

Supplementary information on Platinum nanoparticles supported on carbon nanotube coated carbon fiber as hierarchically structured catalyst layer for oxygen reduction reaction

1. Selection of parameters for electrodeposition

Present study is focused more on the effects of cluster size and loading of Pt on the ORR activity. The parameters for electrodeposition (H_2PtCl_6 concentration and potential) were selected so that the Pt-loading with time varies gradually. For example, large platinum particles were obtained for electrodeposition at -3 V (Fig. S1), which possibly may not be interesting due to high Pt-loading.

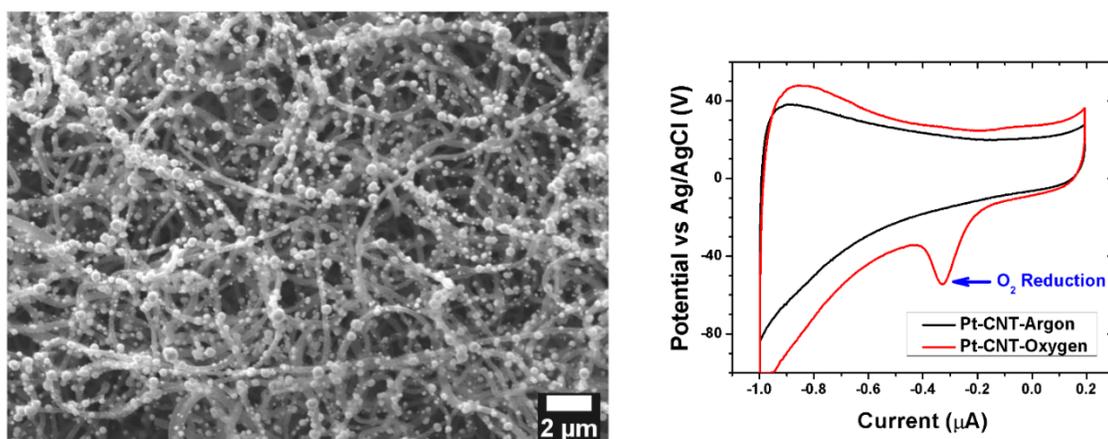


Fig. S1: SEM image and cyclic voltammetry of Pt-CNTCF electrodeposited at -3 V for electrodeposition time of 20 min.

2. Elemental analysis of Pt/CNTCF

EDX spectra of platinum coated CNTCF (Pt/CNTCF) samples synthesized at different electrodeposition times (t_{ed}) are shown in Fig. S2. With increasing t_{ed} , the fractional weight of Pt increases significantly.

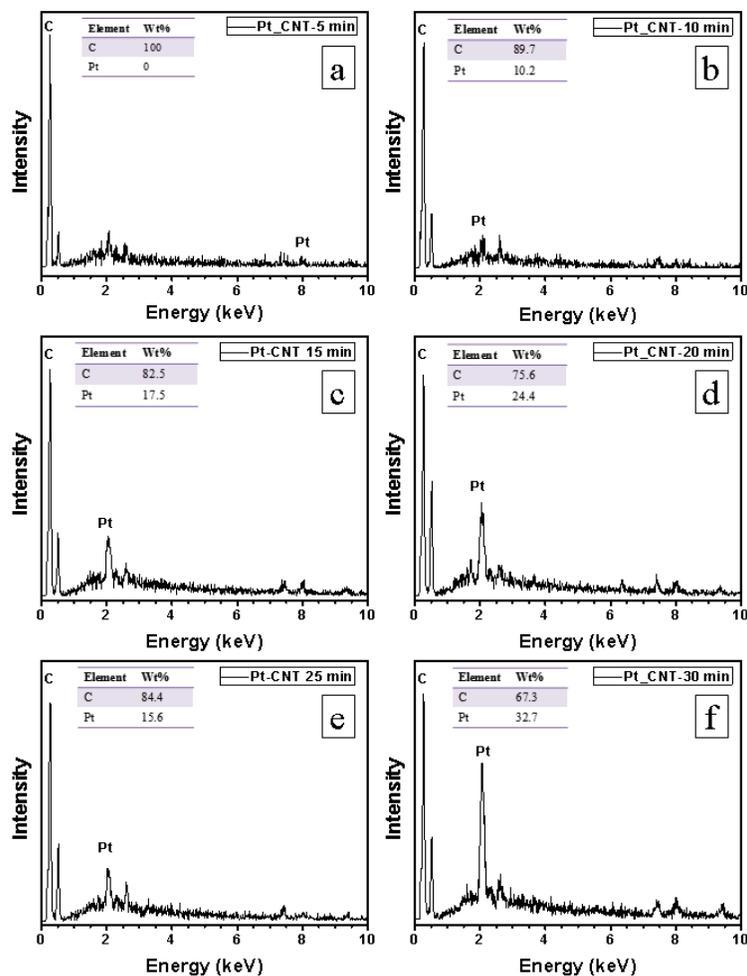


Fig. S2: EDX spectra of Pt/CNTCF synthesized with varying t_{ed} .

3. Determination of Pt-cluster size distribution:

Fig. S3 shows the SEM images and Pt-Cluster size distribution histograms of Pt/CNTCF for varying t_{ed} from 5 to 30 min. A red circle in the image shows the approximate size of the corresponding particle. With increasing t_{ed} , both the % coverage as well as the Pt-cluster size increase significantly. This leads to formation of large clusters for t_{ed} above 15 min. The variations of cluster size and % area coverage with t_{ed} are shown in table S1. The %coverage was calculated by analyzing three images for each sample. However, the average cluster size data include large number of particles from a single image, which makes them statistically more reliable.

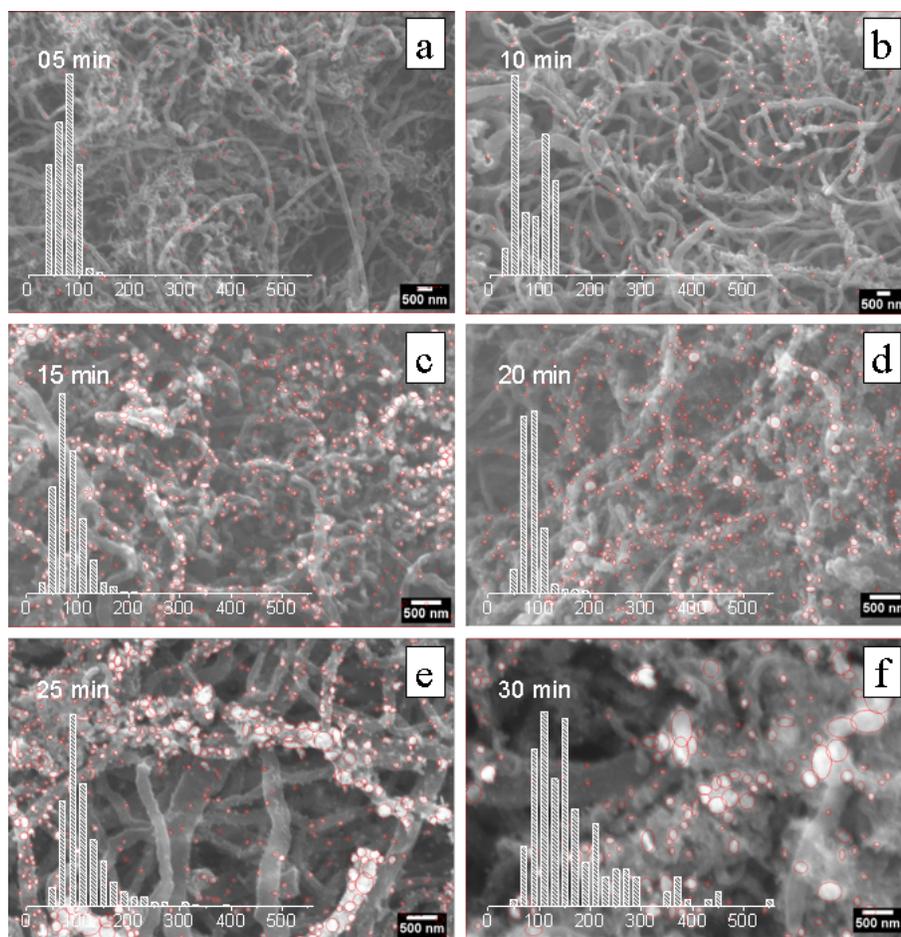


Fig. S3: SEM images and Pt-Cluster size distribution histograms of Pt/CNTCF for t_{ed} of (a) 05, (b) 10, (c) 15, (d) 20, (e) 25 and (f) 30 min. The Pt-particles are approximated to circles/ellipses.

Table S1: Variations of average Pt-cluster size and % area covered by Pt-nanoparticles with the deposition time t_{ed} .

t_{ed} (min)	Pt loading ($\mu\text{g cm}^{-2}$)	Cluster size (nm)	St. deviation (nm)	Area coverage (%)	St. deviation (nm)
5	3.8	71.4	18.8	0.5	0.1
10	5.5	81.7	32.5	2.3	2.1
15	9.3	83.0	28.0	10.9	0.7
20	11.7	85.7	22.8	11.6	3.8
25	14.3	112.9	46.9	15.5	1.5
30	15.7	166.7	86.1	15.3	4.0

4. Copper underpotential deposition (Cu upd) on Pt-CNTCF

Cu upd was also performed to estimate the electrochemical surface area of Pt-CNTCF. However, the CNTCF itself exhibits Cu stripping peak at a potential almost similar to that for Pt (Fig. S4).

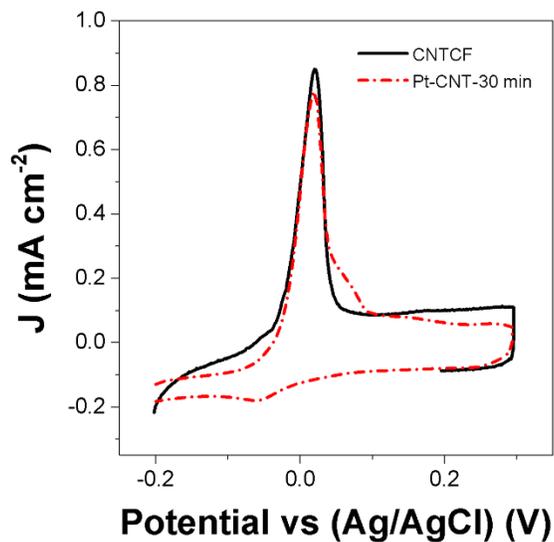


Fig. S4: Cu upd for CNTCF and Pt-CNTCF-30 min performed at a scan rate of 2 mV s⁻¹ after holding at -0.2 V for 100 s in an electrolyte consisting of 0.1 M H₂SO₄ and 2 mM CuSO₄.

5. Cyclic voltammetry in Ar saturated electrolyte

CV scans for Ar saturated 0.1 M KOH electrolyte shown in Fig. S5 exhibit no cathodic peak at ~0.4 V. The disappearance of the peak in absence of oxygen confirms its origin to be the oxygen reduction reaction.

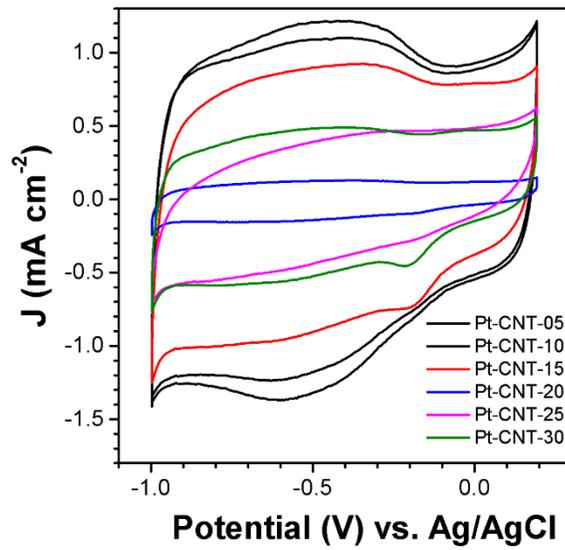


Fig. S5: CV scans of Pt/CNTCF in Ar saturated 0.1 M KOH at a scan rate of 50 mV s⁻¹.