Electronic Supplementary Information for

Germanium and Phosphorus Co-Doped Carbon Nanotubes with High Electrocatalytic Activity for Oxygen Reduction Reaction

Qianqian Li ‡[1], Fang Yuan ‡[1], Chunyun Yan[1], Jianjie Zhu[1], Jin Sun*[1], Yijun Wang [1], Jun Ren*[2] Xilin She*[1]

1 School of Environmental Science and Engineering, Collaborative Innovation Centre for Marine Biomass Fibres, Materials and Textiles of Shandong Province; Qingdao University, Qingdao, P R China.

2 School of Chemical and Environmental Engineering, North University of China, Taiyuan, P R China.

E-mail: xlshe@qdu.edu.cn. sunjin@qdu.edu.cn; jun.ren@nuc.edu.cn

Theoretical calculation details

We performed first-principles calculations based on spin-polarized DFT. The Vienna Ab initio Simulation Package (VASP 5.2) is used to solve Kohn-Sham equations with periodic boundary conditions and a plane wave basis set.[1-2] Electron-ion interactions were described by projector-augmented wave (PAW) potentials;[3,4] exchange and correlation energies were also calculated using the Perdew-Burke-Ernzerhof form of the spin-polarized generalized gradient approximation (GGA-PBE).[5,6] We used a kinetic energy cutoff of 500 eV for all calculations, and the convergence threshold was set to 10^{-5} eV in energy and 10^{-3} eV/Å in force, and cell dimensions along the z direction were 12 Å to avoid interaction between layers. The Monkhorst−Pack k-point grids (1×1×2) are employed for Brillouin zone integration for all the structures, using approximately same k-point density for reciprocal cells of different sizes. In the present work, we have taken a (8, 0) zigzag nanotube having length twice of its lattice constant for the work function of Ge-P-CNTs with different doping-geometries. It has total 64 C atoms and is placed in a 15 Å × 15 Å × 8.572 Å tetragonal supercell. The equilibrium configurations were determined by relaxation of all atoms in the supercell.

The stability of various doping models is evaluated by calculating their formation energies (E_f) as follows,

$$E_f = E_D - E_G + \Delta n_C \mu_C - \Delta n_P \mu_P - \Delta n_{Ge} \mu_{Ge} \quad (1)$$

where E_D and E_G are the energies of doped and pristine CNT (8, 0), respectively, μ_i is the chemical potential of atomic species i (i = C, P and Ge), and Δn_i is the difference of atiomic species i in the doped and pristine CNT (8,0). Here μ_C, μ_P and μ_{Ge} are referred to the energy of the C atom in pristine CNT (8, 0), the energy of the P atom coming from red phosphorus unit cell, and the energy of the Ge atom in bulk, respectively.

According to our computation results shown in Table S1, single P doped CNT (8, 0) is the most stable configuration and its formation energy is lower than the other Ge-P-CNTs system in pristine CNT. The work function of CNT (8, 0) in our work has been calculated to be 4.46 eV, which is closed to the previous study. [7]

Table S1. The calculated formation energies (in eV) of all doped CNT(8, 0) configurations.

	P-CNT	Ge-CNT	P-Ge-CNT	2P-Ge-CNT	3P-Ge-CNT	4P-Ge-CNT	Pristine CNT
E_f/eV	1.75	3.86	4.31	4.43	4.95	5.81	—
Workfunction/eV	4.48	4.72	4.77	4.39	4.28	4.24	4.46

References

1 G. Kresse and J. Hafner, *Physical Review B*, 1993, **47**, 558.
2 G. Kresse and J. Furthmuller, *Physical Review B*, 1996, **54**, 11169-11186.
3 P.E. Blochl, *Physical Review B*, 1994, **50**, 17953-17979.
4 G. Kresse and D. Joubert, *Physical Review B*, 1999, **59**, 1758-1775.
5 J.P. Perdew, K. Burke and M. Ernzerhof, *Physical Review Letters*, 1996, **77**, 3865-3868.
6 J. P. Perdew, K. Burke and M. Ernzerhof, *Physical Review Letters*, 1997, **78**, 1396-1401.
7 W. S. Su, T. C. Leung and C. T. Chan, *Physical Review B*, 2007, **76**, 235413(1)-(8).

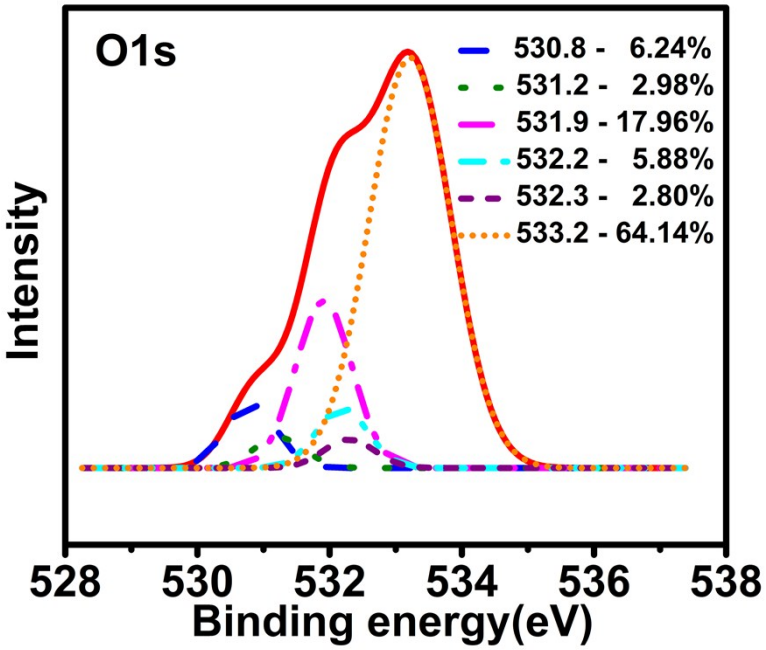

Fig. S1 the deconvoluted XPS O1s spectra for Ge-P-CNTs-2.

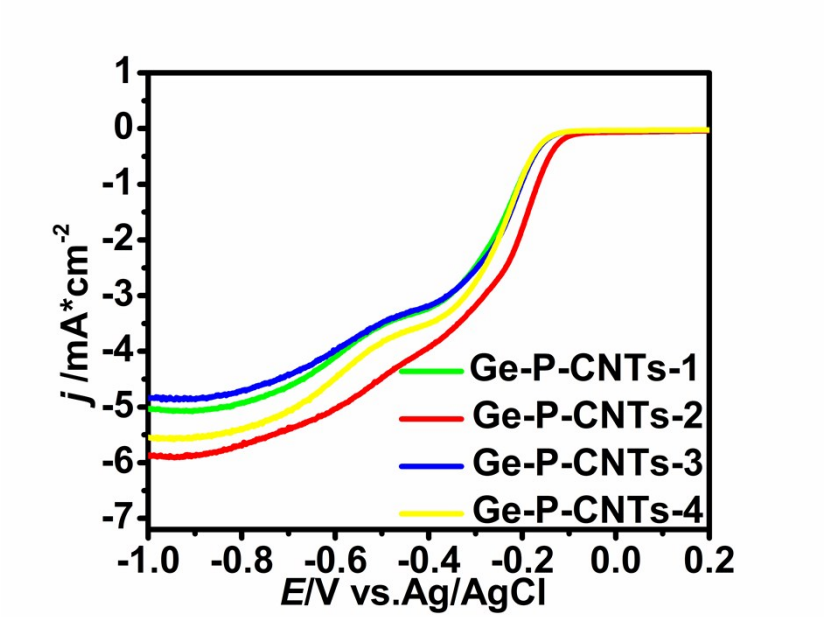

Fig. S2 LSV curves for various materials in O_2-saturated 0.1 M solution of KOH with a rotation rate of 1600 rpm.

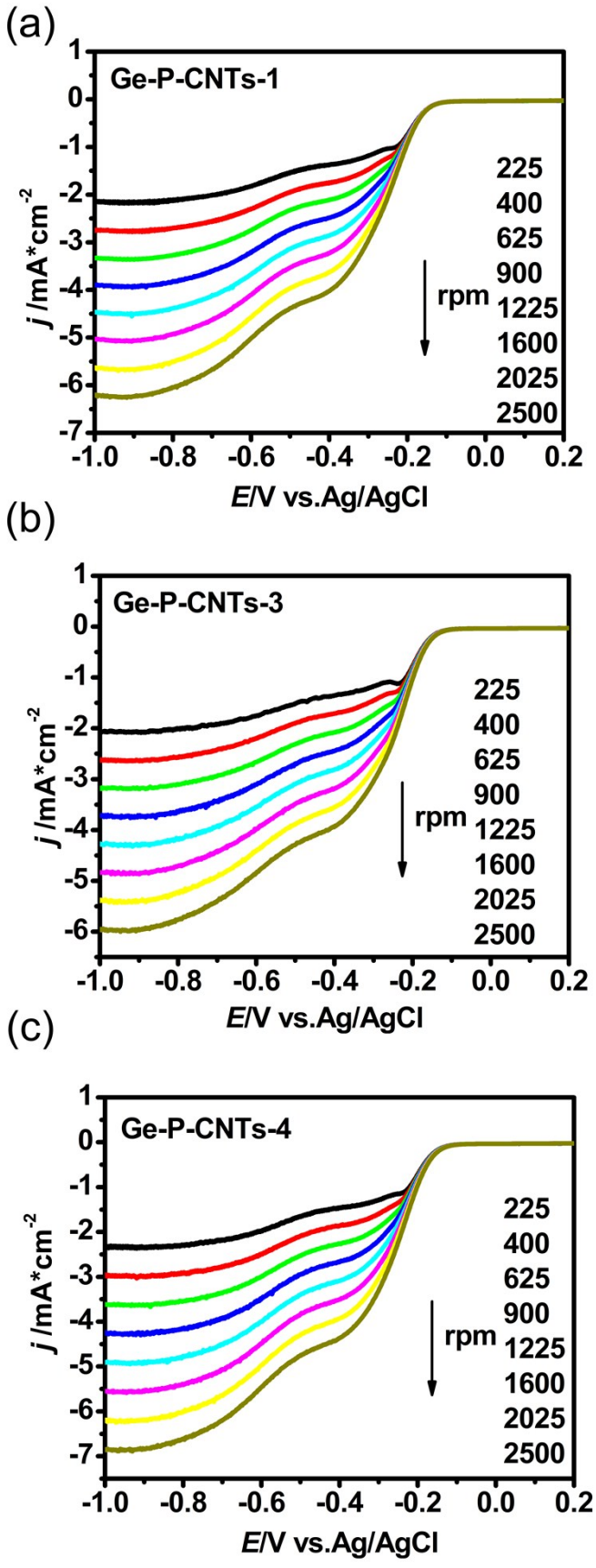

Fig. S3 LSV curves for the Ge-P-CNTs-1, Ge-P-CNTs-3 and Ge-P-CNTs-4 at various rotating speeds.

Table S2 The electron-transfer numbers obtained from K-L plots at different potentials for Ge-P-CNTs-1, Ge-P-CNTs-2, Ge-P-CNTs-3, Ge-P-CNTs-4.

	-0.30 V	**-0.40 V**	**-0.475 V**	**-0.50 V**	**-0.70 V**	**-1.0 V**
Ge-P-CNTs-1	2.6	2.8	3.0	3.2	3.8	3.9
Ge-P-CNTs-2	3.1	3.5	3.8	3.9	4.0	4.0
Ge-P-CNTs-3	2.6	2.8	3.1	3.1	3.6	3.8
Ge-P-CNTs-4	2.8	2.9	3.2	3.4	3.9	3.9