Supplementary Information

1. Experimental Section

1.1 Preparation of materials

In a typical experiment, 0.05 g of $FeMo/Al_2O_3$ in quartz boat was put in the quartz tube loaded in a tubular furnace and 120 sccm Ar flow and 40 sccm H_2 were introduced. After the temperature of the hot zone of the quartz tube arrived to 700 ^oC, 10 mL of 3-aminopropyltriethoxysilane was injected in the vicinity of the hot zone of the quartz tube at a flow rate of 3 ml/h. After the liquid was conveyed into the quartz tube completely, the tubular furnace continued to be kept at 700 ^oC for 30 minutes to make 3-aminopropyltriethoxysilane pyrolysis absolutely. And then the tubular furnace was allowed to cool down to the room temperature with a flow rate of 80 sccm Ar and 20 sccm H_2. When the system was cold, the resulting sample donated as Si,N-CNTs was collected from quartz boats. N-doped carbon nanotubes (N-CNTs) and pure carbon nanotubes were prepared by the same method using ammonia as N precursor and xylene as C precursor. The Si-doped and pure carbon nanospheres (Si-CNSs and CNSs) were synthesized by the same method using dimethylsilicone oil and xylene at 1000 ^oC.

The commercially available Pt-C (47.6 wt% on Vulcan XC-72) catalyst was purchased from BASF Fuel Cell, Inc., USA. All chemicals were purchased and used without any further purification.

1.2 Electrode preparation and electrochemical experiments

The pretreatment procedures of glass carbon electrode (5.0 mm in diameter) were as follows: prior to use, the electrodes were polished mechanically with aluminite powder on an abrasive paper to obtain a mirror-like surface, washed with ethanol and de-ionized water by

sonication for 5 min and dried in a desiccator. 1.5 mg of each grinded sample was dispersed in 0.5 ml of solvent mixture of Nafion (5 %), de-ionized water and acetone (V: V: V=15: 385: 100) by sonication. 10.0 µl suspension was dropped onto the glassy carbon electrode surface. And the electrode was dried at room temperature for 2 h in a desiccator before the electrochemical measurements.

Electrochemical experiments were carried out at room temperature in a three-electrode cell connected to an electrochemical analyzer (Pine Research Instrumentation, USA). Carbon nanospheres/GC, Silicon-doped carbon nanospheres/GC, or commercial Pt/C/GC was used as the working electrode, an Ag/AgCl with saturated KCl as reference electrode, and a Pt electrode or a graphite carbon as counter electrode. All potentials were measured and reported vs the potential of Ag/AgCl electrode. The cyclic voltammetry (CV) experiments were conducted in oxygen-saturated 0.1 M KOH solution with or without 1.0 M CH_3OH in the potential range from +0.2 to -1.0 V at room temperature. The linear sweep voltammetry (LSV) measurements were performed in the oxygen-saturated 0.1 M KOH solution at the scan rate of 10 mV/s.

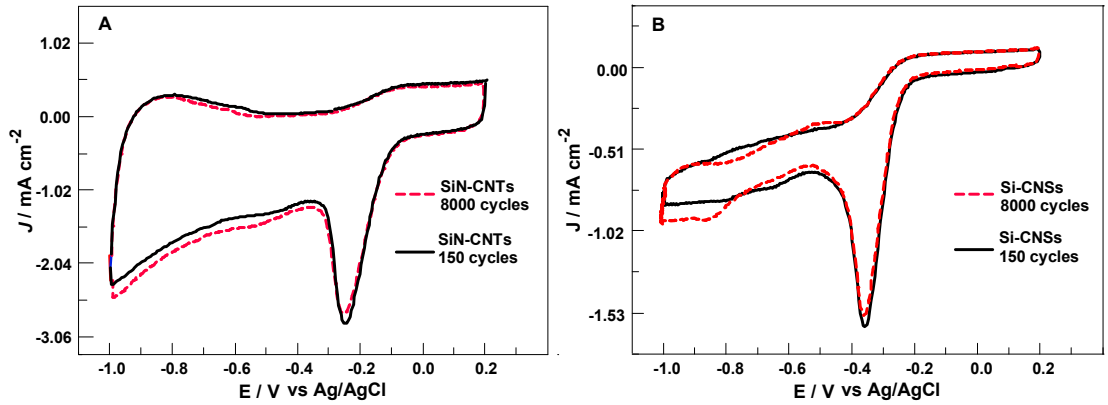


Fig. S1. The CVs of the 150th and 8000th cycles of the SiN-CNTs (A) and Si-CNSs (B) in an oxygen-saturated 0.1 M KOH solution in the three-electrode system with a graphite

carbon as counter electrode.

1.3 Characterizations

The morphologies of the samples and elemental compositions were characterized by scanning electron microscopy (SEM) (MERLIN compact) and transmission electron microscopy (TEM) (JEOL, JEM2010) operating at 200 kV. Elemental compositions of P-doped graphite were analyzed by Energy dispersive spectrometer (EDS) and X-ray photoelectron spectroscopic. XPS measurements were performed on a Thermo Scientific ESCALAB 250XI using Al Kα radiation, and the C1s peak at 284.8 eV was taken as internal standard.

Table S1. Carbon, oxygen, silicon and nitrogen contents in SiN-CNTs and Si-CNSs analyzed by EDS

Samples	C (at.%)	O (at.%)	Si (at.%)	N (at.%)
SiN-CNTs	84.34	8.40	3.98	1.52
Si-CNSs	72.37	11.62	14.91	-

2. Electron-Transfer Numbers and DFT Calculations

2.1 Electron-transfer numbers calculation

The Koutecky-Levich equation (Equation1) [S1]:

$$I^{-1} = I_k^{-1} + (0.62nFCD^{2/3}v^{-1/6}\omega^{1/2})^{-1} \quad (1)$$

In equation (1), I is the measured current density, I_k is the kinetic current density of ORR, n is the overall number of electron transferred in oxygen reduction, F is the Faraday

constant (F=96485 C mol^{-1}), C is the bulk concentration of O_2, D is the diffusion coefficient of O_2 in the KOH electrolyte, v is the kinetic viscosity of the electrolyte, and ω is the angular velocity of the disk (ω=2πN, N is the linear rotation speed). The values of C=1.2 × 10^{-3} mol L^{-1}, D=1.9 × 10^{-5} cm^2 s^{-1}, v=0.01 cm^2 s^{-1} in 0.1M KOH solution were used.

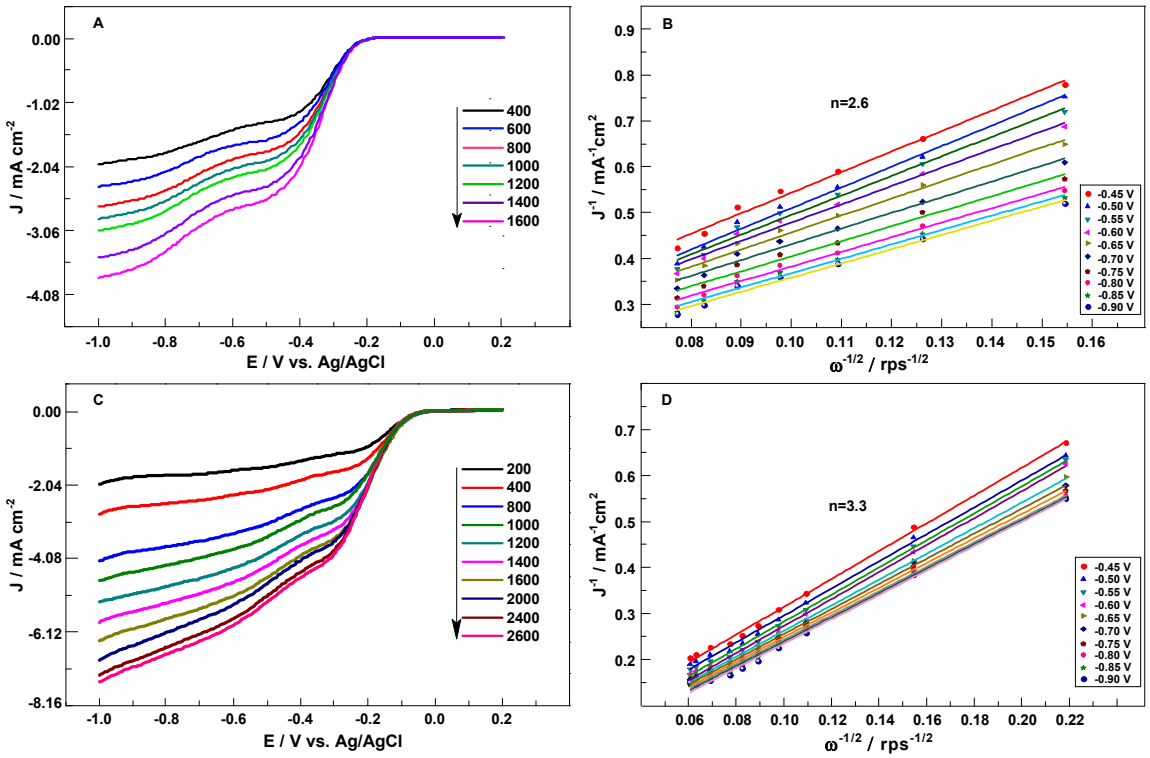
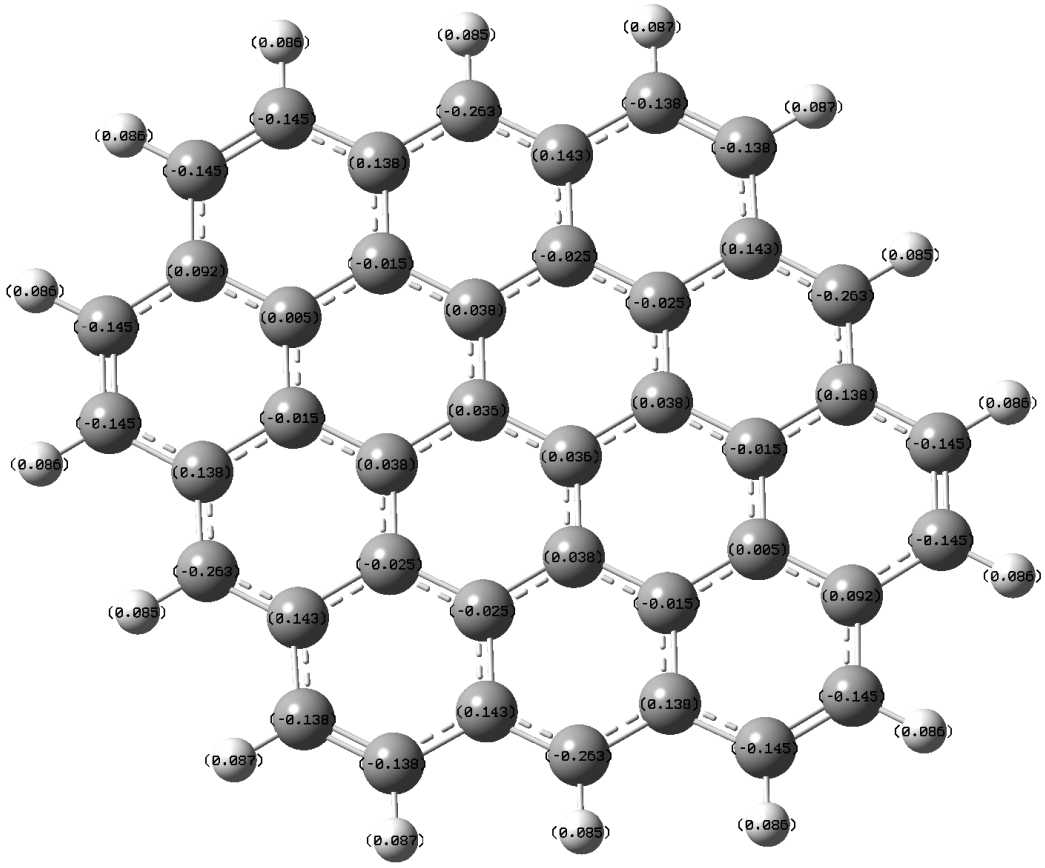


Fig. S2 Koutecky-Levich plots of J^{-1} versus $\omega^{-1/2}$ at different electrode potentials of SiN-CNTs (A, B) and Si-CNSs (C, D) obtained from the LSVs at different rotating speeds from 200 rpm to 2600 rpm.

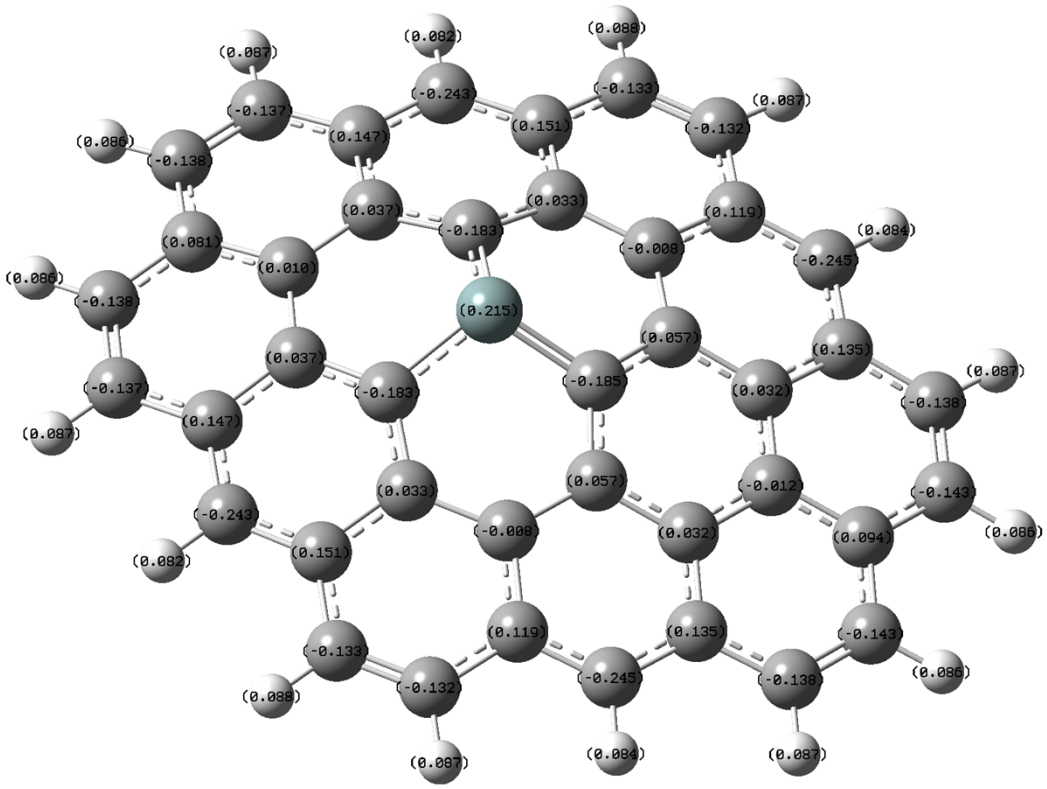
2.2 DFT calculation

To gain insight into the electrocatalytic activity of the Si-doped graphitic carbon material for the ORR, quantum chemical calculations on the basis of hybrid DFT calculations were performed by using Gaussian 09 electronic structure program. All the calculations were carried out using UB3LYP/6-31G(d, p) level of theory with all atoms fully relaxed. The cluster models for pure and Si-and Si, N-doped graphenes shown in Fig. S3 were constructed.

The models contain 14 hexagonal rings terminated with C-H bonds, which have been previously adopted for investigation of ORR on graphene doped with nitrogen or boron.[S2-S3] For Si-doped graphene, the graphene model with one Si and two Si atoms were considered.



(A)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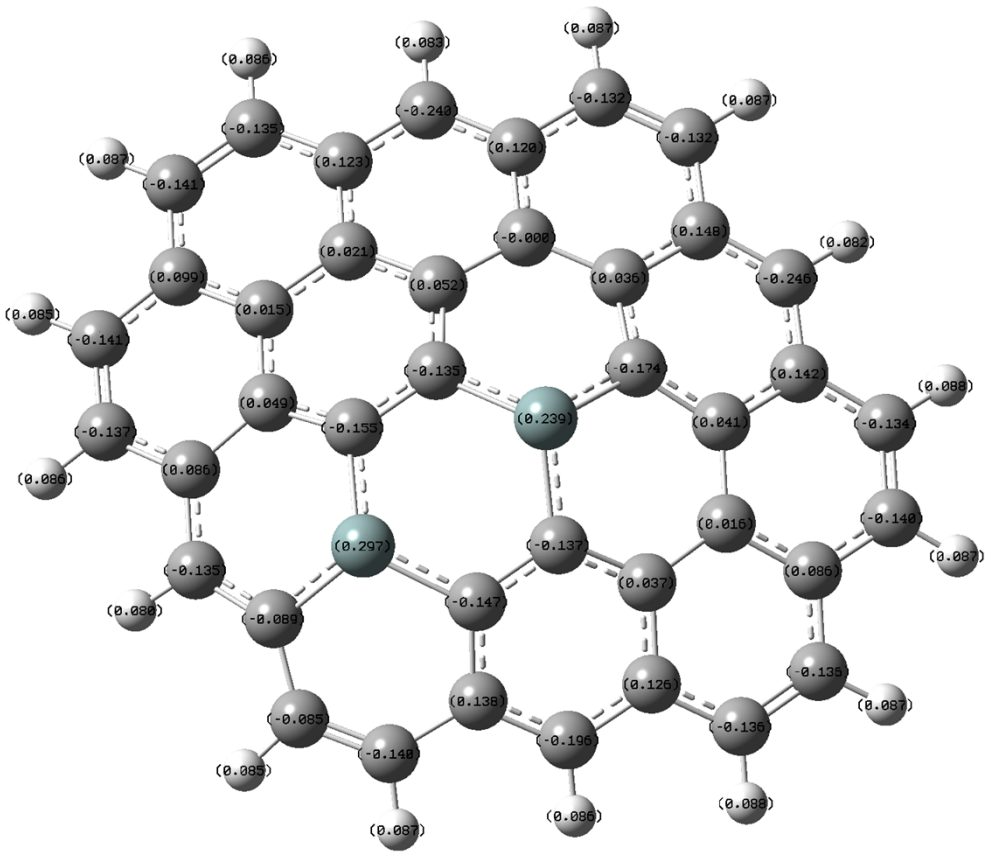
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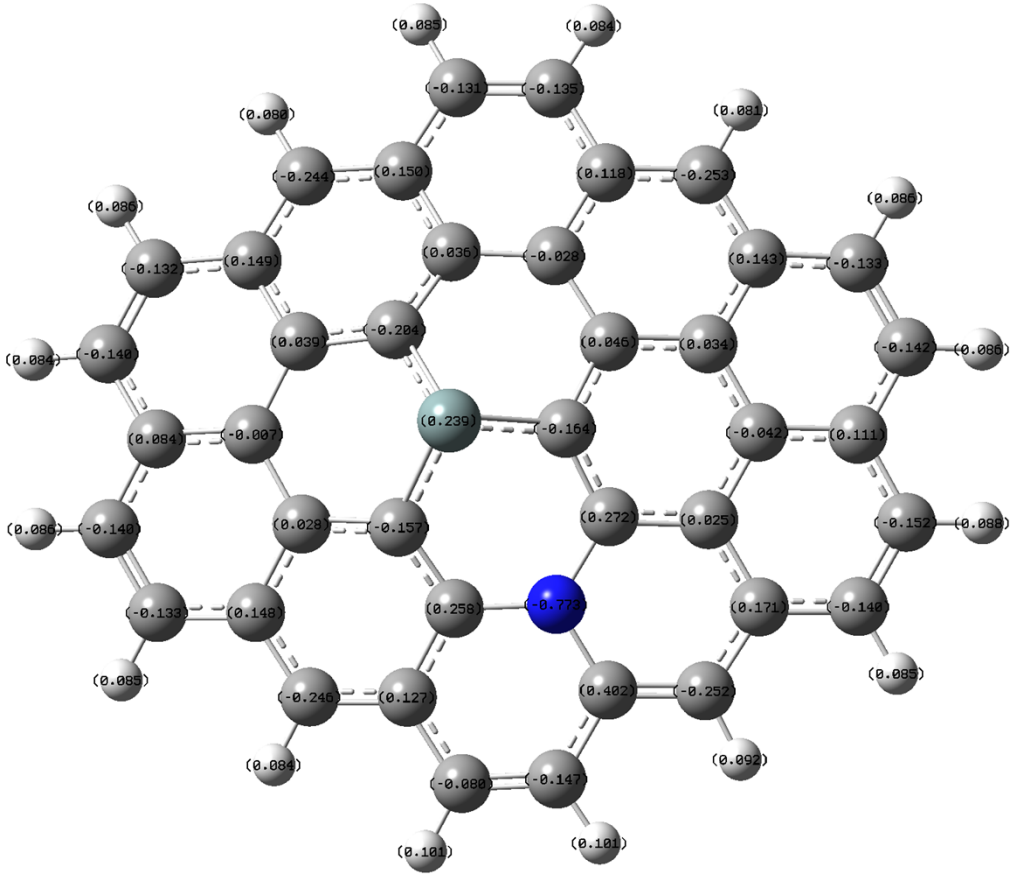

(D)

Fig. S3. The net charge distributions of C, Si and N atoms in pure graphene (A), Si-doped graphene with one silicon (B) or two silicon atoms (C) and Si, N-codoped graphene (D).

References

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