

Molecular Architecture of Cobalt Porphyrin Multilayers on Reduced Graphene Oxide Sheets for High-Performance Oxygen Reduction Reaction**

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Thanks to their lightweight, highly efficient, modular and scalable properties, polymer electrolyte membrane fuel cells (PEMFCs) have long been thought to be a promising candidate for applications in transportation and in both stationary and portable electronics.^[1] Unfortunately, despite the above advantages, until now the fuel-cell technologies have failed to reach mass commercialization, and the main problems include short operational time and high cost of the materials used.^[1b–d] For example, platinum-based materials are generally believed to be ideal catalysts for the oxygen reduction reaction (ORR) at the cathodes of PEMFCs; however, their disadvantages, for example, low tolerance to methanol fuel, high price and scarcity, limit the practical application of platinum-based catalysts.^[2] Therefore, replacement of platinum-based materials with non-precious-metal catalysts, which are of low cost, high catalytic activity, and robust, has become one of the key issues for the realization of mass applications of PEMFCs.^[3a,b]

In recent years, many non-precious-metal electrocatalysts have been investigated, such as non-pyrolyzed transition-metal macrocycles, conductive polymer based complexes, transition-metal chalcogenides,^[3c,d] metal oxide/carbide/nitride materials, and even enzymes.^[3a] One of the most promising types of non-precious-metal catalysts is carbon-supported transition-metal-nitrogen (C/M-N_x) materials (M = Co, Fe, Ni, Mn, etc., and normally $x = 2$ or 4).^[4] The purpose of using carbon substrates to support M-N_x is that they have high surface areas and can offer a sufficient number of reacting sites.^[5] Since the finding in the 1960s that the

carbon-supported transition-metal porphyrins, namely cobalt phthalocyanine (CoPc), could act as the catalysts for ORR,^[6] many C/M-N_x compounds have been investigated and their potential applications in PEMFCs have been demonstrated.^[7] However, all these C/M-N_x catalysts still suffer from low activity and stability toward ORR and are thus far away from satisfying the requirements of fuel cells.^[8] The drawbacks of the C/M-N_x catalysts originate from the absence of control of the interaction between the C substrates and the M-N_x compounds as well as the rational structural design of the M-N_x compounds.^[3a]

Herein, we present a novel strategy to prepare the C/M-N_x catalysts, in which the molecular architecture of the cobalt porphyrin multilayers is incorporated onto the reduced graphene oxide (rGO) sheets using the layer-by-layer (LBL) assembly technique.^[9] In addition to its high specific surface area,^[10] rGO can offer possible electrostatic or coordination interactions with the supported catalysts.^[11] Especially for the cobalt porphyrin catalysts, the planar benzene rings of the rGO sheets could provide additional interactions, for example, π - π stacking and van der Waals forces. Such multiple interactions will favor the stability of the catalysts on the substrates.^[12] Also the rGO sheets have high chemical, thermal, and mechanical stabilities, which are beneficial for improvement of the lifetime of the catalysts.^[13] On the other hand, the LBL assembly method has been broadly used to construct functional nanostructures because of its numerous advantages, such as ease of preparation, versatility, capability of incorporating high loadings of different molecules in the films.^[14a] Therefore, we expect to use the LBL assembly technique to control the structure, thickness, and uniformity of the cobalt porphyrin catalysts on the surface of the rGO sheets at the molecular level, leading to maximization of the catalytic activity for ORR.

Scheme 1 illustrates the typical LBL procedure to synthesize the catalysts. First, the graphene oxide (GO) and Co²⁺ ions are mixed in the solution. The presence of many oxygen-containing groups on the surface of the GO sheets allows the Co²⁺ ions in the solution to be adsorbed onto the GO sheets by coordination/electrostatic interactions.^[11b] Subsequently, the GO sheets with adsorbed Co²⁺ ions are separated from the mixture solution by centrifugation and washed with pure water several times, to remove excess Co²⁺ ions. Then, the Co²⁺-GO sheets are mixed with 5,10,15,20-tetrakis(4-hydroxyphenyl) porphyrin (THPP) in solution.^[9b] Afterwards, the GO sheets with the adsorbed Co²⁺-THPP monolayer are purified again by centrifugation and washing with pure water. As a result, the desired multilayers on the GO substrate can

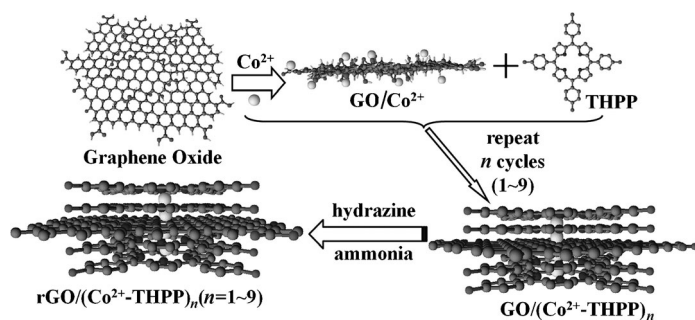
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Scheme 1. Preparation procedure of $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_n$.

be obtain the by many cycles of alternative adsorption of Co^{2+} and THPP. Such nanostructures are named as $\text{GO}/(\text{Co}^{2+}\text{-THPP})_n$, and n stands for the cycle number of one composite layer of Co^{2+} and THPP.^[9c,14b] Finally, the GO supports in the $\text{GO}/(\text{Co}^{2+}\text{-THPP})_n$ composites are reduced by hydrazine in the ammonia solution to obtain the $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_n$ products.^[11b]

The LBL assembly process of the $\text{Co}^{2+}\text{-THPP}$ multilayers on the GO sheets is monitored by the UV/Vis absorption spectra (Figure 1).^[14c] The free THPP molecules in solution display five characteristic absorption bands (Figure 1a), including an intense Soret band at 413 nm and four Q-bands located at 516, 554, 594, and 650 nm. Coordination of THPP with Co^{2+} ions to form the $\text{Co}^{2+}\text{-THPP}$ complexes results in red shift of the Soret bands to 433 nm, while the number of Q-bands decreases to two (inset in Figure 1a).^[15a] Compared to

that of free THPP or $\text{Co}^{2+}\text{-THPP}$ molecules in solution, the Soret band of the $\text{Co}^{2+}\text{-THPP}$ multilayers on the GO sheets is split into two peaks, 425 nm and 452 nm (Figure 1b), which should be assigned to the J-aggregation in the same plane and the H-aggregation along the axial direction, respectively.^[15b] Furthermore, by normalizing the adsorption peak of the GO sheets at 229 nm, it can be seen that the intensity of the Soret bands of $\text{GO}/(\text{Co}^{2+}\text{-THPP})_n$ at 425 nm increases linearly with the assembly cycle, suggesting the uniform growth of the $\text{Co}^{2+}\text{-THPP}$ multilayers perpendicular to the GO substrates.^[16]

Such homogeneous growth can be also confirmed by atomic force microscopy (AFM; Supporting Information, Figure S1). The measured thickness of the single GO layer before deposition of the $\text{Co}^{2+}\text{-THPP}$ complexes is around 1.3 nm (Figure S1a),^[17a] and the average thickness of each layer during the subsequent growth is measured to be about 0.5 nm (Figure S1 and S2). Notably, half of this value ($\text{Co}^{2+}\text{-THPP}$ should be absorbed on both sides of the GO sheets) is very close to the thickness of the $\text{Co}^{2+}\text{-THPP}$ molecule (0.3 nm),^[17b] which suggests that, in each layer, $\text{Co}^{2+}\text{-THPP}$ is homogeneously adsorbed on the GO sheets in the form of monolayer.

To enhance the conductivity in the ORR process, the $\text{GO}/(\text{Co}^{2+}\text{-THPP})_n$ samples are subsequently reduced by hydrazine in ammonia solution.^[11b] As shown in Figure 1c, the resultant $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$ products in solution are very stable and no precipitation is observed even after being left for five months at room temperature. This stability is essential for lowering the overpotential of the ORR catalysts,^[18] whereas the direct reduction of the GO sheets in solution results in considerable precipitation after the same time. Figure 1d shows the UV/Vis absorption spectra of $\text{GO}/(\text{Co}^{2+}\text{-THPP})_7$, $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$, GO and rGO. Both GO and $\text{GO}/(\text{Co}^{2+}\text{-THPP})_7$ show the characteristic absorption peaks of GO at 229 nm (Figure 1d). After reduction, for both the rGO and $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$ products, the peaks at 229 nm are red shifted to 266 nm with a clear increase of the adsorption intensity in the whole UV and visible region.^[11,12] Another prominent absorption feature of the $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$ products is that the characteristic Soret band of $\text{Co}^{2+}\text{-THPP}$ is preserved with slight bathochromic shift to 433 nm, indicating that reduction with hydrazine only results in conversion of GO to rGO rather than any reaction with the $\text{Co}^{2+}\text{-THPP}$ multilayers. The red shift of the Soret band absorption can be assigned to the increased electron transfer from the rGO substrates to the THPP molecules through the Co^{2+} bridge. Such electron transfer gives rise to the electron-rich $\text{Co}^{2+}\text{-THPP}$ complexes, which is beneficial for ORR.^[19] This conclusion is also drawn by microscopy observation (Figure S3a and S3b), and there is no structural alteration to be found after reduction (Figure S4).

Except for the morphology, possible changes in the chemical composition of $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$ by hydrazine reduction are investigated by X-ray photoelectron spectroscopy (XPS). Figure 2 displays the high-resolution

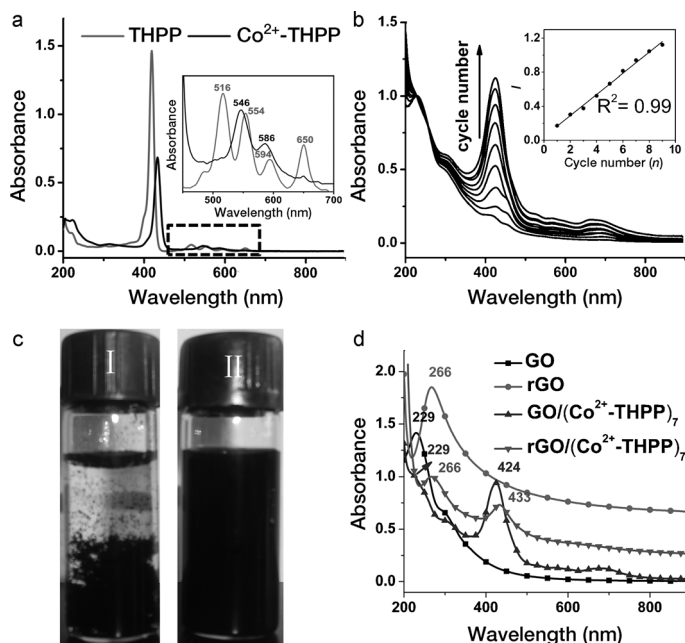


Figure 1. a) UV/Vis adsorption spectra of free THPP or $\text{Co}^{2+}\text{-THPP}$ in solution. Inset: expansion of the selected area. b) UV/Vis adsorption spectra of $\text{GO}/(\text{Co}^{2+}\text{-THPP})_n$ ($n = 1-9$). Inset: relationship of the UV/Vis adsorption intensity at 425 nm with increase of the cycle number. c) Solutions of rGO (I) and $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$ (II) after being stored under ambient conditions for five months. d) UV/Vis adsorption spectra of GO, rGO, $\text{GO}/(\text{Co}^{2+}\text{-THPP})_7$, and $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$.

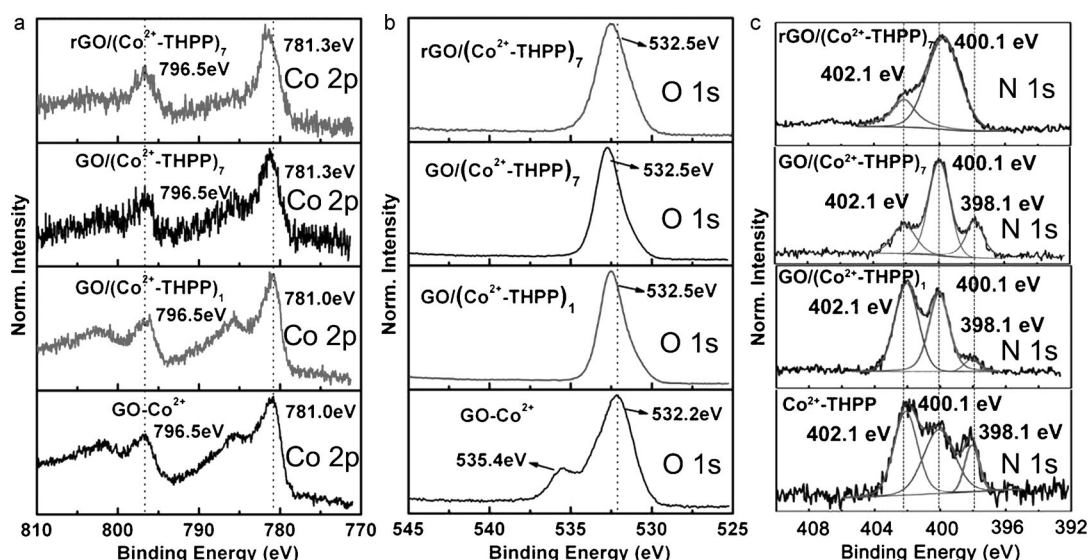


Figure 2. High-resolution XPS spectra of a) Co 2p and b) O 1s of GO/Co^{2+} , $\text{GO}/(\text{Co}^{2+}\text{-THPP})_1$, $\text{GO}/(\text{Co}^{2+}\text{-THPP})_7$, and $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$, and c) N 1s of $\text{Co}^{2+}\text{-THPP}$, $\text{GO}/(\text{Co}^{2+}\text{-THPP})_1$, $\text{GO}/(\text{Co}^{2+}\text{-THPP})_7$, and $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$.

spectra of Co 2p and O 1s of GO/Co^{2+} , $\text{GO}/(\text{Co}^{2+}\text{-THPP})_1$, $\text{GO}/(\text{Co}^{2+}\text{-THPP})_7$, and $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$ and the N 1s of $\text{Co}^{2+}\text{-THPP}$, $\text{GO}/(\text{Co}^{2+}\text{-THPP})_1$, $\text{GO}/(\text{Co}^{2+}\text{-THPP})_7$, and $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$. As shown in Figure 2a, direct mixture of the GO sheets with the Co^{2+} ions leads to appearance of the Co 2p peaks located at 781.0 eV and 796.5 eV. Simultaneously, in addition to the O 1s peak of GO at 532.2 eV (Figure S5b), a new O 1s peak located at 535.4 eV arises (GO/Co^{2+} in Figure 2b), which corresponds to the electrostatic interaction of the Co^{2+} ions and the oxygen-containing groups of the GO substrates.^[20] After injection of the THPP molecules, the O 1s peak at 535.4 eV disappears and the peak located at 532.2 eV shifts to 532.5 eV ($\text{GO}/(\text{Co}^{2+}\text{-THPP})$ in Figure 2b), whereas the Co 2p peaks remain unchanged. Therefore, one can draw the conclusion that after introduction of the N-containing THPP molecules, the $\text{Co}^{2+}\text{-THPP}$ complexes are formed while the interactions between the Co^{2+} ions and the O-containing groups of the GO substrates are weakened. This deduction is also supported by analyzing the XPS spectra of the N species. As for the $\text{Co}^{2+}\text{-THPP}$ complexes in solution, a new peak with respect to pure THPP (Figure S5c)^[21a] appears at 402.1 eV, which is assigned to the N atoms binding Co^{2+} ions (Figure 2c). The coexistence of the three types of N 1s signals indicates that the N atoms of the THPP macrocycles only partially coordinate with the Co^{2+} ions to form the complexes. Similarly to the $\text{Co}^{2+}\text{-THPP}$ complexes, the three types of N 1s signals are distinguished in $\text{GO}/(\text{Co}^{2+}\text{-THPP})_1$, though the intensity of the iminic N at 398.1 eV is decreased through more coordination with Co^{2+} ions. When the cycle number is increased to 7, the intensity of the $\text{Co}^{2+}\text{-N}$ peak at 402.1 eV in $\text{GO}/(\text{Co}^{2+}\text{-THPP})_7$ is considerably decreased, revealing that many THPP molecules in the $\text{Co}^{2+}\text{-THPP}$ multilayers may not coordinate with the Co^{2+} ions. The strong intermolecular π - π interactions between the adjacent THPP layers should be responsible for stabilization of such uncoordinated THPP molecules in the multilayer structure. After production of $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$ by reduction with hydra-

zine, the signal corresponding to the iminic N atom at 398.1 eV has almost disappeared, indicating that the iminic N atom of the THPP molecules is reduced to a pyrrolic N atom.^[21b] Nevertheless, the signal of $\text{Co}^{2+}\text{-N}$ at 402.1 eV is well-preserved in $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$, highlighting the high stability of $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_n$ even in the strong reductive environment. This high-stability feature will aid use of the composites as durable ORR catalysts.

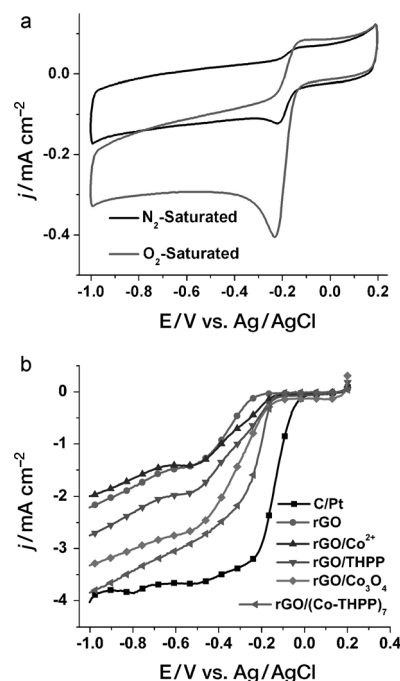


Figure 3. a) CV curves of $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$ on glass carbon electrodes in O_2 -saturated or N_2 -saturated 0.1 M KOH solution. b) LSV on RDE of rGO , $\text{rGO}/\text{Co}^{2+}$, rGO/THPP , $\text{rGO}/\text{Co}_3\text{O}_4$, $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$, and C/Pt in O_2 -saturated 0.1 M KOH solution with a sweep rate of 10 mV s^{-1} . The rotation rate of RDE is 1600 rpm .

The electrocatalytic activity of $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_n$ for ORR is evaluated by cyclic voltammetry (CV) scanning in a 0.1 M KOH aqueous solution saturated with either N_2 or O_2 gas at room temperature.^[22] The $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$ sample is selected as a typical catalyst for examining the ORR activity. As shown in Figure 3a, a well-defined O_2 reduction peak centered at -0.22 V emerges as the electrolyte solution is saturated with O_2 (the gray curve in Figure 3a), which is close to the value of -0.18 V of the commercial carbon-supported Pt (C/Pt) and superior to other rGO-based catalysts (Figure S6 and S7). The impressive electrocatalytic activity of $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$ is confirmed by recording the linear sweep voltammetry (LSV) curves on a rotating disk electrode (RDE; Figure 3b). The limiting current density of $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$ at -1.0 V is up to about -4.0 mA cm^{-2} , which is much higher than other rGO-based materials and comparable to C/Pt. The electrocatalytic activity of $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$ should originate from the synergistic effect of the adsorbed $\text{Co}^{2+}\text{-THPP}$ complexes and the rGO substrates in the hybrid materials.

The LBL assembly technique allows us to accurately control the structure and the thickness of the $\text{Co}^{2+}\text{-THPP}$ complexes on the rGO substrates.^[14] As shown in Figure S8, with the increasing layer number of the $\text{Co}^{2+}\text{-THPP}$ complexes, the peak position of ORR is positively shifted until the layer number reaches 5. The $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_n$ composites with $n > 5$ have similar ORR peaks at around -0.18 V. Such a change in the ORR activity could be understood in that when the adsorbed amount of $\text{Co}^{2+}\text{-THPP}$ is small, an increase in the number of $\text{Co}^{2+}\text{-THPP}$ layers enhances the catalytic activity; however, when the adsorbed amount of $\text{Co}^{2+}\text{-THPP}$ is high enough, a further increase in the number of adsorption layers impedes diffusion of both O_2 and electrolyte towards the inner $\text{Co}^{2+}\text{-THPP}$ layers, resulting in no additional improvement in the ORR activity and even some extent in a decrease that can be seen in the LSV curve of $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_9$ (Figure S8).

To gain further insight into ORR involving the $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_n$ catalysts, LSV curves on RDE at different rotation rates are recorded (Figure 4a). The electron-transfer number is then calculated to be approximately 3.85 between -0.3 and approximately -0.5 V from the slopes of the Koutecky–Levich plots (the inset in Figure 4a, see details in see details in part S1 in the Supporting Information),^[23a] which is consistent with the rotating ring-disk electrode (RRDE) measurements (Figure S9) and similar to the commercial C/Pt (Figure S10), indicating the ORR at the $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$ electrodes proceeds by an approximate four-electron reduction pathway.

Except for the activity, the stability is another key parameter for high-performance catalysts.^[23b] As seen in Figure 4b, though the current density of both $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$ and C/Pt decreases with time, $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$ has a much slower decay rate. For instance, 80 % of the initial catalytic current could be maintained at the $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$ electrode after continuous reaction for about 40 000 s, whereas only 50 % of that is kept for the commercial C/Pt, demonstrating the remarkably stability of $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$ in the ORR process.

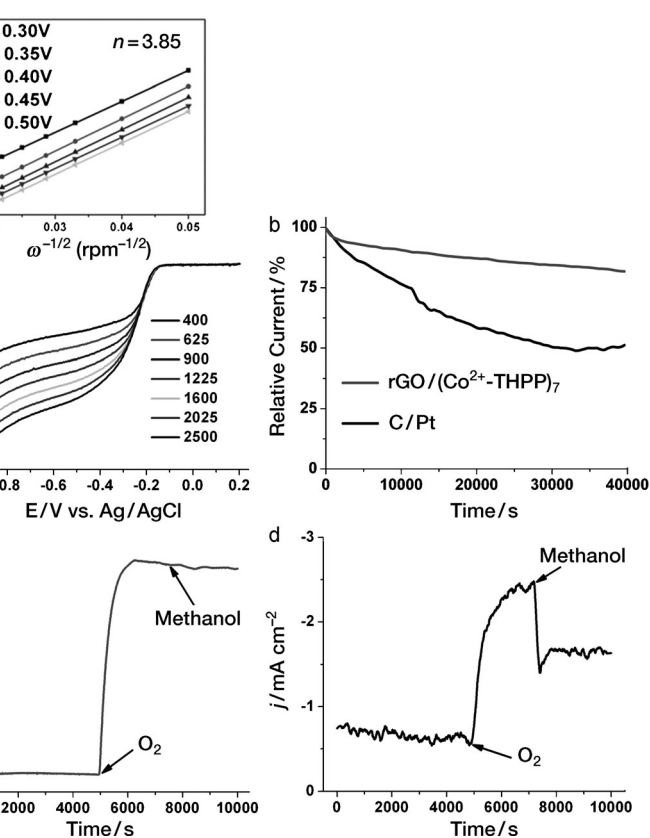


Figure 4. a) LSV on RDE of $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$ in O_2 -saturated 0.1 M KOH solution with a sweep rate of 10 mV s^{-1} at different rotation rates. Inset: corresponding Koutecky–Levich plots (j^{-1} versus $\omega^{-1/2}$) at different potentials. b) Normalized $I-t$ chronoamperometric responses of $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$ and C/Pt at -0.25 V in O_2 -saturated 0.1 M KOH solution at a rotating rate of 1000 rpm. $I-t$ chronoamperometric responses of c) $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$ and d) C/Pt at -0.25 V in 0.1 M KOH solution. The solution is saturated with N_2 from 0 to 5000 s, then by an immediate introduction of O_2 . The arrows indicate the point at which 3.0 M methanol is added into the O_2 -saturated 0.1 M KOH solution (at 7000 s).

The catalysts should also be robust in the real application environment.^[22a] Specific to the ORR catalysts, the crossover effect must be considered.^[23c] As shown in Figure 4c and d, an immediate response in the chronoamperometric curve is observed for C/Pt in O_2 -saturated KOH solution with 3.0 M methanol, while no noticeable change for $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$ is discerned under the same conditions. The big difference in resistance to methanol is also noted by investigating the CV behaviors of $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$ and C/Pt in the O_2 -saturated 0.1 M KOH solution containing 3 M methanol (Figure S11). These experimental results unambiguously reveal that $\text{rGO}/(\text{Co}^{2+}\text{-THPP})_7$ has a much better methanol tolerance towards ORR than the commercial C/Pt, namely, a great tolerance to possible crossover effect.

In summary, we have designed and prepared novel C/M-N_x catalysts, rGO/(Co²⁺-THPP)_n, for ORR. Compared to other rGO-based materials including rGO/Co²⁺, rGO/THPP, and rGO/Co₃O₄, rGO/(Co²⁺-THPP)_n exhibits much high electrocatalytic activity. Moreover, in respect to the commercial C/Pt catalysts, rGO/(Co²⁺-THPP)_n shows the comparable electrocatalytic activity, but better stability and increased tolerance to the crossover effect. Such electrocatalytic performances arise from accurate structural control over the rGO/(Co²⁺-THPP)_n composites at the molecular level and corresponding maximization of the synergistic coupling between the Co²⁺-THPP complexes and the graphene substrate.^[24] It can be expected that the LBL approach we employed will open a new avenue for the development of low-cost and high-performance catalysts.

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