Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Supplementary information

Self-assembled Hierarchical PEDOT Micro/nanostructures for High Efficient Oxygen Reduction Catalysts in a Wide pH Range

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1. SEM pictures of micro-structured PEDOT prepared under different molar ratio of the monomer and oxidant.

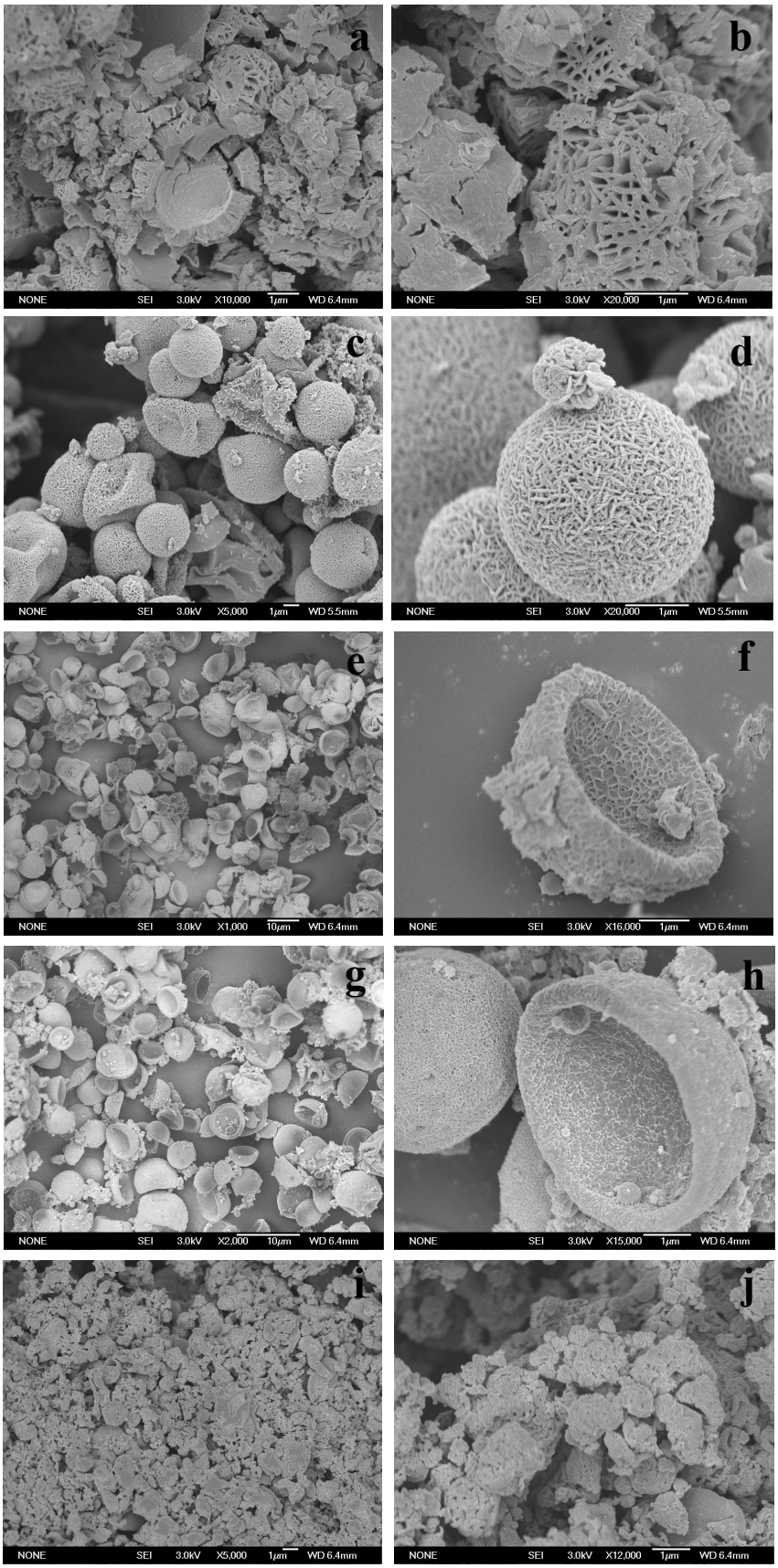

Fig. S1 Representative SEM pictures of micro-structured PEDOT prepared under different molar ratio of the EDOT and $FeCl_3$: (a)(b)-1 : 1.3; (c)(d)-1 : 4.0; (e)(f)-1 : 8.0; (g)(h)-1 : 12.0; (i)(j)-1 : 16.0, with PFSEA concentration 8 mM (0.08 g, 0.16 mmol) under 70 ºC for 5 h.

As shown in Fig. S1, the microstructures of as-prepared PEDOT are dependent on the molar ratio of $FeCl_3$ to EDOT. Only when the molar ratio of $FeCl_3$ to EDOT is properly controlled between 4.0 and 12.0, the microstructures of polymerized product can change from hollow micro-spheres to double-layer micro-bowls, as well as the subtle variance of the nano-fibers on the surfaces of micro-structures. When the molar ratio of oxidant ($FeCl_3$) to monomer (EDOT) is either too high (16.0) or too low (1.3), there are hardly homogeneous micro-structured PEDOT appeared in the product. It was proposed that excessive or insufficient oxidants can break the balanced formation mechanism of EDOT/PFSEA soft-templates, which leads to none structurally ordered product.

2. XRD spectra of the as-prepared micro-structured PEDOT.

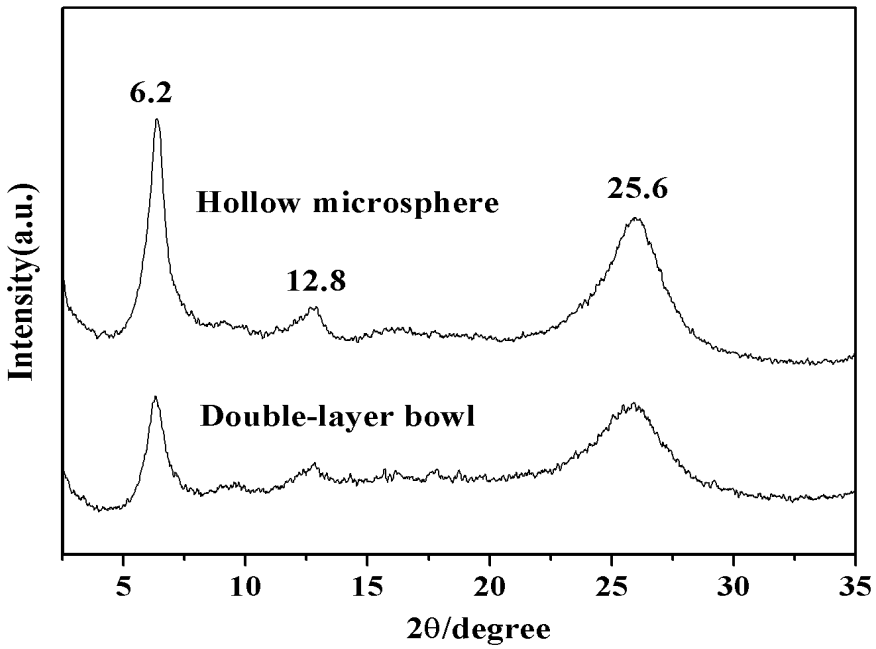

Fig. S2 XRD spectra of the hollow spheres and double-layer bowls

Three shape peaks centered at 2θ = 6.4º, 12.8 º and 25.6 º are observed in the XRD spectra of

the hollow microspheres and double-layer bowls. The peak at 2θ = 6.4º with high intensity seems to be (100) reflection of the polymer with a d-space of 13.6 Å. The peak at 2θ = 12.8º with low intensity may correspond to (200) reflection, and its d-space is about half of the (100) reflection.[1] The peak at 2θ = 25.6º with broad width can be ascribed to (020) reflection, which likely corresponds to the thiophene rings in the amorphous structures of PEDOT.[2] The varied peak intensity of the PEDOT hollow microspheres and double-layer bowls indicates the respective different orderings of the polymer chains[1].

3. XPS spectra of the as-prepared micro-structured PEDOT.

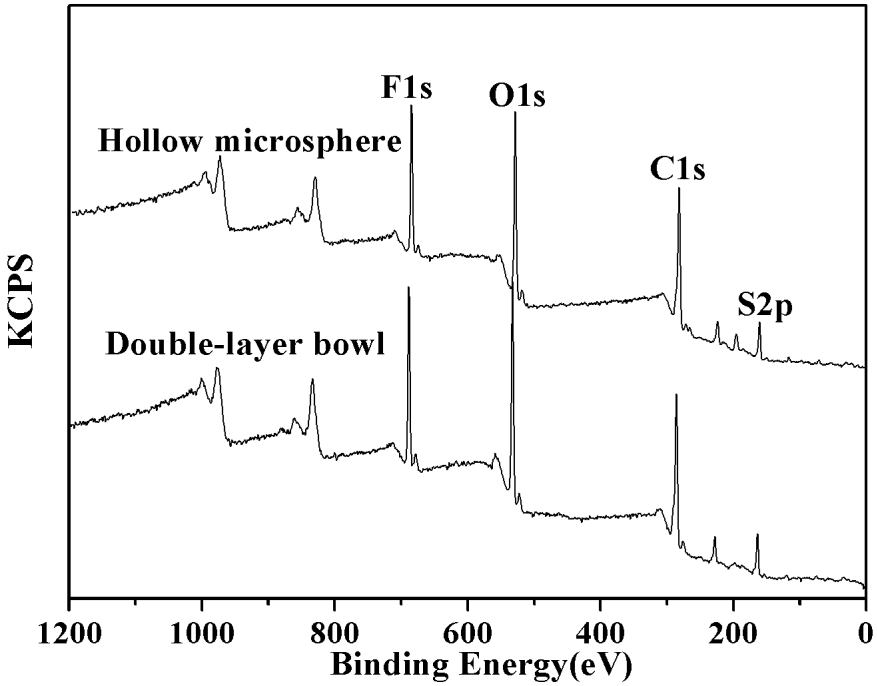

Fig. S3 XPS spectra of the hollow spheres and double-layer bowls

The X-ray photoelectron spectroscopy (XPS) analysis show that the PEDOT compositions are respectively 57.8 at.% C, 23.2 at.% O, 6.2 at.% S and 12.8 at.% F for the hollow microspheres, and 54.5 at.% C, 22.2 at.% O, 6.3 at.% S, 14.5 at.% F and 2.5 at.% for the double-layer bowls. However, difference in the element composition is observed. It noted that content of the fluorine in the double-layer bowls is slightly higher than the microspheres. From the element analysis, it's obvious that all the sulfur atoms come from thiophene rings in PEDOT, while all fluorine atoms should be attributed to the C-F chains in PFSEA. The doping levels of

PEDOT can be calculated from atomic ratios of F and S and were about 12.9% for the hollow spheres and 10.4% for the double-layer bowls at 4.0 $g.L^{-1}$ PFSEA concentrations, respectively.

4. Time course of cathodic ORR current catalyzed by as-prepared micro-structured PEDOT in acid and alkaline solutions.

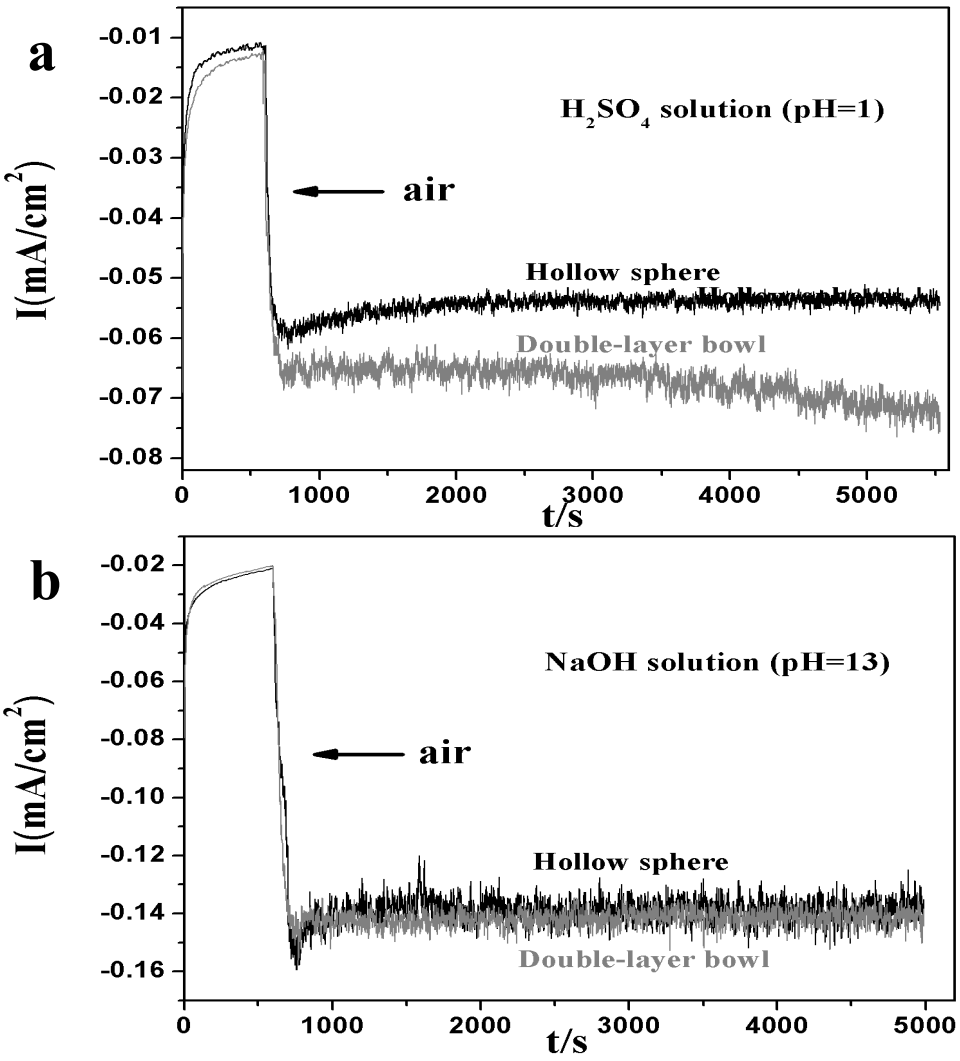

Fig. S4 I-t curves of the hollow spheres and double-layer bowls in acid (a) and alkaline (b) solutions

5. Rotating disk electrodes (RDE) voltammograms and Koutecky-Levich (K-L) plots (-0.8 V) of PEDOT micro-structures in 0.1 M PBS.

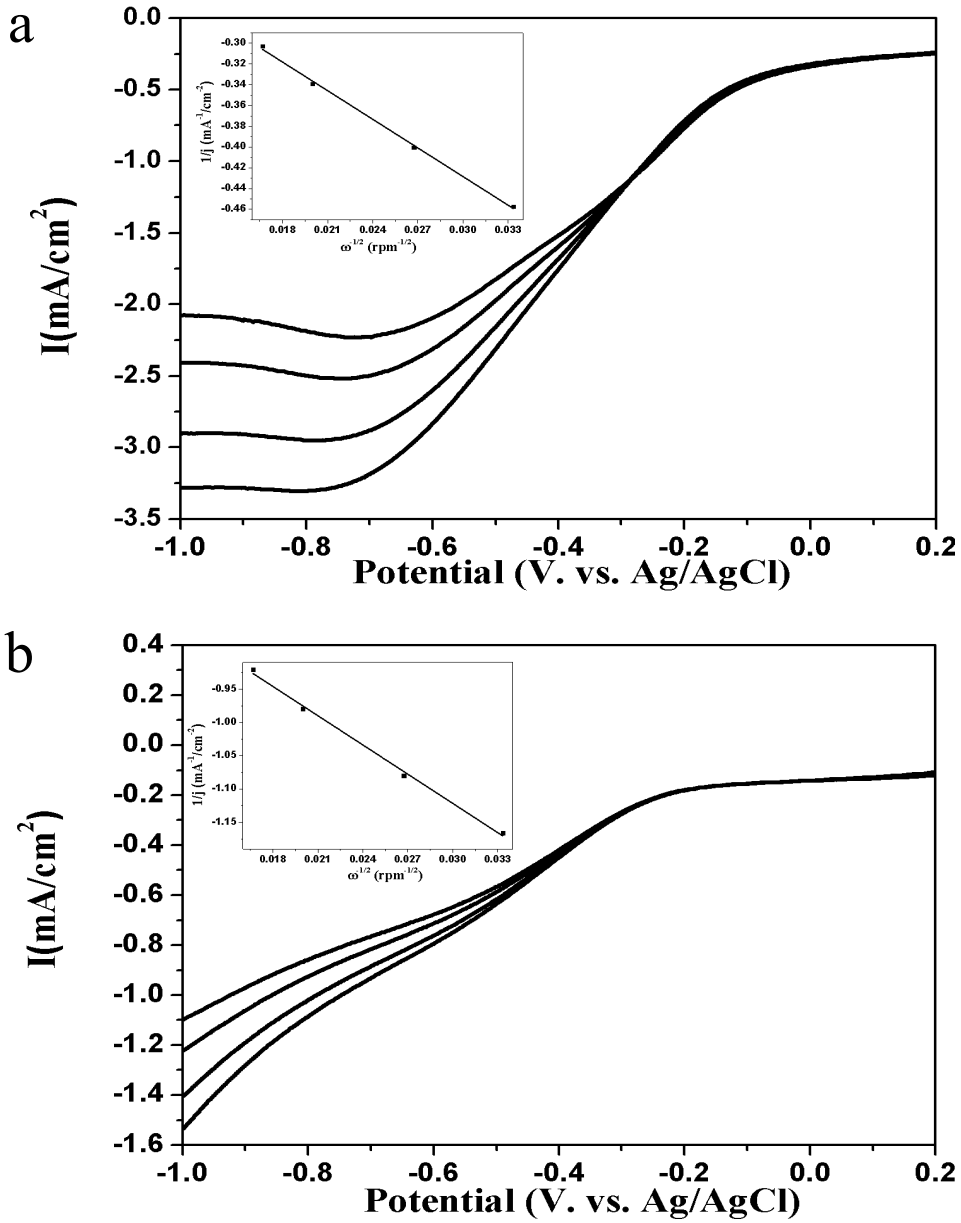

Fig. S5 RDE voltammograms for oxygen reduction of PEDOT microstructures (a) hollow spheres (b) double-layer bowls on GC electrode in O_2 saturated 0.1 M PBS solutions at a scan rate 10 $mV \cdot s^{-1}$ with different rotation rates of 900, 1400, 2500 and 3600 rpm. The insets show the Koutecky-Levich plots at the potential of -0.8V.

The calculated number of transferred electron is 3.11 for hollow spheres, which indicate a

reduction process between 2-electron and 4-elecron. The number of transferred electron for double-layer bowls is 1.96, which gives a proof of 2-electron reduction mechanism.

6. RDE voltammograms and K-L plots (-0.6 V) of PEDOT micro-structures in 0.05 M H_2SO_4.

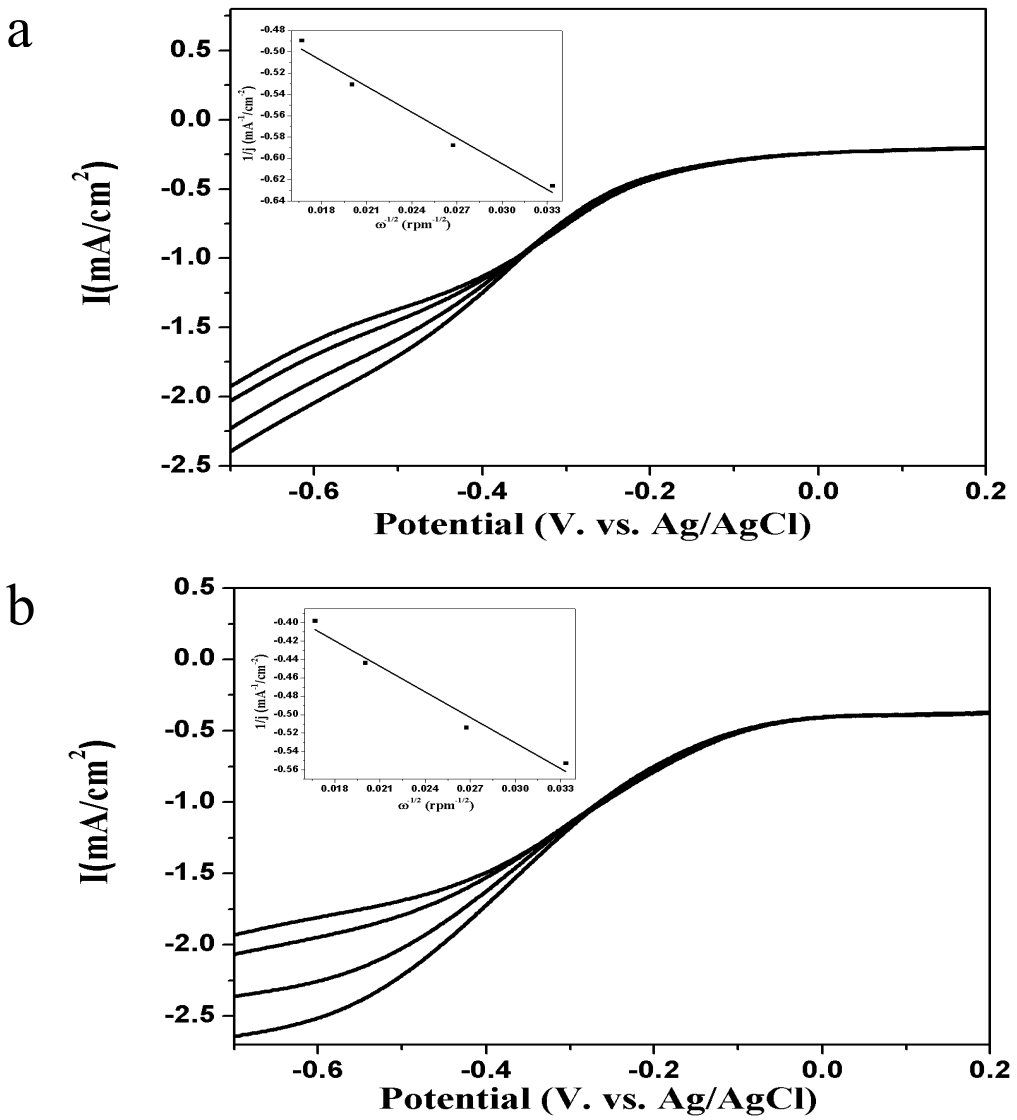

Fig. S6 RDE voltammograms for oxygen reduction of PEDOT microstructures (a) hollow spheres (b) double-layer bowls on GC electrode in O_2 saturated 0.1 M NaOH solutions at a scan rate 10 mV·s^{-1} with different rotation rates of 900, 1400, 2500 and 3600 rpm. The insets show the Koutecky-Levich plots at the potential of -0.6 V.

The calculated number of transferred electron is 3.55 for hollow spheres and 3.07 for the double-layer bowls.

Reference

1. J. W. Choi, M. G.Han, *Synthetic Met*. 2004, **141**, 293–299.
2. L. Zhang, H. Peng, *Macromolecules* 2008, **41**, 7671-7678.