Supporting Information

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Title: Electrochemically Reduced Graphene Oxide Multilayer Films as Metal-free Electrocatalysts for Oxygen Reduction

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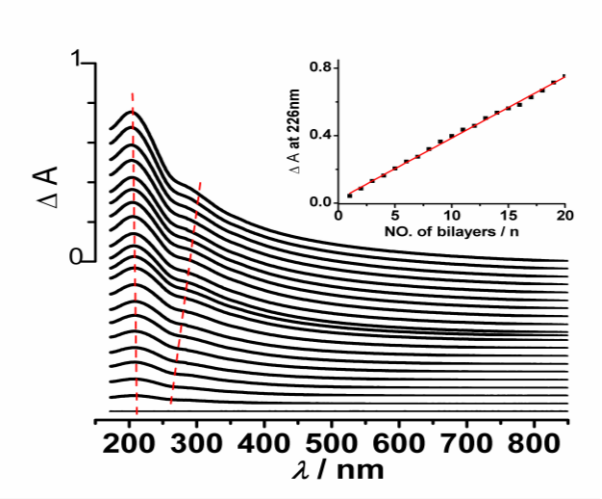

Figure S1. UV/vis absorbance spectra of $[PDDA@GO]_n$ with different numbers of bilayers from 0 to 20. Inset shows the linear relation between the absorbance at the peak and the number of bilayers.

Figure S1 shows the corresponding UV-vis absorption spectra of various nanocomposited films. The as-prepared $[PDDA@GO]_n$ based nanocomposite films stay stably, as revealed by the fact that no detectable change of the UV-vis spectra occurred during long time storage at room temperature.

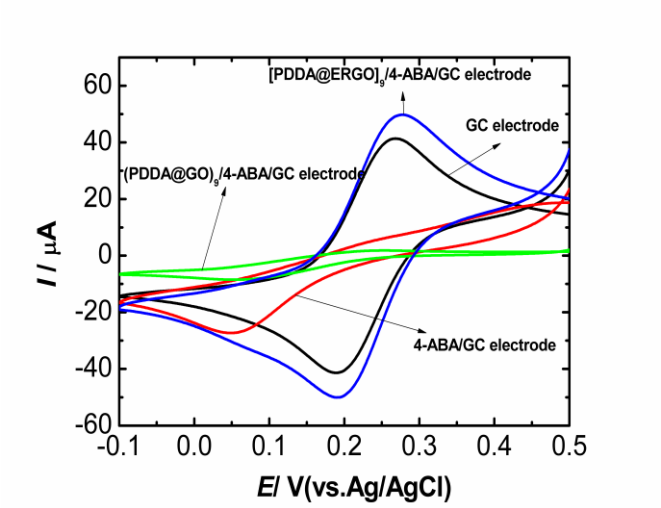

Figure S2. CV curves recorded at GC, 4-ABA/GC, $[PDDA@GO]_9$/4-ABA/GC, and $[PDDA@ERGO]_9$/4-ABA/GC electrodes for 5 mM $[Fe(CN)_6]^{3-/4-}$ in 0.1 M KCl solution at the scan rate of 5 mV s^{-1}.

The redox probe $[Fe(CN)_6]^{3-/4-}$ is sensitive to surface chemistry of carbon nanomaterials. In figure S2, the current of the $[Fe(CN)_6]^{3-/4-}$ probe varied at different modified electrodes. The bare GC electrode showed the reversible electrochemical response for the $[Fe(CN)_6]^{3-/4-}$ probe. After modified with 4-ABA, the GC electrode was negatively charged due to the ionization of -COOH, which generated the repulsive force over the negatively charged $[Fe(CN)_6]^{3-/4-}$ probe and blocked its electron transfer. When the electrode fabricated with $[PDDA@GO]_9$ film by LBL assembly method, the current was seriously suppressed. This result indicates that the heterogeneous electron transfer was inhibited on the insulating GO. After the electrochemical reduction of as-prepared multilayer films, the electrochemical behavior of the $[Fe(CN)_6]^{3-/4-}$ probe was significantly enhanced due to the improved conductivity and reactive edge defects on ERGO, which was an obvious evidence of the change of GO into ERGO.

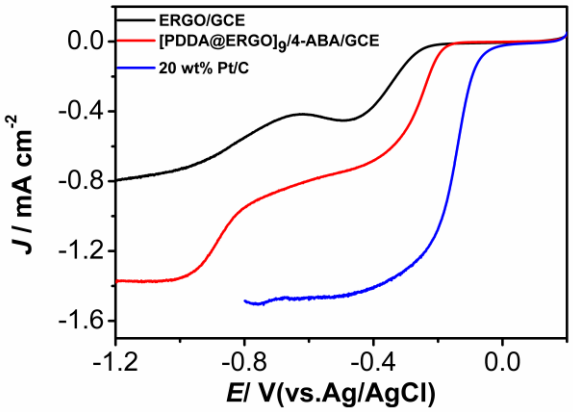

Figure S3. RDE linear sweep vltammograms for oxygen reduction on the ERGO/GC and $[PDDA@ERGO]_9$/4-ABA/GC electrodes and 20 wt% Pt/C in air-saturated 0.1 M KOH at a rotation rate of 2500 rpm. Scan rate: 10 mV s^{-1}.

As shown in Figure S3, compared to the ERGO/GC electrode, which was prepared by drop-casting 25 μl 0.1 mg/ml GO onto the GC electrode and subsequent an electrochemical reduction procedure, the $[PDDA@ERGO]_9$ film showed more positive onset potential and higher current density of ORR, which suggested the positive effect of PDDA on the ORR activity. Though our prepared $[PDDA@ERGO]_9$ multilayer film does not present both the onset potential and current density as good as that of the commercial Pt/C electrocatalyst (Figure S3), the high selectivity and stability make the $[PDDA@ERGO]_n$ film a promising inexpensive cathodic material for fuel cells.

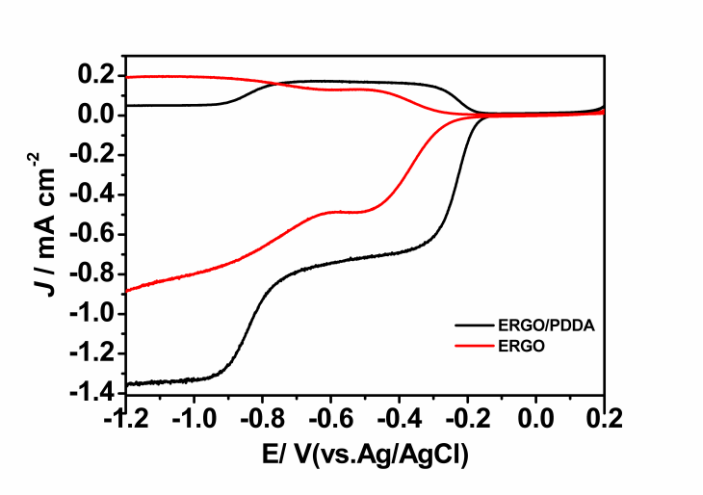

Figure S4. RRDE of ERGO/GC and (ERGO/PDDA)/GC electrodes in air-saturated 0.1 M KOH with the rotation rate of 2500 rpm.

The influence from PDDA was further investigated by a direct attachment PDDA onto the ERGO film (See Figure S4). The resulted material also shows an augment of the catalytic activity towards ORR. This indicates the key role of PDDA in these films towards oxygen reduction reaction.

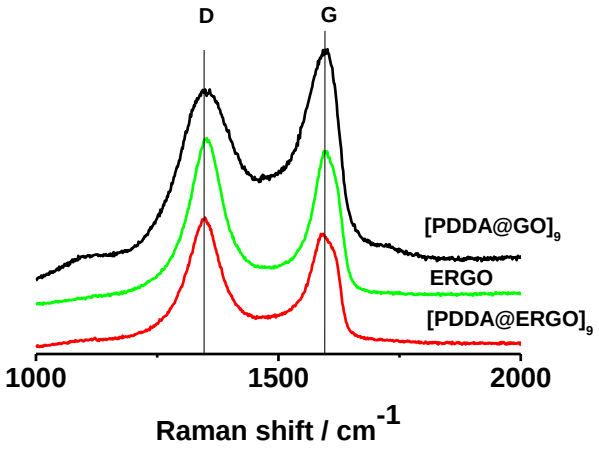

Figure S5. The Raman spectra of $[PDDA@ERGO]_9$, pure ERGO and $[PDDA@GO]_9$.

Figure S5 shows the Raman spectra for $[PDDA@GO]_9$, $[PDDA@ERGO]_9$ and pure ERGO films. The $[PDDA@GO]_9$ film displays a strong G band at 1594 cm^{-1} and a weak D band at 1351 cm^{-1}. The D/G intensity ratio increased from $[PDDA@GO]_9$ to $[PDDA@ERGO]_9$ film, suggesting a decrease of sp^2 domain induced by electrochemical reduction. G band of $[PDDA@ERGO]_9$ film shifts downward to 1591 cm^{-1}, which is π-electron conjugation within the sp^2 carbon framework. The G band of graphene down-shifted from 1594 to 1591 cm^{-1}, further indicating no occurrence of electron transfer from the ERGO to the adsorbed PDDA.