In this work, a nitrogen doped carbon nanotubes encapsulated cobalt nanoparticles (Co@N-CNTs) catalyst was prepared by assembling the precursors of melamine and cobalt nitrate hexahydrate, followed by gradient temperature carbonization in the presence of glucose as a reducing agent. The as prepared Co@N-CNTs composite exhibited electroactivity and long-term stability toward oxygen reduction reaction (ORR) in both alkaline and acidic solutions. It was found that the gradient temperature synthesis and reduction of the gels in the presence of glucose played an important role in the formation of a thin carbon shell on the Co nanoparticles, which protected it from being destroyed during the electrochemical procedures. These processes also facilitated to the ordered arrangement of nitrogen-carbon precursors and the formation of enriched pyridinic, pyrrolic and quaternary nitrogen functional groups that led to the highly activity of Co@N-CNTs. In addition, the catalyst also presented tolerance to methanol oxidation. This synthetic method and mechanism enlighten the future design of state-of-the-art nanostructured materials as an alternative for precious metal based catalysts for highly efficient ORR.

© The Author(s) 2018. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.010181jes]
nanomaterials. In addition, the Co@N-CNTs also showed superior tolerance to methanol oxidation during the ORR procedures, which enlighten the future design of state-of-the-art nanostructured materials as an alternative for precious metal based ORR catalysts.

Materials and Methods

Synthesis of the Co@N-CNTs catalysts.—Briefly, melamine (9 mmol) was mixed with Cobalt(II) nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O, 9 mmol) and glucose (6 mmol), then the pH of homogenous mixture was adjusted to 2.5 with HCl solution. It formed a stable gel (Figure S1). After centrifugation, redundant Co ions were removed to avoid the damage of the structure by acidification. After freeze-drying, the xerogel was placed on an alumina boat and heated at a ramp of 5°C min$^{-1}$ in a tube furnace and kept at 550°C for 3 h in Ar atmosphere. Then the temperature in the tube furnace was further raised to 900°C for 3 h in Ar atmosphere, and pyrolysis to 900°C for 3 h in Ar atmosphere to pyrolyze the Co$_2$g-C$_3$N$_4$. Subsequently, the pyrolysis product was washed with 0.1 mol L$^{-1}$ H$_2$SO$_4$ solution to remove a small amount of cobalt particles on the surface. After washing with water and ethanol for three times, the final product of Co@N-CNTs-1 was obtained after drying. In addition, the product that prepared with the same procedure but in the absence of glucose was assigned as Co@N-CNTs-2. The composite that synthesized with the same procedure as Co@N-CNTs-1 but without the calcination aging treatment at 550°C for 3 h was named Co@N-CNTs-3.

Characterization.—Field emission scanning electron microscopy (SEM) images were obtained with Hitachi SU-8010. The microscopic features of the samples were observed by high-resolution transmission electron microscope (HRTEM, JEM-2100F) operated at 200 kV. X-ray diffraction (XRD) characterization was carried out on a Bruker D8 with a Cu-Kα radiation ($\lambda = 1.5418$ Å). Raman spectra were obtained under ambient conditions by using a RUM 2000 microscope confocal Raman spectrometer (Renishaw PLC) using 514 nm laser. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI Quantera Scanning X-ray Microprobe using a monochromatic Al-Kα (1486.7 eV).

Preparation of the electrodes.—The glassy carbon electrode (GCE) was successively polished with 0.3 μm and 0.05 μm α-Al$_2$O$_3$ slurry on an abrasive cloth, followed by cleaning with distilled water and ethanol under sonication. After being dried with nitrogen gas, the catalyst homogeneous ink was prepared by dispersing catalyst (1 mg) in Nafion solution (1 mL, 0.5 wt%, aq.) with at least 30 min sonication. Then 6 μL of the catalyst ink was coated onto a clean GCE (with diameter of 3 mm) for cyclic voltammetry (CV) measurements and 20 μL of the catalyst ink was coated onto GCE (with diameter of 5 mm) for rotating disk electrode (RDE) measurements. All experiments were performed at room temperature.

Results and Discussion

Characterization of Co@N-CNTs.—The Co@N-CNTs-1 was synthesized by the assembly of melamine and cobalt nitrate. After freeze-drying procedure, the precursors were calcinated at 550°C for 3 h in Ar atmosphere, and pyrolysis to 900°C and kept at 900°C for 3 h in Ar atmosphere, and the final products were obtained. SEM image (Figure 1A) shows that the products consist of carbon nanotubes with several micrometers long and approximate 100 nm of diameter. Figure 1B exhibits TEM image of the product, and some nanoparticles dispersed inside the nanotubes especially on the end point of the nanotubes. Figure 1C shows the enlarged TEM image of the Co@N-CNTs-1, and the corresponding elemental mapping pictures of carbon and cobalt were presented as presented in Figures 1D and 1E, respectively. Homogeneous distribution of carbon element on the carbon nanotube was observed, and the cobalt element was located on the nanoparticles. Moreover, the HRTEM pattern (Figure 1F) shows that the nanoparticles are coated with carbon shells with a thickness of about 10 nm. The lattice spacing of the carbon shell is 0.356 nm which is slightly larger than that of graphite of 0.335 nm, suggesting that there is graphitic carbon with turbostratic structure in the stacking of graphitic carbon coating. Additionally, the carbon networks of the graphitic layers were disordered, which may be attributed to the
doping of hetero-atoms N that could lead to the stacking disorder and a turbostratic structure of the graphitic planes. The structure and components of Co@N-CNTs-1 nanocomposites were further studied by XRD as shown in Figure 1G. The XRD peaks are in agreement with the structural feature of graphite carbon and the metallic cobalt (JCPDS: 15-0806). The similar components were observed for Co@N-CNTs-3 (Figure S2a), while a complex composite consist of Co, Co$_3$O$_4$ and graphite carbon were appeared in Co@N-CNTs-2 (Figure S2b), which revealed that glucose may act as a reducing agent and carbon source in the process of pyrolysis.

Figure 2A shows the XPS spectra of the Co@N-CNTs-1 composite, and the elements of C, N, and Co in Co@N-CNTs-1 are observed. The quantification results showed that the atomic concentrations of Co and N in the Co@N-CNTs-1 composite are 0.24% and 1.75%, respectively. In addition, the cobalt was assigned to metallic cobalt according to the Co 2p, which is similar to that of XRD result (Figure S3). Figure 2B shows the high resolution XPS of nitrogen in the Co@N-CNTs-1. The N 1 s spectra of Co@N-CNTs-1 present three types of nitrogen species at 398.4 eV, 399.3 eV and 401.1 eV, corresponding to pyridinic nitrogen (N1), pyrrolic nitrogen (N2) and quaternary nitrogen (N3), respectively. The contents of the three types of nitrogen in the products were summarized (Table S1). Especially, the atomic ratios of N$_2$/N$_{total}$ and N$_3$/N$_{total}$ in the Co@N-CNTs-1 are 26.7% and 59.3%, respectively. The results suggested that the formation of pyrrolic nitrogen and quaternary nitrogen is suppressed in the absence of glucose. Furthermore, the calcination aging at 550°C facilitates the transformation of pyridinic nitrogen to pyrrolic nitrogen. Figure 2C shows the Raman spectra of Co@N-CNTs. Three remarkable peaks at approximately 1330 cm$^{-1}$, 1600 cm$^{-1}$ and 2700 cm$^{-1}$ in the Raman spectra of Co@N-CNTs (Figure 2C) are corresponding to the D, G and 2D bands of CNTs, respectively. The D band is often referred to as the disorder or defect band, which originates from hybridized vibrational mode associated with the edges of CNTs, and the G band is related to the tangential oscillations and vibrations of all the sp$^2$ carbon atoms in the CNTs. The intensity ratio between D and G bands (I$_D$/I$_G$) could generally reflect the defect density in CNTs. In addition, the 2D band, also known as G' band, is a two-phonon resonance Raman bands that reflect the thickness of the carbon film directly.\textsuperscript{32,33} The I$_D$/I$_G$ of the Co@N-CNTs-1 is calculated to be 1.05. As a comparison, the Co@N-CNTs-3 was 0.88 (curve b), and the Co@N-CNTs-2 was 0.98 (curve c). The highest I$_D$/I$_G$ value for Co@N-CNTs-1 means that more defects formed in the carbon of Co@N-CNTs-1. In addition, the sharp 2D peak of Co@N-CNTs-1 means that a thinner carbon film formed than that of Co@N-CNTs-3.

Electrocatalytic activities of Co@N-CNTs toward the ORR.—The electrocatalytic activity of Co@N-CNTs-1 for ORR was measured by CV in N$_2$ and O$_2$ saturated KOH solution. As shown in Figure 3, there is no redox peak within the potential range for the N$_2$-saturated solution (curve a). When the solution was enriched with O$_2$, a well-defined peak with high current density at 0.82 V vs. RHE was observed, and the onset potential ($E_{onset}$) was 0.94 V (curve b), suggesting the
excellent electrocatalytic activity of the Co@N-CNT-1 for ORR. For a comparison, the CVs of multi-walled carbon nanotubes (curve c) and commercial Pt/C (20 wt%) (curve d) modified electrode were also measured. It was observed that both the onset potential and the current density for Co@N-CNT-1 were superior to that of multi-walled carbon nanotubes (curve c), and was comparable to Pt/C catalyst (curve d). In addition, the electrocatalytic activity of Co@N-CNTs-2 was also studied as shown in Figure S4, and its electrocatalytic activity was obviously lower than that of Co@N-CNT-1, which could be attributed to the existence of Co$_3$O$_4$ in the products that impress the electrocatalytic activity.

To better understand the electrocatalytic performance of Co@N-CNTs catalysts during the ORR process, linear sweep voltammetry (LSV) curves were measured using RDE in O$_2$ saturated 0.1 mol L$^{-1}$ KOH solution at a rotation rate of 1600 rpm. As shown in Figure 4A, the ORR $E_{\text{onset}}$ of the Co@N-CNTs-1 (0.975 V, curve c) is very close to the commercial Pt/C (1.01 V, curve d) and is better than that of Co@N-CNTs-2 (0.963 V, curve b) and Co@N-CNTs-3 (0.970 V, curve a). Moreover, the limiting current density at 0.4 V of Co@N-CNTs-1 (2.697 mA cm$^{-2}$, curve c) is close to that of the commercial Pt/C catalyst, which is much larger than that of Co@N-CNTs-2 (2.318 mA cm$^{-2}$, curve b) and Co@N-CNTs-3 (2.004 mA cm$^{-2}$, curve a). These results confirmed that the good electrocatalytic activity of Co@N-CNTs-1 toward the ORR. ORR activity of the Co@N-CNTs-1 was also gleaned from the smaller Tafel slope of 49 mV/decade (Figure 4B, curve c) at low over-potentials compared to Co@N-CNTs-2 (65 mV/decade, curve a) and Co@N-CNTs-3 (59 mV/decade, curve b). It’s known that the activity of nitrogen doped carbon is associated with the types of nitrogen. As it was described in the XPS spectra, the content of pyrrolic nitrogen in Co@N-CNTs-1 was higher than that of Co@N-CNTs-3. The Co@N-CNTs-2 had the highest content of pyridinic nitrogen. The results are similar to those reported that the content of the three types nitrogen achieved a balance contributes to more active site for ORR. The facts suggested that glucose in the experiments facilitates the formation of pyrrolic nitrogen and quaternary nitrogen. Furthermore, the calcination aging at 550 $^\circ$C increased the transformation of pyridinic nitrogen to pyrrolic nitrogen, which may be resulted in the good electrocatalytic activity toward the ORR. These results were also confirmed by Raman spectrum that after the calcination aging at 550 $^\circ$C, the Co@N-CNTs-1 has the higher $I_D/I_G$ (1.05) and the sharper 2D peak than the Co@N-CNTs-3. These results implied that Co@N-CNTs-1 has a thinner carbon film therefore has more significant structural defects and N dopants which has more active site for ORR.

RDE voltammetry was further performed to study the kinetics of the electrochemical catalytic ORR for Co@N-CNTs-1. The polarization curves were obtained by scanning the potential from 0.3 to 1.0 V at a scan rate of 5 mV s$^{-1}$ in O$_2$-saturated 0.1 mol L$^{-1}$ KOH solution with a variety of rotation rates ranging from 400 rpm to 2025 rpm. As shown in Figure 5, the limiting current density increased with increasing rotation rate. The corresponding Koutecky-Levich (K-L) plots showed good linearity with parallelism over the potential range.
Figure 4. (A) RDE linear sweep voltammetrys (LSV) of (a) Co@N-CNTs-3, (b) Co@N-CNTs-2, (c) Co@N-CNTs-1 and (d) Pt/C modified electrode at 1600 rpm in O2-saturated 0.1 mol L\(^{-1}\) KOH solution with a scan rate of 5 mV s\(^{-1}\). (B) Tafel plots of (a) Co@N-CNTs-2, (b) Co@N-CNTs-3, (c) Co@N-CNTs-1 and (d) Pt/C modified electrode.

Figure 5. (A) RDE linear sweep voltammetrys (LSV) of Co@N-CNTs-1 modified electrode at different rotating speeds in O2-saturated 0.1 mol L\(^{-1}\) KOH solution with a scan rate of 5 mV s\(^{-1}\). (B) Koutecky-Levich (K-L) plots of the material from RDE voltammetrys at different potentials.

Figure 6. RDE linear sweep voltammograms (LSV) of (a) MCNTs, (b) Co@N-CNTs-3, (c) Co@N-CNTs-2, (d) Co@N-CNTs-1 and (e) Pt/C modified electrode at 1600 rpm in O2-saturated 0.5 mol L\(^{-1}\) H\(_2\)SO\(_4\) solution with a scan rate of 5 mV s\(^{-1}\).
activity of the materials was first increased as the pyrolysis temperature increased from 700 °C to 900 °C, and then decreased after 900 °C. The highest ORR current density was obtained at 900 °C.

The electrocatalytic performance of Co@N-CNTs in acidic medium was also investigated. The LSV curves were obtained at different electrodes with an electrode rotation rate of 1600 rpm in O2-saturated 0.5 mol L\(^{-1}\) H\(_2\)SO\(_4\) solution. As shown in Figure 6, all these Co@N-CNTs catalysts show larger current densities and more positive \(E_{\text{onset}}\) compared with the MCNTs in acidic medium (curve a). Particularly, the \(E_{\text{onset}}\) of the Co@N-CNTs-1 (curve d) is 0.77 V, which is more positive than the Co@N-CNTs-3 (0.710 V, curve b) and the Co@N-CNTs-2 (0.720 V, curve c).

The resistance to crossover effects and stability of the catalyst materials are important considerations for their practical application in fuel cells. Chronoamperometric responses of Co@N-CNTs-1 were measured to evaluate the methanol crossover and stability (Figure 7A). It could be seen that the Co@N-CNTs-1 exhibited a consistent ORR curve after the addition of 3 mol L\(^{-1}\) methanol to an O2-saturated 0.1 mol L\(^{-1}\) KOH solution, whereas the ORR curve of the commercial Pt/C suffered a sharp decrease after the addition of methanol. These results indicate that Co@N-CNTs-1 exhibit high ORR selectivity and have a good ability to avoid crossover effects. The durability of Co@N-CNTs-3 and commercial Pt/C were also tested (Figure 7B). The Co@N-CNTs-1 were held at 0.81 V for 25000 s in an O2-saturated 0.5 mol L\(^{-1}\) KOH solution. It could be seen that the chronoamperometric response for Co@N-CNTs-1 exhibited a slight decrease of less than 17%, which was much better than that of commercial Pt/C of approximately 40% decline after 25000 s. These results demonstrated that Co@N-CNTs-1 have superior stability and have potential use in direct methanol and alkaline fuel cells. In addition, the durability of Co@N-CNTs-3 in O2-saturated 0.5 mol L\(^{-1}\) H\(_2\)SO\(_4\) solution was also evaluated. As shown in Figure S7, the chronoamperometric response for Co@N-CNTs-3 exhibited a decrease of less than 30%, while the commercial Pt/C lost approximately 75% after 25000 s, indicating a better stability of the Co@N-CNTs-3 than the commercial Pt/C in acidic medium. The above results demonstrate that the Co@N-CNTs-1 also presents excellent the ORR catalytic activity in acidic medium.

As far as the excellent performances on ORR and the unique structure features of Co@N-CNTs-1, there are three reasons should be responsible for its superior electrocatalytic performance for ORR: (i) The assembling process of the precursors to form novel superstructures, adding glucose as a reducing agent and the gradient temperature synthesis mechanism are indispensable for catalyzing the ordered assembled N-doped nanocarbon. (ii) The calcination aging temperature of 550 °C facilitates the formation of pyridinic nitrogen and pyrrolic nitrogen at a suitable ratio which are valuable active sites for ORR. (iii) Glucose added during calcination procedures acts as a reducing agent and carbon source for the formation of carbon encapsulated Co metallic nanoparticles, avoiding the formation of cobalt oxides and the exposure of Co nanoparticles during electrochemical reduction procedures. These synergies effects are attributed to the excellent electrocatalytic activity toward the ORR.

Conclusions

In summary, the nitrogen doped carbon nanotubes encapsulated cobalt nanoparticles (Co@N-CNTs-1) was fabricated by assembling the precursors of melamine, glucose and cobalt nitrate hexahydrate. The as-prepared Co@N-CNTs-1 catalyst exhibited activity with highly positive onset potential and preferable current density, excellent tolerance to methanol oxidation and high stability in both alkaline and acidic medium. The glucose added during gradient temperature plays an important role in formation of a thin carbon shell on the Co nanoparticles, which protects it from being destroyed during the electrochemical procedures, and facilitates to the ordered arrangement of nitrogen-carbon precursors and the formation of enriched pyridinic, pyrrolic and quaternary nitrogen, resulting in the highly activity of Co@N-CNTs. The strategy enlightens the future design of state-of-the-art nanostructured materials as an alternation for precious metal-based ORR catalysts.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (No. 21475071, 51572139, 21874080, 21622506, 21621003), National Basic Research Program of China (No. 2013CB934004), National Key Research and Development Program of China (No. 2016YFA0203101), Tsinghua University Initiative Scientific Research Program (2014z1027), Beijing municipal science and technology commission (Z171100001171135), the Taishan Scholar Program of Shandong Province (No. ts201511027).

ORCID

Feifei Zhang https://orcid.org/0000-0002-9828-750X
Zonghua Wang https://orcid.org/0000-0003-4138-6328

References

1. W. J. Zhou et al., “N-Doped Carbon-Wrapped Cobalt Nanoparticles on N-Doped Graphene Nanosheets for High-Efficiency Hydrogen Production.” Chemistry of Materials, 27(6), 2026 (2015).
2. L. M. Dai et al., “Metal-Free Catalysts for Oxygen Reduction Reaction.” Chemical Reviews, 115(11), 4823 (2015).

3. Y. Lv and X. B. Wang, “Nonprecious Metal Phosphides as Catalysts for Hydrogen Evolution, Oxygen Reduction and Evolution Reactions.” Catalysis Science & Technology, 7(17), 3676 (2017).

4. S. B. Jin et al., “An Oxygen Reduction Electrocatalyst based on Carbon Nanotube-Graphene Complexes.” Nature Nanotechnology, 7(6), 394 (2012).

5. S. Jiang, C. Z. Zhu, and S. J. Dong, “Cobalt and Nitrogen-Cofunctionalized Graphene as a Durable Non-Precious Metal Catalyst with Enhanced ORR Activity.” Journal of Materials Chemistry A, 1(11), 3593 (2013).

6. Y. Z. Dong and J. H. Li, “Heating Treated Carbon Nanotubes As Highly Active Electrocatalysts for Oxygen Reduction Reaction.” Nano Letters, 10(10), 780 (2011).

7. Y. Y. Liang et al., “Cobalt and Nitrogen Co-Doped Carbon Nanotubes and Their Catalytic Activity for the Oxygen Reduction Reaction.” Applied Surface Science, 427, 262 (2018).

8. Y. Hou et al., “An Advanced Nitrogen-Doped Graphene/Cobalt-Embedded Porous Carbon Polyhydroxynitrogen for Highly Efficient Catalysis of Oxygen Reduction and Water Splitting.” Advanced Functional Materials, 35(6), 872 (2015).

9. A. Indra et al., “Unification of Catalytic Water Oxidation and Oxygen Reduction Reactions: Amorphous Beat Crystalline Cobalt Iron Oxides.” Journal of the American Chemical Society, 136(50), 17530 (2014).

10. M. J. Liu and J. H. Li, “Copper Nitride Nanocubes: Size-Controlled Synthesis and Their Catalytic Activity for the Oxygen Reduction Reaction.” Nature Nanotechnology, 7(6), 394 (2012).

11. S. T. Yang et al., “Onion-Derived N, S Self-Doped Carbon Materials as Highly Efficient Metal-Free Electrocatalysts for the Oxygen Reduction Reaction.” Applied Surface Science, 427, 262 (2018).

12. Y. Z. Dong and J. H. Li, “Heating Treated Carbon Nanotubes As Highly Active Electrocatalysts for Oxygen Reduction Reaction.” Nano Letters, 10(10), 780 (2011).

13. Y. G. Li et al., “An Oxygen Reduction Electrocatalyst based on Carbon Nanotube-Graphene Complexes.” Nature Nanotechnology, 7(6), 394 (2012).

14. S. F. Fu et al., “One-Step Synthesis of Cobalt and Nitrogen Co-Doped Carbon Nanotubes and Their Catalytic Activity for the Oxygen Reduction Reaction.” Journal of Materials Chemistry A, 3(24), 12718 (2015).

15. M. Sun et al., “Graphene-Based Transition Metal Oxide Nanocomposites for the Oxygen Reduction Reaction.” Nanoscale, 7(4), 1250 (2015).

16. L. J Cao et al., “Synergistic Effects of C/Go-Mo and Ag for Efficient Oxygen Reduction Reaction.” The Journal of Physical Chemistry Letters, 9(4), 779 (2018).

17. Y. Y. Liang et al., “Coo:O Nanocrystals on Graphene as a Synergistic Catalyst for Oxygen Reduction Reaction.” Nature Chemistry, 10(10), 780 (2011).

18. Y. Y. Liang et al., “Cobalt and Nitrogen Co-Doped Carbon Nanotubes on Graphene Framework as a Highly Efficient Electrocatalyst for Oxygen Reduction Reaction.” Journal of the American Chemical Society, 136(10), 3676 (2014).

19. L. B. Wu and W. Chen, “Copper Nitride Nanocubes: Size-Controlled Synthesis and Application as Cathode Catalyst in Alkaline Fuel Cells.” Journal of the American Chemical Society, 133(39), 15236 (2011).

20. Y. Z. Dong and J. H. Li, “Tungsten Nitride Nanocrystals on Nitrogen-Doped Carbon Black as Efficient Electrocatalysts for Oxygen Reduction Reactions.” Chemical Communications, 51(3), 572 (2015).

21. Y. S. Jun et al., “Mesoporous, 2D Hexagonal Carbon Nitride and Titanium Nitride/Carbon Composites.” Advanced Materials, 21(42), 4270 (2009).

22. Z. W. Chen et al., “A Review on Non-Precious Metal Electrocatalysts for PEM Fuel Cells.” Energy & Environmental Science, 4(9), 3167 (2011).

23. G. Wu et al., “High-Performance Electrocatalyst for Oxygen Reduction Derived from Polyaniline, Iron, and Cobalt.” Science, 332(6028), 443 (2011).

24. G. Wu et al., “Nitrogen Doped Graphene-Rich Catalysys Derived from Heteroatom Polymers for Oxygen Reduction in Nonaqueous Lithium-0.2 Battery Cathodes.” ACS Nano, 6(11), 9764 (2012).

25. A. Indra et al., “Unification of Catalytic Water Oxidation and Oxygen Reduction Reactions: Amorphous Beat Crystalline Cobalt Iron Oxides.” Journal of the American Chemical Society, 136(50), 17530 (2014).

26. Z. W. Chen et al., “A Review on Non-Precious Metal Electrocatalysts for PEM Fuel Cells.” Energy & Environmental Science, 4(9), 3167 (2011).

27. A. Indra et al., “Unification of Catalytic Water Oxidation and Oxygen Reduction Reactions: Amorphous Beat Crystalline Cobalt Iron Oxides.” Journal of the American Chemical Society, 136(50), 17530 (2014).

28. K. S. Kim et al., “Large-scale Pattern Growth of Graphene Films for Stretchable Transparent Electrodes.” Nature, 457(7230), 706 (2009).

29. J. S. Shen et al., “Anion-Triggered Melamine based Self-assembly and Hydrogel.” Chemical Communications, 46(36), 6786 (2010).

30. S. T. Yang et al., “Onion-Derived N, S Self-Doped Carbon Materials as Highly Efficient Metal-Free Electrocatalysts for the Oxygen Reduction Reaction.” Nanoscale, 6(24), 15066 (2014).

31. A. Weinstabl et al., “Melamine Salts as Hardeners for Urea Formaldehyde Resins.” Journal of Applied Polymer Science, 83(7), 1654 (2001).

32. Y. S. Jun et al., “Mesoporous, 2D Hexagonal Carbon Nitride and Titanium Nitride/Carbon Composites.” Advanced Materials, 21(42), 4270 (2009).

33. K. S. Kim et al., “Large-scale Pattern Growth of Graphene Films for Stretchable Transparent Electrodes.” Nature, 457(7230), 706 (2009).

34. L. T. Qu et al., “Nitrogen-Doped Graphene as Efficient Metal-Free Electrocatalyst for Oxygen Reduction in Fuel Cells.” ACS Nano, 4(3), 1321 (2010).