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Strong-Coupled Co-g-C$_3$N$_4$/SWCNTs Composites as High-Performance Electro catalysts for Oxygen Reduction Reaction

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The hybrid materials of cobalt doped graphitic carbon nitride (g-C$_3$N$_4$) attached on single-walled carbon nanotubes (SWCNTs) were synthesized by a simple pyrolysis process. Electrochemical measurements revealed that the composites exhibited excellent electrocatalytic activity for oxygen reduction reaction (ORR), with a more positive onset potential (-0.03 V), half-wave potential (-0.15 V), high efficient four-electron process (n=3.97) and much higher stability than that of commercial Pt/C catalysts in alkaline media. The ORR activity mainly originates from the strong coupling of Co-g-C$_3$N$_4$ derived active sites on the SWCNTs.

High-performance, low-cost and stabilized electrocatalysts for oxygen reduction reaction (ORR) is urgently needed to renewable energy applications, such as fuel cells and metal-air batteries. The ORR, for which is the bottleneck of electrochemical catalytic performance, suffers from a series of problems, including slow charge transfer, low stability under fuel cell and poisoning effects. Currently, the commercial Pt-based materials are considered as the most promising ideal scaffolds for the fabrication of high-performance catalyst and Li-insertion materials.

As a consequence, exploring non-precious metal catalysts with high ORR activity has become a major challenge in fuel cells. In order to overcome these obstructions, extensive efforts are underway to develop high-activity catalytic materials. Previous studies implied that transition metals (Co, Fe, Mn, etc.) might act as the active sites of the new non-precious metal electrocatalysts. However, the sluggish kinetics of non-precious metal catalysts limits the efficiency and performance of the ORR. Recently, carbon-based nanomaterials doped with heteroatoms, especially N-doped carbon materials, have been explored as alternative electrocatalysts for ORR due to their relatively high abundance and low cost.

Graphitic carbon nitride (g-C$_3$N$_4$) polymer with N-rich and facile synthesis procedure has been proven to provide more active sites than other N-carbon materials for ORR electrocatalysts. However, the catalytic activity of g-C$_3$N$_4$ alone is still far inferior to commercial Pt-based catalysts, due to the extremely low electrical conductivity of g-C$_3$N$_4$ sheet. With the aim of nitrogen-rich and high conductivity, a variety of carbon materials have been introduced into g-C$_3$N$_4$, including carbon black, mesoporous carbon, and graphene oxides. But the effect of the structure of these composites is still unknown. Therefore, choosing suitable substrate is a key point to improve the ORR performance of g-C$_3$N$_4$.

Single-walled carbon nanotubes (SWCNTs), especially those synthesized by arc-discharged method, due to their high electron conductivity, high specific surface area and integrated structures, are one of the most promising ideal scaffolds for the fabrication of ORR electrocatalyst and Li-insertion materials.

Herein we develop a new electrocatalyst, composed of cobalt doped graphitic carbon nitride (Co-g-C$_3$N$_4$) and SWCNTs, which is the Co-g-C$_3$N$_4$ strong coupled with SWCNTs via π-π interactions. The electrocatalyst displayed excellent electrocatalytic activity and superior stability, resultant from the strong-coupling of Co-g-C$_3$N$_4$ and SWCNTs, thus making it as the promising candidate for the non-precious metal ORR catalysts.

Microscopic structure analyses of the Co-g-C$_3$N$_4$/SWCNTs samples with respect to pure-SWCNTs were performed by transmission electron microscopy (TEM), as displayed in Figure 1a-b. Compared to the bare surface of pure-SWCNTs (Fig. 1a), the Co-g-C$_3$N$_4$/SWCNTs demonstrate homogeneous distribution of Co-g-C$_3$N$_4$ on SWCNTs, as observed clearly in Fig. 1b. The uniform dispersion of C, N and Co elements was also observed in elemental-mapping (see Fig. S1 for detail information). It should be noted that without cobalt anticipation, the size of g-C$_3$N$_4$ particles on the SWCNTs appear severe aggregation (Fig. 1c). It implied that the metal cobalt helpfully disperse the pyrolyzed g-C$_3$N$_4$ on the SWCNTs. The HR-TEM image of Co-g-C$_3$N$_4$ nanosheet (inset in Fig. 1b) reveals clear...
lattice fringes with a distance of 0.326 nm, corresponding to the (002) plane of g-C$_3$N$_4$. The reduced crystal size of Co-g-C$_3$N$_4$/SWCNTs was also confirmed by XRD, as comparatively displayed in Fig. S2. Compared to the pure-g-C$_3$N$_4$ at 27.4°, the (002) diffraction peak of Co-g-C$_3$N$_4$ shows a significant decrease in intensity, indicating the reduce layers of g-C$_3$N$_4$ nanosheet. Together with the absence of (100) peak at 13.2°, it confirmed that cobalt ions are embedded into graphitic carbon nitride networks.

For the Co-g-C$_3$N$_4$/SWCNTs, the (002) diffraction peak at 27.4° of g-C$_3$N$_4$ disappeared, while a new diffraction peak assigned to a layer to tube distance between Co-g-C$_3$N$_4$ and SWCNTs appears at 26.6°. All these indicate that the Co-doped g-C$_3$N$_4$ is well dispersing on SWCNTs with a strong interaction. Nitrogen physisorption of Co-g-C$_3$N$_4$/SWCNTs was measured to investigate the surface structure (Fig. S3-a). The Brunauer-Emmett-Teller surface areas are 426 m$^2$/g and the diameters of the pores are in the range of 1.2 to 30 nm. The surface areas of Co-g-C$_3$N$_4$/SWCNTs are higher than that of pure-SWCNTs (166 m$^2$/g, Fig. S3-b), which might derive from the melamine pyrolysis. Moreover, the presence of micro-pores (< 2 nm) is beneficial to the formation of metal-nitrogen active sites in catalysts.

Raman spectroscopy was used to detect the charge transfer between the Co-g-C$_3$N$_4$ and SWCNTs. The Raman results of pure SWCNTs, g-C$_3$N$_4$/SWCNTs and Co-g-C$_3$N$_4$/SWCNTs are shown in Fig. 1d. The Raman peaks centered at about ~ 1346 cm$^{-1}$ and ~ 1593 cm$^{-1}$ are attributed to the D and G bands of SWCNTs, respectively. It is well-known that the frequency of G band is sensitive to the interfacial charge transfer. After being incorporated with Co-g-C$_3$N$_4$, the G band of SWCNTs red shifted (approximately 11 cm$^{-1}$) obviously, due to the charge transfer between the Co-g-C$_3$N$_4$ and the host SWCNTs. For Co-g-C$_3$N$_4$/SWCNTs composites, Co-g-C$_3$N$_4$ can bind to the SWCNTs sidewall via strong n-p stacking interaction, which promote electron-transfer between Co-g-C$_3$N$_4$ and the host SWCNTs. On the contrary, when SWCNTs were coupled with undoped g-C$_3$N$_4$, the G band shifted barely. It confirmed that Co embedded into graphitic carbon nitride greatly enhanced the charge transfer between Co-g-C$_3$N$_4$ and SWCNTs. The intensity of D band normalized toward G band ($I_D/I_G$) was used to measure the disorder degree of SWCNTs in three samples. The Co-g-C$_3$N$_4$/SWCNTs sample has an $I_D/I_G$ ratio of 0.40, which is much higher than that of the original pure SWCNTs (0.094) and that of the g-C$_3$N$_4$/SWCNTs (0.23). The results indicated the higher defects concentration of the SWCNTs in Co-g-C$_3$N$_4$/SWCNTs.

As expected, X-ray photoelectron spectroscopy (XPS) shows the existence of carbon, oxygen, nitrogen and cobalt (Fig. 2a). The O 1s peak most likely arises from the incorporation of physicochemical absorbed oxygen and trace amounts of metal-oxygen coordination. The high resolution N 1s spectrum reveals with several N species at different binding energy (Fig. 2b). The dominant peak at 398.6 eV corresponds to the sp$^3$-bonded N atoms in triazine rings (C-N-C). The peak at 400.8 eV can be assigned to N atoms in triazine rings and N (-C$\equiv$N). The Co 2p XPS spectrum of Co-g-C$_3$N$_4$/SWCNTs can be deconvoluted into two peaks with binding energies of 781.3 and 795.8 eV (Fig. 2c), which correspond to nitrogen- and oxygen-coordinated metals, respectively. The Co-g-C$_3$N$_4$/SWCNTs samples with a high N content (~15.2 at %) might benefit from the coordinated Co-g-C$_3$N$_4$ structure. A referenced sample of g-C$_3$N$_4$/SWCNTs was also measured to prove Co-N coordination. The N content of g-C$_3$N$_4$/SWCNTs (~8.7 at %) are much lower than that of Co-g-C$_3$N$_4$/SWCNTs. Moreover, the Co/N atomic ratio of Co-g-C$_3$N$_4$/SWCNTs was calculated to be 0.13, higher than that of bulk Co-g-C$_3$N$_4$ (0.09), suggesting a more stable Co-g-C$_3$N$_4$ substructure originated from the potential electronic coupling.

**Scheme. 1** Schematic presentations showed the ORR on the envisaged microstructures of Co-g-C$_3$N$_4$/SWCNTs.
between SWCNTs and Co-g-C$_3$N$_4$. The high Co/N atomic ratio can be attributed to the nitrogen transfer from g-C$_3$N$_4$ to SWCNTs during the pyrolysis of melamine.\textsuperscript{15, 31, 35} To further demonstrate that the cobalt embedded into g-C$_3$N$_4$, the Co-g-C$_3$N$_4$/SWCNTs composites were washed by 1 mol/L HCl (50 ml) solution at 50 °C for 6 h. The Co spectrum was shown in Fig. S4. With respect to the Co-g-C$_3$N$_4$/SWCNTs, the pickling composites peak intensity (at 795.8 eV) decreases significantly, while the peak intensity (at 781.3 eV) decreases barely.

The cathodic ORR electrocatalytic properties of Co-g-C$_3$N$_4$/SWCNTs were estimated in a three-electrode system at room temperature. Firstly, the cyclic voltammetry of Co-g-C$_3$N$_4$/SWCNTs was performed in both O$_2$ and N$_2$-saturated 0.1 M NaOH solution (Fig. 3a). CV curves show no any significant peak in the N$_2$-saturated electrolyte. On the contrary, a characteristic ORR peak at about -0.22 V was observed in the presence of oxygen, indicating the electrocatalytic activity of Co-g-C$_3$N$_4$/SWCNTs for ORR. The current response shows a weak oxidation peak at 1.9 V, possibly due to the cobalt ions transform from low valent state to high valent state. For understanding the strong coupling of Co-g-C$_3$N$_4$ component and SWCNTs in Co-g-C$_3$N$_4$/SWCNTs catalysts, the ORR performance of referred samples of g-C$_3$N$_4$, Co-g-C$_3$N$_4$, SWCNTs and g-C$_3$N$_4$/SWCNTs were also measured. As displayed in Fig. 3b and Fig. 55. The largest ORR peak-current and most positive ORR peak-potential on the Co-g-C$_3$N$_4$/SWCNTs electrode suggest the highest ORR activity for Co-g-C$_3$N$_4$/SWCNTs as compared to the g-C$_3$N$_4$, Co-g-C$_3$N$_4$/SWCNTs and g-C$_3$N$_4$/SWCNTs catalysts. The results indicated that the electrocatalytic activity originates from the Co-g-C$_3$N$_4$ derived active sites and SWCNTs with a high conductivity. The composites cyclic voltammograms shows a half-wave potential of -0.163 V, much more positive than the reported g-C$_3$N$_4$@carbon catalyst in 3D structure,\textsuperscript{16, 18} and comparable to those of the state-of-the-art commercial noble-metal catalysts.\textsuperscript{36}
Fig. 4 Linear sweep voltammetry curves of different samples with Pt/C in comparison in an O$_2$-saturated 0.1 M NaOH solution at a scan rate of 10 mV s$^{-1}$ and 1600 rpm.

To gain further insight into the role of Co-g-C$_3$N$_4$/SWCNTs during the ORR electrochemical process, the reaction kinetics was studied by rotation disk voltammetry. Fig. 5a shows RDE current-potential curves at different rotation rates for Co-g-C$_3$N$_4$/SWCNTs electrodes in the O$_2$-saturated 0.1 M NaOH electrolyte. The measured current density shows the typical increase with increasing rotation rate (from 500 to 2500 rpm). The transferred electron number of per O$_2$ molecule for ORR was determined by the Koutecky-Levich equation given below:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{A_\omega^{1/2}}$$

Where $j_k$ is the kinetic current and $\omega$ is the electrode rotation rate. $B$ would be determined from the slope of K-L plots (Fig. 5b) based on Levich equation as follows:

$$B = 0.62nFA \left(D_{O_2}\right)^{2/3}v^{-1/6}C_{O_2}$$

In which $n$ represents the number of electrons transferred per O$_2$ molecule; $F$ is the Faraday constant ($F = 96485$ C mol$^{-1}$); $A$ is the geometric electrode area ($0.196$ cm$^2$); $D_{O_2}$ is the diffusion coefficient of O$_2$ in 0.1 M NaOH solution ($1.9 \times 10^{-5}$ cm$^2$ s$^{-1}$); $v$ is the kinetic viscosity ($0.01$ cm$^2$ s$^{-1}$); and $C_{O_2}$ is the bulk concentration of the O$_2$ in 0.1 M NaOH solution ($1.2 \times 10^{-6}$ mol cm$^{-3}$). The constant 0.62 is adopted when the rotation rate expressed in rad s$^{-1}$.

The Koutecky-Levich equation corresponding curves are plotted for different potentials in Fig. 5b. The $n$ value for Co-g-C$_3$N$_4$/SWCNTs was calculated to be 3.97 at the potential of -0.35 V, comparable to that of Pt/C ($n=3.91$, calculated from Fig. 5a), suggesting a high efficient four-electron process for the ORR on the Co-g-C$_3$N$_4$/SWCNTs electrode. From the slope of the Koutecky-Levich equation, the number of transferred electrons per O$_2$ molecule was determined to be 3.97 at the potential of -0.35 V.
Fig. 5 (a) Linear sweep voltammetry curves of Co-g-C₃N₄/SWCNTs in an O₂-saturated 0.1 M NaOH solution at a sweep rate of 10 mV s⁻¹ under various rotation rates. (b) Koutecky-Levich plot for Co-g-C₃N₄/SWCNTs and Pt/C at -0.35 V obtained from Fig. 5a and Fig. S6, respectively. (c) Current-Time chronoamperometric response of Co-g-C₃N₄/SWCNTs and Pt/C in O₂-saturated 0.1 M NaOH solution at a rotation rate of 1600 rpm.

Levich plots (Fig. S8) derived from the data in Fig. 5a. The parallel and straight fitting lines of 1/β vs 1/ω⁰.₅ imply a first-order reaction toward dissolved oxygen. The n value for Co-g-C₃N₄/SWCNTs is derived to be 3.90-3.97 at the potential ranging from -0.25 to -0.45 V (Fig. S8). This further confirmed the high ORR efficiency of Co-g-C₃N₄/SWCNTs. In addition, the n value of Co-g-C₃N₄/SWCNTs also confirmed by RRDE results (Figure S9, Supporting Information). The Co-g-C₃N₄/SWCNTs also exhibited an ORR process approximating a 4e transfer pathway.

In order to test the stability of the electrocatalytic activity, a chronoamperometry at -3.0 V in O₂-saturated 0.1 M NaOH electrolyte at a rotation rate of 1600 rpm was carried out for 12 h. As shown in Fig. 5c, the corresponding current-time chronoamperometric response of Co-g-C₃N₄/SWCNTs exhibits a very slow attenuation and a high relative current of 82.3% still persists after 12 h. The stability of Co-g-C₃N₄/SWCNTs higher than that of the graphene supported Co-g-C₃N₄, confirming a strong coupling between Co-g-C₃N₄ and SWCNTs on the Co-g-C₃N₄/SWCNTs catalyst. In contrast, commercial Pt/C shows a gradual decrease with a current loss of approximately 35.5% measured after 12 h. This result clearly suggests that the durability of Co-g-C₃N₄/SWCNTs catalysts is superior to that of the Pt/C catalyst.

Conclusions

In summary, we have successfully synthesized a high-performance electrocatalyst coupled by Co-g-C₃N₄ and SWCNTs. The ORR activity for Co-g-C₃N₄/SWCNTs electrocatalyst arises from the Co-g-C₃N₄ derived active sites and the excellent conductivity of SWCNTs. Within the context of simple synthesis, more positive onset potential, number of electron transfer and the reliable stability, the Co-g-C₃N₄/SWCNTs Composites actually exhibited remarkable ORR performance compared to commercial Pt/C catalysts. All these superior properties make Co-g-C₃N₄/SWCNTs a potentially promising and suitable substitute for Pt/C catalyst, especially in alkaline fuel cell.

Notes and references