy granules and potential-time profile of pyrrole polymerization using V<sub>2</sub>O<sub>5</sub>/H<sub>2</sub>O<sub>2</sub>/HCl system; (B, D) SEM image of PPy nanofibers and potential-time profile of pyrrole polymerization using V<sub>2</sub>O<sub>5</sub>/H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O system. Scale bar: 2  $\mu$ m



*Figure S2.* (A, C) SEM image of PPy granules and potential-time profile of pyrrole polymerization using FeCl<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/HCl system; and (B, D) SEM image of PPy nanospheres and potential-time profile of pyrrole polymerization using FeCl<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O system. Scale bar: 2  $\mu$ m



*Figure S3.* Dynamic light scattering test for particle size distribution of PPy nanospheres dispersed in (A) AOT surfactant and (B) Triton X-100 surfactant. Concentrations from a-e: 0.1, 0.2, 0.6, 1, and 2 g/L.