



## Short communication

# Novel As-doped, As and N-codoped carbon nanotubes as highly active and durable electrocatalysts for O<sub>2</sub> reduction in alkaline medium

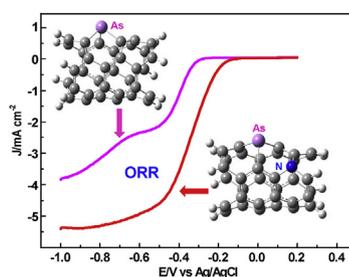
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## HIGHLIGHTS

- Novel arsenic-doped, arsenic and nitrogen-codoped CNTs are designed.
- As doping improves the activity of CNTs or N-CNTs for oxygen reduction reaction.
- Activities of CNTs or N-CNTs increase and then decrease with the As content increase.
- DFT calculations indicate the As doping changes the electronic structure of CNTs.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 1 September 2015

Received in revised form

3 December 2015

Accepted 16 December 2015

Available online 24 December 2015

## Keywords:

Arsenic-containing carbon nanotubes

Metal-free electrocatalysts

Oxygen reduction reaction

Fuel cells

## ABSTRACT

To develop more efficient metal-free cathode electrocatalysts for fuel cells, novel arsenic (As)-doped, As and N-codoped carbon nanotubes are synthesized by chemical vapor deposition in this work. The as-prepared As-containing carbon nanotubes exhibit significantly enhanced activity and long-term durability for the oxygen reduction reaction (ORR) in alkaline medium, indicating that the doping of As or codoping As with other heteroatoms into carbon matrix could improve the ORR activity of carbon materials due to the changes in electronic and physical properties of carbon nanotubes evidenced by density functional theory calculations. Moreover, As-containing carbon nanotubes also display much better methanol tolerance, showing a good potential application for future fuel cells.

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## 1. Introduction

Since nitrogen (N)-doped ordered mesoporous graphitic arrays [1] and phosphorus (P)-doped graphite layers [2] without any metal were proved to exhibit much superior activity for the oxygen reduction reaction (ORR) than pure carbon ones in alkaline medium, the doubt that the improvement of ORR activity of carbon materials derived from the metal catalyst residue was removed thoroughly and novel metal-free heteroatom-doped carbon

electrocatalysts began to attract many researchers' attention in the field of fuel cells. Thenceforward, boron (B) [3], sulfur (S) [4], selenium [5], fluorine [6,7], iodine, chlorine and bromine [8,9]-doped metal-free carbon materials emerged in succession at the forefront of ORR electrocatalytic technology. Most recently, the doping of silicon (Si) into carbon nanomaterials was also reported to effectively improve the ORR activity of carbon materials in alkaline medium [10,11]. More interestingly, the dual or multiple doping of these foreign atoms such as N/S, N/P, N/B, N/Si, N/B/P into carbon framework was found to bring much more striking enhancement in the ORR activity of carbon materials [11–15] in comparison with the unitary doping due to the synergistic coupling effect between

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these doped heteroatoms. Currently, heteroatom-doped or codoped carbon materials with excellent performances such as high electrocatalytic activity and long-term durability toward the ORR have been considered to be one of the most promising alternatives to noble metal platinum-based catalysts.

Arsenic (As), as one of VA elements in the periodic table, contains same valence electron numbers with N and P. Like N or P-doped carbon materials, the As-doped or codoped carbon materials should exhibit much high enhanced ORR activity if arsenic atoms are doped into carbon matrix. To verify this hypothesis, we rationally selected triphenylarsine (TP) with low toxicity as As source and tried to synthesize novel As-doped carbon nanotubes (As-CNTs) and AsN-codoped carbon nanotubes (AsN-CNTs) by chemical vapor deposition and estimated their electrocatalytic performance by electrochemical measurements. The results showed that As could be doped into the framework of CNTs and the doping of arsenic atoms also could significantly improve the ORR activities of CNTs and N-CNTs in alkaline medium as other reported foreign atoms. It is noted that, to the best of our knowledge, this is the first time to report the syntheses and high ORR activities of As-doped and AsN-codoped carbon nanomaterials.

## 2. Experiment

The commercially available Pt–C (47.6 wt% on Vulcan XC-72) catalyst was purchased from BASF Fuel Cell, Inc., USA. Other chemicals were purchased and used without any further purification. As-CNTs1, As-CNTs2, As-CNTs3 and AsN-CNTs1, AsN-CNTs2, AsN-CNTs3 were prepared by the thermolyses of TP xylene solutions and TP aniline solutions containing 2.0, 4.0 and 8.0 wt.% of TP using FeMo/Al<sub>2</sub>O<sub>3</sub> as catalyst according to Re. [11], respectively. For comparison, pure CNTs and N-CNTs were also synthesized by the same method using xylene and aniline.

Electrochemical experiments were carried out at room temperature in a three-electrode cell connected to an electrochemical analyzer (Pine Research Instrumentation, USA). The detailed preparation of electrodes was described in our previous work [11]. 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 = 15: 385: 100) by sonication. 10.0  $\mu$ l suspension was dropped onto the glassy carbon electrode surface. Consequently, 0.31 mgcm<sup>-2</sup> of each example was loaded onto the surface of bare glassy carbon electrode. Every as-made sample/GC and Pt/C/GC were used as the working electrodes, 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 an oxygen-saturated 0.1 M KOH solution with or without 3.0 M CH<sub>3</sub>OH in the potential range of +0.2 to –1.0 V at room temperature at the scan rate of 100 mV s<sup>-1</sup>. The linear sweep voltammetry (LSV) measurements were performed in a nitrogen-protected or oxygen-saturated 0.1 M KOH solution in the potential range of +0.2 to –1.0 V at the scan rate of 10 mV s<sup>-1</sup>. The Koutecky–Levich plots were obtained by  $I^{-1} = I_k^{-1} + (0.62nFCD^{2/3}v^{-1/6}\omega^{1/2})^{-1}$ , where  $I_k^{-1}$  is the kinetic current density,  $\omega$  is the rotational speed,  $n$  is the number of electron transferred,  $F$  is the Faraday constant ( $F = 96485 \text{ C mol}^{-1}$ ),  $C$  is the bulk concentration of O<sub>2</sub> ( $C = 1.2 \times 10^{-3} \text{ mol L}^{-1}$ ),  $D$  is the diffusion coefficient of O<sub>2</sub> ( $D = 1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ),  $\nu$  is the kinetic viscosity of the electrolyte ( $0.01 \text{ cm}^2 \text{ s}^{-1}$ ),  $\omega$  is the angular velocity of the disk ( $\omega = 2\pi N$ ,  $N$  is the linear rotation speed).

The morphologies of the samples and elemental compositions were characterized by scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and energy dispersive spectrometer (EDS) (MERLIN compact). X-ray photoelectron

spectroscopic (XPS) measurements were performed on a Thermo Scientific ESCALAB 250XI using Al K $\alpha$  radiation.

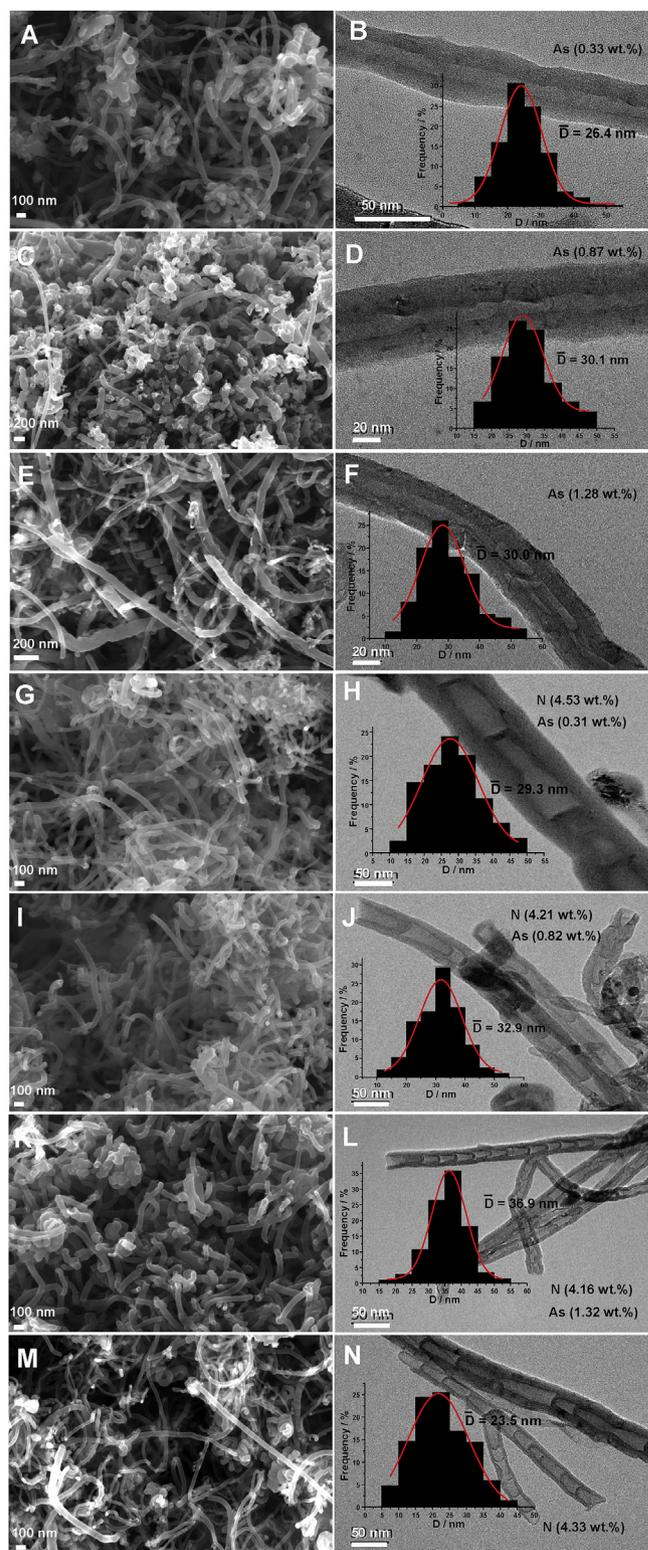


Fig. 1. SEM and TEM images of the As-CNTs1 (A, B), As-CNTs2 (C, D), As-CNTs3 (E, F), AsN-CNTs1 (G, H), AsN-CNTs2 (I, J), AsN-CNTs3 (K, L) and N-CNTs (M, N). The inset in TEMs shows the corresponding tube diameter distribution, As and N contents.

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