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Highly Efficient Oxygen Reduction Electrocatalysts based on Winged Carbon Nanotubes

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Developing electrocatalysts with both high selectivity and efficiency for the oxygen reduction reaction (ORR) is critical for several applications including fuel cells and metal-air batteries. In this work we developed high performance electrocatalysts based on unique winged carbon nanotubes. We found that the outer-walls of a special type of carbon nanotubes/nanofibers, when selectively oxidized, unzipped and exfoliated, form graphene wings strongly attached to the inner tubes. After doping with nitrogen, the winged nanotubes exhibited outstanding activity toward catalyzing the ORR through the four-electron pathway with excellent stability and methanol/carbon monoxide tolerance. While the doped graphene wings with high active site density bring remarkable catalytic activity, the inner tubes remain intact and conductive to facilitate electron transport during electrocatalysis.

Precious metals based catalysts (such as Pt and its alloys) are widely used in fuel cells to catalyze the ORR due to their high activity[1]. However, such catalysts are not suitable for widespread mass production because of their prohibitive high cost, instability over long-term operations (via sintering, dissolution and corrosion reactions) and susceptibility to fuel crossover effect and carbon monoxide poisoning[2]. Consequently, considerable research efforts have been devoted to develop advanced electrocatalysts with improved efficiency, stability and selectivity[3]. In addition to developing Pt-based electrocatalysts with minimized Pt loading and improved stability[4,5], alternative non-Pt electrocatalysts including metal-N complex on carbon matrices, transition metal chalcogenides and doped carbonaceous materials have also been actively pursued[6–9].

Carbonaceous materials play critical roles over the course of the developments of ORR catalysts and their physicochemical properties have significant influences on their overall activity and durability[10]. Recent developments of carbon nanotubes and graphene that possess graphitic structure, corrosion resistance and remarkable electrical conductivity bring tremendous opportunities toward developing advanced catalysts[11]. Several previous studies have documented that both graphene and nanotubes can support catalysts with enhanced performance[12,13]. Besides, they can also function as metal-free catalysts after doping with heteroatoms (such as nitrogen, sulfur and/or boron)[14,15]. Such doped materials can be obtained by either direct synthesis in the presence of appropriate precursors (such as NH_3 for N-doping) or doping of pre-synthesized carbon materials[16,17]. Even though significant progresses have been achieved, the developed catalysts still suffer from limited activity and efficiency owning to inherent drawbacks such as low active site densities and low electrical conductivity[16]. In general, highly conductive carbon nanotubes usually have limited surface area (for example, ~ 100 m²/g for N-doped carbon nanotubes[18]) with relatively low density of active catalytic sites. A possible approach to increase its surface area is through harsh oxidations to introduce defects and functional groups[19]. This approach, however, also results in compromises of the inherent structural integrity, stability and conductivity of pristine nanotubes. Graphene and graphene oxide (GO) have high surface area and high density of active sites (in GO) in principle but their electrical conductivity is much lower than carbon nanotubes[20]. More importantly, when used as powders, graphene sheets tend to restack and form "graphite" structure with substantially decreased surface area (typically ~ 300 m²/g) that is well below the theoretical value (2630 m²/g)[21]. In light of these limitations, one would expect that a rational combination of graphene and nanotubes could form a hybrid with much better properties than either of them alone. In fact, several approaches have been developed for making such hybrids[22,23]. One type of approaches involves simply mixing pre-synthesized nanotubes and graphene but this approach has limited success due to weak coupling between the nanotubes and graphene[23]. Another type of approaches is direct growth

of nanotubes on graphene sheets. Despite such approaches yielded hybrids with better nanotube-graphene interactions, these methods are either labor intensive or difficult to scale-up[22]. Therefore, further developments in preparing these hybrid materials are highly desired and such hybrids could make substantial impacts on the development of future ORR catalysts.

In this study, carbon nanotubes with strongly attached graphene wings (denoted as winged carbon nanotubes, wNT) were prepared through selective partial outer-wall oxidation and exfoliation of ultralong stacked-cup nanotubes under controlled processes. This unique wNT have dramatically higher surface area than pristine nanotubes and thus could provide abundant catalytic sites. After doping with nitrogen, the N-wNT exhibited high activity for catalyzing the ORR as a metal-free catalyst in an alkaline electrolyte through the four-electron pathway with outstanding stability and methanol/CO tolerance owning to their unique carbon frame, which provided both high electric conductivity and mechanical stability. In addition to functioning as metal-free catalysts, the high surface area and conductive N-wNT could also be used as advanced catalyst supports. We show that N-wNT containing 0.9 at% Fe exhibited catalyst activity comparable with commercial Pt-based catalysts in ORR reactions.

Results

Stacked-cup carbon nanotubes (SC-CNT, also known as herringbone carbon nanofibers) with heat-treatment at 3000°C were selectively used as the starting material due to their outstanding electrical conductivity, good graphitic structure (Figure S1) and ultra-long length (50 ~ 200 μm, Figure 1a,b) compared with typical multi-walled nanotubes[24]. More significantly, they are commercially available at lower prices than other types of nanotubes and hence economically more attractive for large-scale applications. A high-resolution transmission electron microscopy (TEM) image shown in Figure 1c revealed that such nanotube has stacked-cup carbon structure as inner core and an assembly of concentric cylinders of graphene as external layer. Because of this unique structure, the external layer was more prone to be oxidized when subjected to the oxidization condition as described in the method section. Consequently, these external layers were heavily oxidized after oxidizing whereas the inner tubular structures remained intact (as shown by the fact that their d-spacing did not increase obviously, Figure S2). The defect-rich nature of the as-oxidized nanotubes (ox-NT) is evident from its high D-band/G-band ratio in Raman spectroscopy (Figure S1). After a sonication step (30 min) that was applied to unzip and exfoliate the heavily oxidized external layers, we found

that the average diameter of nanotubes was substantially increased from 100 nm to 180 nm (Figure 1d). More importantly, the ultra-long nature of the initial materials was largely preserved due to, presumably, the intact inner core and they were much longer than few-walled carbon nanotubes subjected to a similar condition (hundreds of nanometers) used in our other research projects[19]. A closer examination of the products (Figure 1e) revealed that the outer layers of the original SC-CNT were successfully exfoliated through the unzipping process as clearly revealed in the TEM images (Figure 1d, inserted)[25], forming graphene wings strongly attached to nanotubes. Figure 1f shows a collection of several wNT and all of them exhibit winged structure and the yield of wNT of this method is high. Additionally, we also found that the graphene wings were strongly attached to nanotubes as the winged structure was preserved even after subjecting a prolonged sonication process (10 hours, Figure S3).

Upon unzipping and exfoliation, the BET specific surface area increased from ~ 40 m²/g for pristine SC-CNT to ~ 480 m²/g for wNT. Noticeably, the wNT has surface area higher than typical N-doped carbon nanotubes (~100 m²/g) and comparable or higher than N-doped graphene (~300 m²/g)[18,21] and it should have outstanding activity when used as catalyst. The surface area result further proved that the outer-layers of ox-NT were effectively exfoliated and they were unlikely to restack owning to the unique winged structure (otherwise the surface area would be much lower). Elemental analysis using X-ray photoelectron spectroscopy (XPS) (Figure 2a) revealed a nominal ~ 30 at% of oxygen in the ox-NT in the form of hybroxyl, carbonyl and carboxyl groups (Figure 2b) that is indicative of abundant defective and functionalized sites. Subsequently, the ox-NTs were doped with nitrogen using a method similarly as described by Müllen et al.[26]. In this method, solid and homogeneous mixtures of ox-NTs and cyanamide were firstly annealed at 550°C under Ar to thermally condense cyanamide and provide polymeric carbon nitride (CN)[27]. Afterwards the mixture was heated to 900°C to decompose CN and generate nitrogen doped wNT (N-wNT)[26]. The structure of the N-wNT (a set of its TEM images is shown in Figure S4) resembled that of wNT and graphene sheets strongly attached to nanotubes were clearly identified, indicating that the doping process did not affect the winged structure.

Along with the doping process, most oxygen functionalities were removed and the oxygen level was reduced significantly to only ~ 2.6 at%. In the meantime, nitrogen was successfully doped with a nominal concentration of 6.6 at% (Figure 2a), which is similar with previous studies on doped graphene oxide[21]. Analysis of N 1s spectra
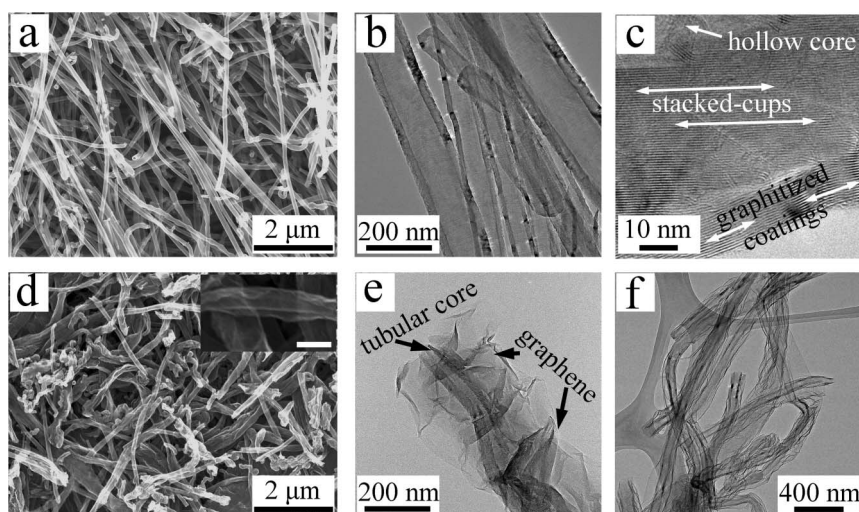

Figure 1 | Structural characterization of pristine SC-CNT and winged nanotubes: (a) SEM and (b), (c) TEM images of pristine SC-CNT; (d) SEM and (e), (f) TEM images of winged nanotubes (The scale bar for the inserted image in (d) is 200 nm).
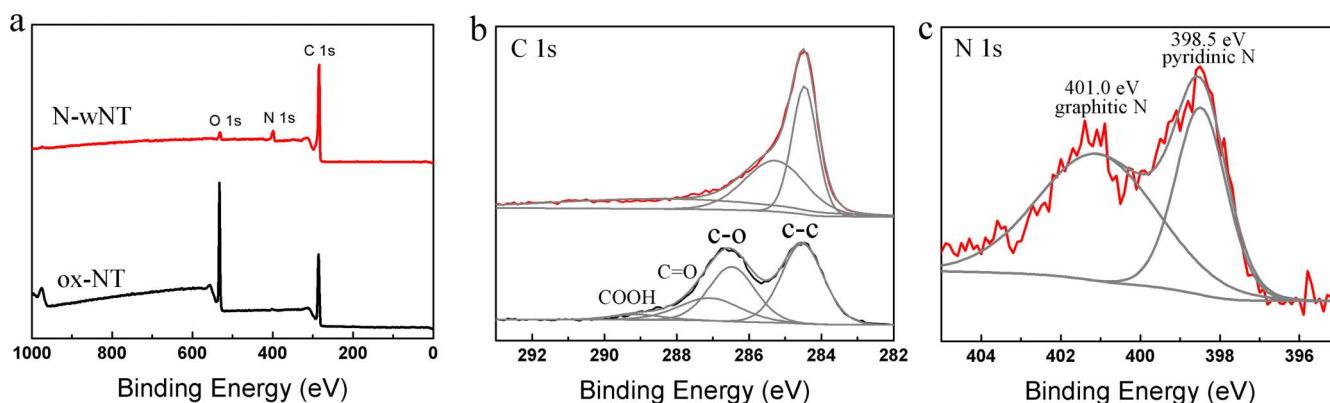
Figure 2 | Compositional characterizations using XPS: (a) survey spectra and (b) C 1s regional spectra of as-synthesized ox-NT (black) and N-wNT (red); (c) N 1s regional spectrum of N-wNT.

revealed the presence of both pyridinic and graphitic nitrogen, corresponding to binding energies of 398.4 and 401.0 eV, respectively (Figure 2c). No metallic species were detected in either ox-NT or N-wNT. The nitrogen doping was likely resulted from reactions of CN with oxygen functionalities and other defects in the heavily oxidized graphene wings of the ox-NT complexes. Additionally, we measured the electrical conductivity of winged nanotubes after nitrogen doping. Our results indicate that the N-wNT exhibited conductivity as high as ~ 4300 s/m. Such high electrical conductivity is beneficial for fast electron transport, which is desired for electrocatalysts.

We performed cyclic voltammetry (CV) and rotating disk electrode (RDE) measurements in 0.1 M KOH to assess the catalytic activity of N-wNT material that had been deposited onto a glassy carbon electrode. The N-wNT catalyst exhibited a symmetrical and rectangular CV curve when the electrolyte was saturated with Ar (Figure 3a). In strong contrast, a pronounced catholic ORR peak with an onset potential of ~ 0.91 V versus reversible hydrogen electrode (RHE) was observed in O_2 saturated electrolyte. Noticeably, the ORR peak is much stronger with more positive onset voltage than most of the metal-free catalyst developed[15,26,28], suggesting large surface area of winged nanotubes. The high ORR activity is also evident from its onset potential (~ 0.93 V) and half-wave potential (~ 0.79 V) in the RDE polarization curve (Figure 3b). The corresponding Koutecky-Levich plot (J^{-1} vs $\omega^{-1/2}$) obtained on the basis of analyzing the RDE curves of different electrode rotating speeds (in rpm, Figure 3b) at various potentials exhibited excellent linearity (Figure 3c). The average number of electrons transferred per oxygen molecule involved in the ORR can be analyzed on the basis of the Koutecky-Levich equations (Supporting Information)[8]. The number of electrons transferred were determined to be all around 4 at different potentials examined (Figure 3c, inserted), demonstrating N-wNT was highly efficient and catalyzing the ORR though the four-electron pathway with oxygen being directly reduced to water. The kinetic currents (J_k) were 12.5 mA cm^{-2} at 0.4 V and 14.2 mA cm^{-2} at 1.0 V, indicating highly active catalytic activity. The N-wNT was free from metal species as discussed above, and this enables a solid correlation between the winged structure and electrochemical performance.

Discussion
The effects of structure and composition on the ORR activity of the catalysts were studied. Figure 3d compares the RDE voltammograms (acquired at 10 mV/s and 1600 rpm in 0.1 M O_2-saturated KOH) of the N-wNT catalyst with control catalysts including N-doped graphene and N-doped simple mixture of graphene and functionalized nanotube without strong coupling (N-G/fCNT). As can be seen, both N-graphene ($E_o = 0.84$ V) and N-G/fCNT ($E_o = 0.87$ V) showed inferior activity compared with N-wNT with more negative onset

voltages and lower steady state currents. These results demonstrated advantages of the winged structure with strongly coupled graphene wings and nanotubes on improving catalytic activities: whereas the doped graphene wings bring catalytic activity with high active site density, the nanotubes bring both mechanical stability and superior electrical conductivity, which could facilitate electron transport during electrocatalysis.

The results presented above demonstrated that the N-wNT catalysts have remarkable activity as metal-free electrocatalysts. Additionally, it was shown that non-precious metals, such as Fe and Co, could enhance the activity of ORR catalysts[26,29,30]. We have also performed similar studies using the N-wNT materials. In this study, Fe was intentionally incorporated with ~ 0.9 at% to the N-wNT catalyst (Figure S5) through an in-situ deposition process. The N-wNT-Fe catalyst exhibited enhanced catalysis activity with onset potential (~ 0.95 V) and half-wave potential ($E_{1/2} = 0.83$ V) close to that of Pt/C ($E_o = 0.98$ V, $E_{1/2} = 0.86$ V). More significantly, the N-wNT-Fe has comparable current density with Pt/C (Figure 3d). These results indicate that the winged carbon nanotubes could also have promising applications as a high performance catalyst support.

The N-wNT catalyst was further tested for possible fuel crossover and poisoning effects in the presence of methanol and carbon monoxide (CO), respectively. For comparison, the behavior of Pt/C under the same conditions was also studied. The strong amperometric response of N-wNT was very stable upon introduction of 1 M methanol (Figure 4a). In contrast, more than 40% of the initial electrocatalytic current was lost for Pt/C. The high selectivity could be attributed to the lower ORR potential than that required for oxidization of methanol using the N-wNT catalyst[6]. The effect of CO on the electrocatalytic activity of N-wNT was also tested since CO poisoning is a major concern for noble-metal catalysts. Being nonmetallic, the activity of N-wNT was stable even with 10% (v/v) CO (Figure 4b), whereas the Pt/C catalyst was rapidly poisoned with dramatically decreased current density (~ 40% within 300 s). Hence, it is clear that the N-wNT catalyst have excellent tolerance for both methanol and CO, indicating high selectivity toward catalyzing the ORR. The reliability of the catalyst was also examined and compared with that of Pt/C by recording the current at 0.5 V and 1600 rpm using RDE and the current retentions were compared in Figure 4c. Additional data on long-term stability measurement is provided in Figure S6. The results show that the N-wNT catalyst exhibite good stability (~ 30% activity loss after 12 hours operation at 0.5 V) and is more stable than commercial Pt/C catalyst.

In summary, we developed a facile strategy to prepare unique winged carbon nanotubes and demonstrated their promising applications as electrocatalyst. After doping with nitrogen, the wNT exhibited high activity and efficiency, excellent selectivity and superior stability toward catalyzing the ORR through the 4-electron trans-
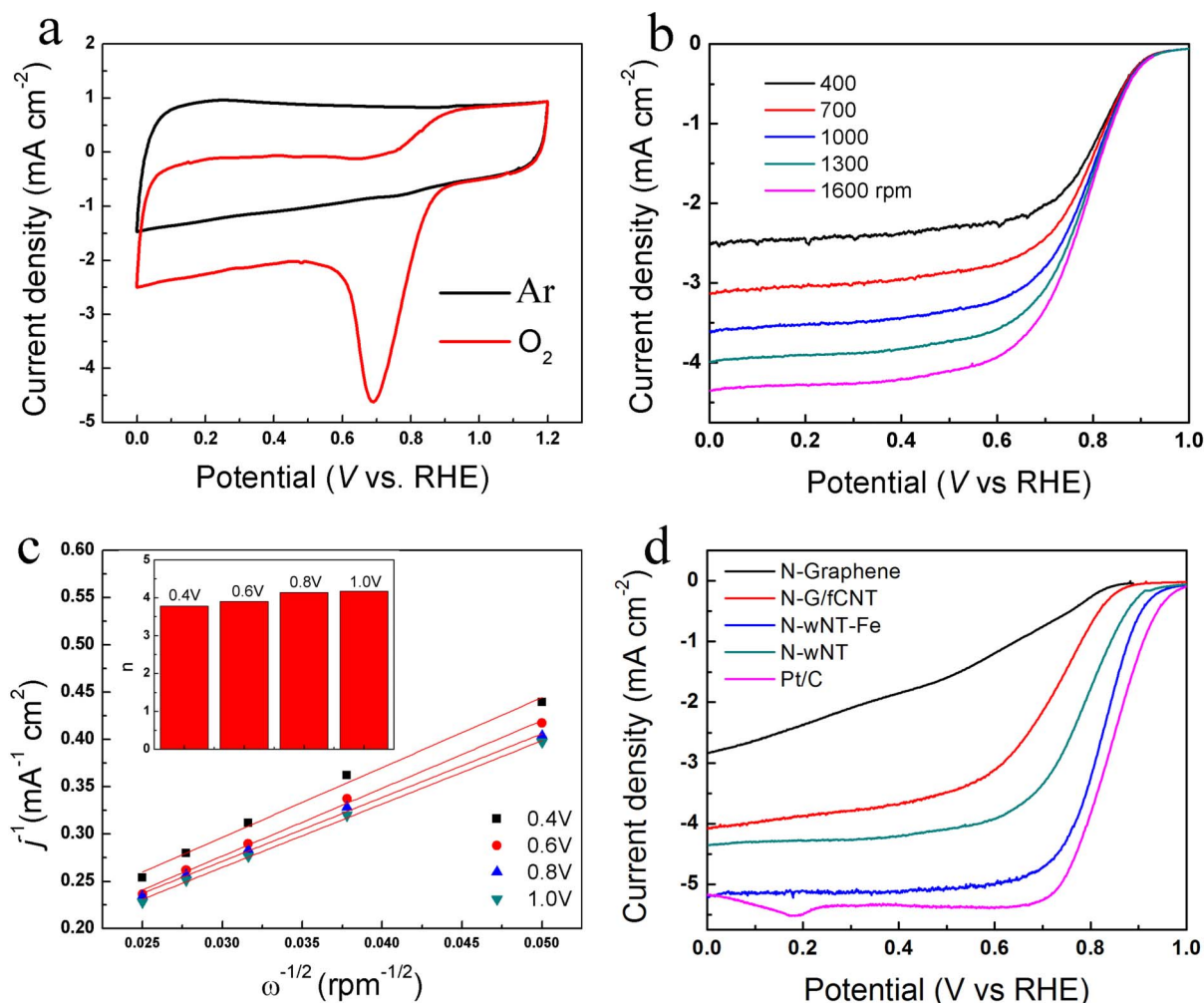
Figure 3 | Electrocatalytic activity of the N-wNT catalyst: (a) CV curves acquired at 100 mV/s in O_2 or Ar saturated 0.1 M KOH. (b) Rotating-disk voltammograms in O_2-saturated 0.1 M KOH acquired at 10 mV/s and different rotating speeds. (c) Koutecky-Levich plots of J^{-1} versus $\omega^{-1/2}$ at different electrode potentials, the inserted image shows estimated number of electrons transferred at different potentials. (d) Comparison of the RDE voltammograms for catalysts with different structure and composition as specified (all acquired at 1600 rpm and 10 mV/s).

fer pathway. Such high activity can be attributed to the unique and strongly coupling between graphene and nanotube in the wNT that bring increased surface area, good electrical,mechanical stability and porosity. In addition to their promising applications as metal-free catalyst with improved efficiency and durability, the N-wNT could also be used as advanced catalyst support. The work described in this paper could represent as a general approach to highly efficient and durable electrocatalysts for a range of important electrochemical reactions.

Methods

Material synthesis. ox-NT was prepared using a method adapted from the Hummers' method. SC-CNT with average diameter of 100 nm (PR-24-XT-HHT, Pyrograf Products, Inc.) was used as the starting material. Typically, 0.2 g of SC-CNT and 1.0 g
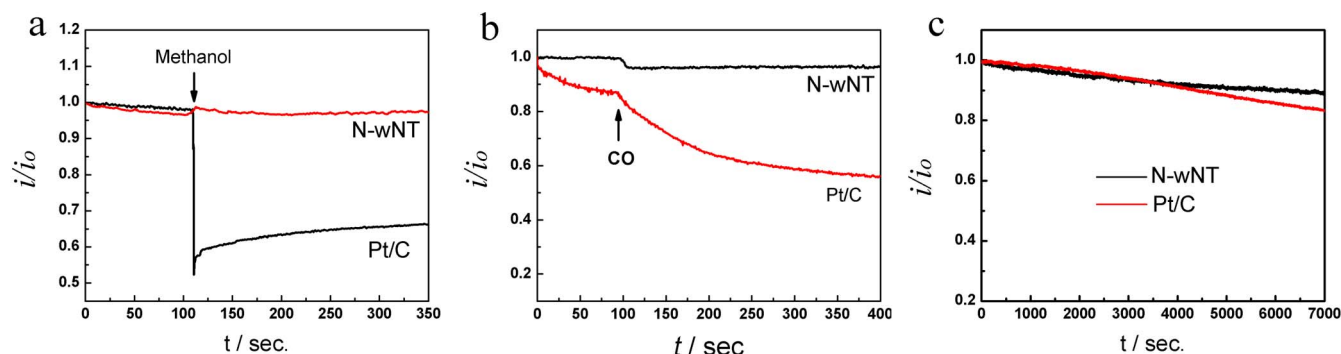

Figure 4 | Comparison of the selectivity and durability of the N-wNT catalyst with Pt/C: (a) with the presence of 1 M methanol (b) 10% (v/v) carbon monoxide and (c) relative current as a function of time at 0.5 V (1600 rpm).

of $NaNO_3$ were mixed in 40 ml of concentrated H_2SO_4 at 0°C. Afterwards $KMnO_4$ (6 g) was added slowly. The mixture was stirred for 90 min at 0°C, then at 35°C for 60 min. The mixture was then poured slowly into 250 ml of water, followed by addition of 10 ml of 30% H_2O_2. After 10 min of stirring, the products were collected by vacuum filtration using a filter membrane (1.2 μm, Millipore) and washed repeatedly with water until pH neutral. The collected solid was dispersed in water and vigorously sonicated for 30 min. For comparison, surface functionalized SC-CNT (fCNT) was also prepared by refluxing pristine material in 6 M HNO_3 for 12 hours.

Nitrogen doping of the ox-NT was achieved by annealing their homogenous mixtures with cyanamide at 900°C[26]. Typically, 30 mg of ox-NT and 400 mg of cyanamide were mixed in 10 ml of water. The mixture was stirred continuously at 100°C to evaporate water. The resulting solid was annealed in two continuous steps: 550°C for 2 hours and then 900°C for 1 hour, both under argon flow (200 sccm). For comparison, both nitrogen doped graphene and simple mixture of graphene and fCNT (1 : 1 weight ratio) were also prepared under identical conditions. Additionally, wNT with both nitrogen doping and iron loading were prepared by adding appropriate amount of $Fe(NO_3)_3$ into the precursor before drying. The annealing procedure is identical as described above.

Electrochemical measurements. N-wNT catalyst (6 mg) and 20 μl of 5 wt% Nafion solution were dispersed in 2 ml ethanol and 0.2 ml of water by sonication for > 1 hour to form a homogeneous ink. CV and RDE measurements were conducted with a Bio-logic SP300 Potentiostat using a standard calomel electrode as the reference electrode. The potential was converted to be in reference with the reversible hydrogen electrode (RHE) using $E_{(RHE)} = E_{(SCE)} + 0.998\ V$[19]. Typically, 20 μl of the catalyst ink was loaded onto a 5.6 mm glassy carbon disk electrode. 0.1 M KOH was used as the electrolyte. Before the start of each measurement, the electrolyte was bubbled with the appropriate gas (O_2 or Ar) for > 10 min and continuous gas flow was maintained during the measurement to ensure gas saturation. A scan rate of 10 mV/s was used for all RDE measurements.

For comparison, commercial 20 wt% platinum on Vulcan carbon black (E-tek) was also measured. The catalyst ink was prepared by mixing 4 mg of Pt/C and 20 μl of 5 wt% Nafion in 1.0 ml ethanol with sonication for > 1 hour. Other experimental conditions were same as for the N-wNT catalyst.

Characterization. Scanning electron microscopy (SEM) images were collected using a FEI XL30 FEGSEM. Transmission electron microscopy (TEM) images were obtained by using a FEI Tecnai G² Twin operating at 200 kV. Samples for TEM analysis were prepared by placing a drop of the ethanol dispersion of the sample on a lacey Formvar/carbon copper grid (200 mesh, Ted-Pella). Raman spectra of the powder samples were recorded with a LabRAM HR Raman microscope with a laser excitation wavelength of 633 nm. XPS spectra were acquired using a Kratos Analytical Axis Ultra X-ray Photoelectron Spectrometer. Electrical conductivity of the material was measured using a four-probe station (Keithley multimeter).

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Author contributions

Y.C. and J. L. conceived and designed the experiments. Y.C. and H.Z. performed the experiments. Y.C. analyzed the data. Y.C., C.V.V. and J.L. wrote the paper, and all authors discussed the results and commented on the manuscript.

Additional information

Supplementary information accompanies this paper at http://www.nature.com/scientificreports

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Cheng, Y.W., Zhang, H.B., Varanasi, C.V. & Liu, J. Highly Efficient Oxygen Reduction Electrocatalysts based on Winged Carbon Nanotubes. *Sci. Rep.* **3**, 3195; DOI:10.1038/srep03195 (2013).