Metal-Free Selenium Doped Carbon Nanotube/Graphene Networks as a Synergistically Improved Cathode Catalyst for Oxygen Reduction Reaction

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Supporting Information

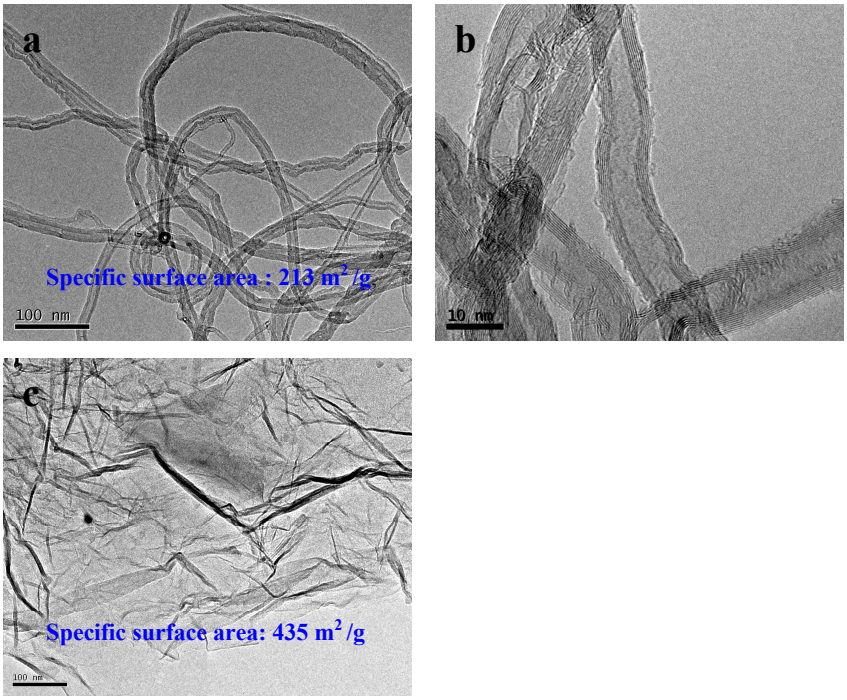

Figure S1 TEM images of CNTs (a, b) and GO (c)

S2 Electrochemical impedance spectroscopy measurements

The changes of interfacial electron-transfer properties resulting from changes of interfacial structures can be monitored by electrochemical impedance spectroscopy (EIS). It can be seen as shown in Figure S2 that all the Se-doped carbon materials (Se-CNTs-900, Se-graphene-900, and Se-CNTs-graphene-900) have the smaller value of the interfacial charge-transfer resistance than those of the corresponding carbon materials without dopants (CNTs-900, Graphene-900, and CNTs-graphene-900). Moreover, from Figure S2, we also find that the value of the interfacial charge-transfer resistance on these CNTs/graphene composites whether with or without Se dopant are much smaller than that of the corresponding single CNTs or graphene. The observations above-mentioned confirm that both Se doping and combing CNTs with graphene can accelerate the electron transfer of electrochemical interface.

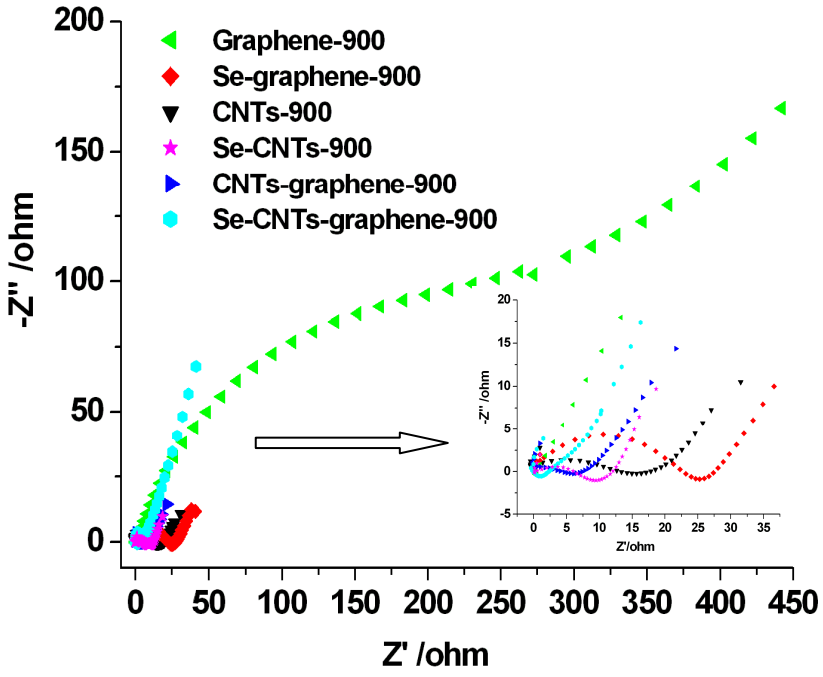

Figure S2 Electrochemical impedance spectroscopy plots of various carbon materials

S3 Rotating-disk voltammetry measurements

To further study the ORR electrochemical procedures of Se-CNTs-graphene-900, we performed rotating-disk electrode (RDE). The RDE current-potential curves at various rotating speeds are shown in Figure S3a .The limited diffusion currents are dependent on the rotating rates. The number of electrons involved in the ORR can be calculated from the Koutecky-Levich (K-L) equation:

(1) $J^{-1}=J_L^{-1}+J_K^{-1}=(B\omega^{1/2})^{-1}+ J_K^{-1}$

(2) $B=0.62nFC_0(D_0)^{2/3}v^{-1/6}$

(3) $B=nFkC0$

(4) $J_K^{-1} = J^{-1} -(0.62nFC_0(D_0)^{2/3}v^{-1/6}\omega^{1/2})^{-1}$.

Where J is the measured current density, J_K and J_L are the kinetic- and diffusion-limiting current densities, ω is the angular velocity of the disk (ω=2pN, N is the linear rotation speed), n is the overall number of electrons transferred in oxygen reduction, F is the Faraday constant (F=96485 $C\cdot mol^{-1}$), C_0 is the bulk concentration of O_2, (C_0 =$1.2\times10^{-6}mol\cdot cm^{-3}$),v is the kinematic viscosity of the electrolyte (v=0.01 $cm^2\cdot s^{-1}$), D_0 is the diffusion coefficient of O_2 in 0.1 M KOH (1.9×10^{-5} $cm^2\cdot s^{-1}$). According to Equations (1) and (2), the number of electrons transferred (n) can be calculated to be 3.95 at -0.60 V, which indicates that the Se-CNTs-graphene-900 lead to a four-electron-transfer reaction to reduce directly oxygen into OH^-. The calculated J_k value is 10.04 mA•cm^{-2} at –0.40 V from equation (4).

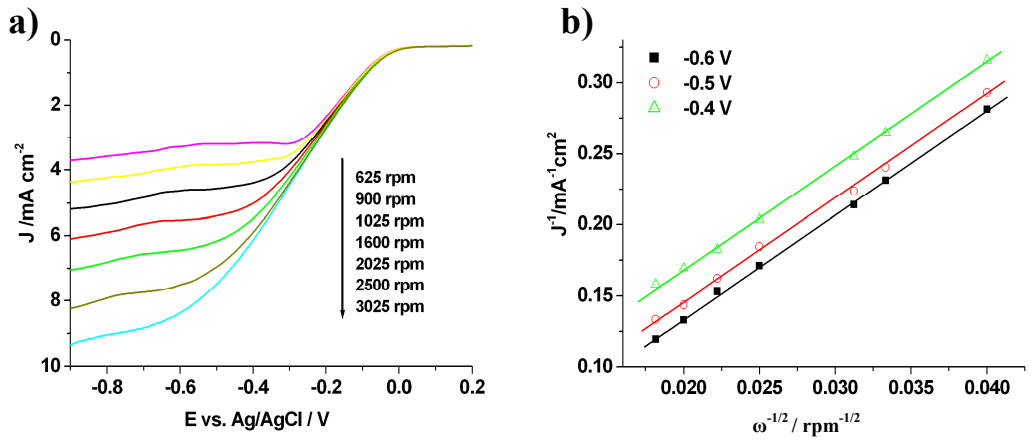

Figure S3 (a) Rotating-disk voltammograms recorded for the Se-CNTs-graphene-900 electrode in an O_2-saturated 0.1M solution of KOH at a scan rate of 10 mV s^{-1} and different rotation rates. (b,) Koutecky–Levich plot of J^{-1} versus $\omega^{-1/2}$ at different electrode potentials and the experimental data were obtained from (Figure S3a).

S4 Control experiments

As a control experiment, we investigated the influences of the annealing temperature and the mass ratios of carbon materials and DDS on the electrocatalytic properties of these carbon materials. The contents of Se in these Se-doped carbon materials can be adjusted by varying the mass ratios of carbon materials and DDS. Figure S4a show the CV measurement curves for these Se-CNTs obtained from the mass ratios of CNTs and DDS of 4:2 at 800-1000Ⅲ. From Figure S4a, it can be found that the Se-CNTs obtained at 900Ⅲ shows the highest peak current and most positive ORR peak potential of all the samples. Figure S4b show the CV measurement curves for these Se-CNTs obtained from the different mass ratios of CNTs and DDS at 900Ⅲ. From Figure S4b, it can be found that the mass ratios of ratios CNTs and DDS of 4:2 is the optimum. Furthermore, Figure S4c shows that the optimum mass ratio of ratios of graphene and DDS is also 4:2. More importantly, compared to these Figures (Figure S4a, b, c and d), we find finally that the Se-CNTs-graphene obtained from the mass ratios of CNTs, GO and DDS of 4:4:4 at 900°C holds the most outstanding ORR activity amongst all the carbon materials.

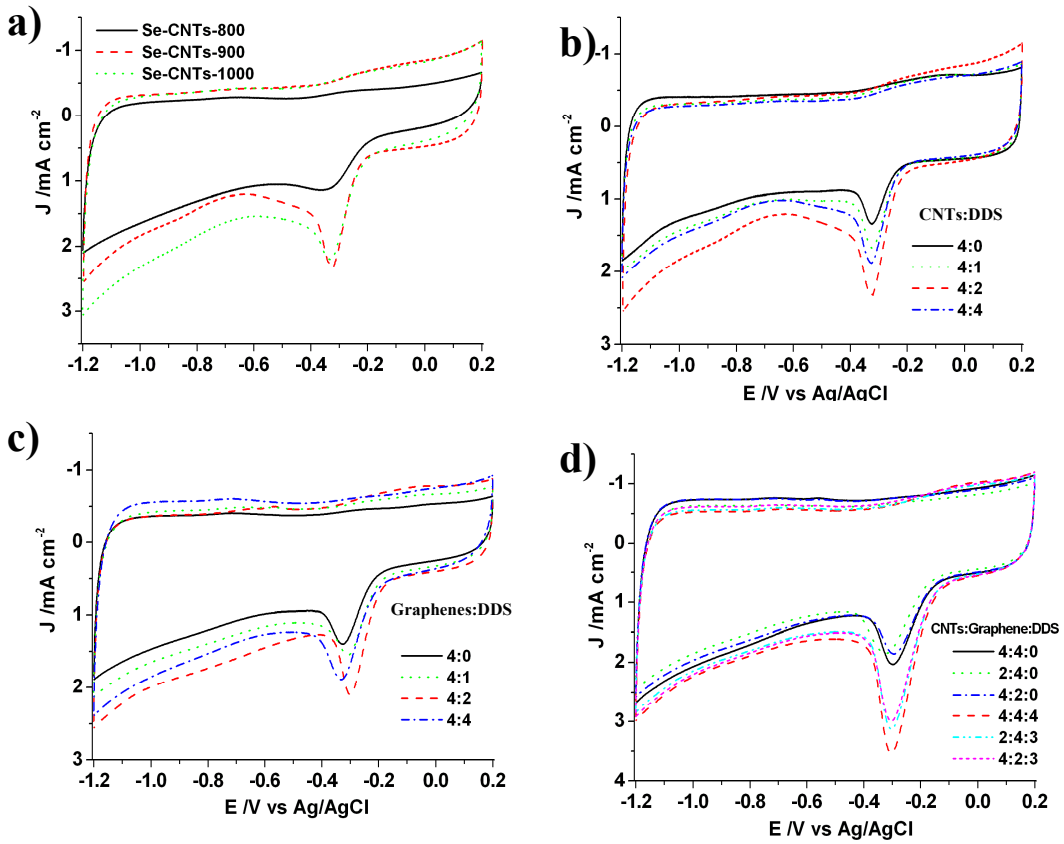

Figure S4 Cyclic voltammograms for Se-CNTs obtained at different temperatures (a) and mass ratios of CNTs and DDS (b), Se-graphene obtained at different the mass ratios of graphene and DDS (c), and Se-CNTs-graphene at different mass ratios of CNTs, GO and DDS (d)

Table S1 Physical parameters, electrochemical properties for various carbon materials obtained at various annealing temperature and mass ratios of carbon materials and DDS

Number	Samples	Annealing temperature (℃)	DDS:CNTs:GO	Se content (wt.%)	Peak Potential (V)	Peak current density, (mA cm^{-2})
1	Se-CNTs-800	800	2:4:0	1.26	-0.35	0.75
2	Se-CNTs-900	900	2:4:0	1.03	-0.32	1.76
3	Se-CNTs-1000	1000	2:4:0	0.98	-0.32	1.52
4	CNTs-900	900	0:4:0	0	-0.33	0.93
5	Se-CNTs-900-1	900	1:4:0	0.84	-0.32	1.08
6	Se-CNTs-900-2	900	2:4:0	1.03	-0.32	1.76
7	Se-CNTs-900-3	900	4:4:0	1.16	-0.32	1.45
8	Graphene-900	900	0:0:4	0	-0.32	0.92
9	Se-graphene-900-1	900	1:0:4	0.83	-0.31	1.01
10	Se-graphene-900-2	900	2:0:4	1.09	-0.30	1.62
11	Se-graphene-900-3	900	4:0:4	1.18	-0.33	1.23
12	CNTs-graphene-900-1	900	4:4:0	0	-0.30	1.41
13	CNTs-graphene-900-2	900	2:4:0	0	-0.32	1.15
14	CNTs-graphene-900-3	900	4:2:0	0	-0.30	1.08
15	Se-CNTs-graphene-900-1	900	4:4:4	1.05	-0.29	2.41
16	Se-CNTs-graphene-900-2	900	2:4:3	0.85	-0.30	2.15
17	Se-CNTs-graphene-900-3	900	4:2:3	0.86	-0.30	2.11