Bio-inspired Multinuclear Copper Complexes Covalently Immobilized on Reduced Graphene Oxide as Efficient Electrocatalysts for the Oxygen Reduction Reaction

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Inspired by the multicopper active site of laccase, which efficiently catalyzes the oxygen reduction reaction (ORR), herein we report a novel bio-inspired ORR catalyst composed of a multinuclear copper complex that was immobilized on the surface of reduced graphene oxide (rGO) via the covalent grafted triazole-dipyridine (TADPy) dinucleating ligand. This rGO-TADPyCu catalyst exhibited high ORR activity, and superior long-term stability to Pt/C in alkaline media.

The lack of availability of efficient cathodic oxygen reduction reaction (ORR) catalysts is the major barrier to the large-scale commercialization of low-temperature fuel cells. Currently, the noble-metal platinum (Pt) and its alloys are predominantly used as the ORR catalysts in low-temperature fuel cells such as hydrogen/air polymer electrolyte fuel cells, direct methanol fuel cells, and metal-air batteries. However, the sluggish ORR at the cathode generally requires a higher loading of Pt on the cathode. The disadvantages of high cost and scarce reserves together with a low tolerance to fuel crossover of Pt-based catalysts mean that developing low-cost, non-precious-metal catalysts for ORR is of paramount importance for the large commercial fuel cell market. The non-precious-metal catalysts have been extensively pursued mainly through the traditional method of pyrolysis of various precursors, including transition metal complexes of nitrogen-containing precursors, transition metal oxides, and chalcogenides, as well as metal-organic frameworks. This pyrolysis approach largely depends on trial-and-error-based experiments for optimizing the ORR activity, while the actual nature of the active sites remains a subject of debate.

On the other hand, ORR catalysts prepared in a non-pyrolyzed manner have attracted interest because they provide the ability to adequately control the ORR catalyst structure and the underlying support material, thus fine tuning the ORR activity in a structure-function controllable way. In addition, the design of new ORR catalysts using a biomimetic approach could benefit from the relatively clean O2 activation/reduction mechanisms, and thus high efficiency of the enzymatic catalytic reactions. For instance, taking inspiration from the naturally occurring oxygen activation/reduction metalloenzymes such as the heme-containing enzymes, we have reported a biomimetic ORR electrocatalyst, an axial imidazole-coordinated porphyrin covalently grafted to multiwalled carbon nanotubes, which showed remarkable and superior ORR activity and stability compared to commercial Pt/C catalysts in both acidic and alkaline environments.

Copper ions have been implicated in various copper enzymes for O2-binding, activation, and reduction. The multicopper oxidase enzymes, such as laccase, very efficiently catalyze the four-electron reduction of O2 to H2O with very low overpotential, where the active center features in a tri-copper O2-binding/reduction site. For their biological relevance, numerous Cu complexes including multinuclear Cu compounds have been explored as ORR catalysts, although most of the systems exhibited relatively low ORR activity as well as poor catalyst stability. Among all those reported copper complexes, the most efficient Cu-complex-based ORR electrocatalyst is a triazole copper compound [Cu(Hdatrz)]. However, the long-term stability of the [Cu(Hdatrz)] catalyst is poor, and it degrades substantially over repeat potential cycles in alkaline media.

Recent ORR studies of mononuclear Cu complexes covalently immobilized on the surface of glassy carbon have suggested that two proximal coordinated Cu sites are required for efficient O2 reduction, and a Cu polynuclear assembly is the key to attaining four-electron reduction of O2 at low overpotential. Bearing this consideration in mind, we accordingly designed a new bio-inspired multicopper ORR catalyst in which a dinuclear Cu complex was immobilized on the surface of reduced graphene oxide (rGO) via the covalent grafted triazole-dipyridine (TADPy) dinucleating ligand.
Due to its high specific surface area and high electrical conductivity, graphene has emerged as a promising support material for electrocatalysts. In most cases, electrocatalysts were physically adsorbed on the surface of a graphene sheet, which improved the dispersibility of indissolvable catalysts such as Pt nanoparticles. In this work, we chose the alternative method of direct functionalization of graphene with an ORR catalyst via covalent surface modification. This covalent immobilization approach may benefit from the facile electron transfer between the catalyst and the supporting material as well as from tightly holding the catalyst without detaching it from the support.

The preparation route for the covalent functionalization of graphene with TADPy is shown in Scheme 1. We employed in situ generation of an aryl diazonium for covalent functionalization of graphene oxide (GO) using isoamyl nitrite and pyridin-ethynyl-amine. This reaction was evidenced by the FTIR spectrum of the GO-pyridin-ethyl product where a prominent peak at 2198 cm⁻¹ was assignable to the stretching vibration of the grafted pyridine-ethyl groups (Figure 2a), which shifted from 2146 cm⁻¹ in the pyridin-ethyl-amine reactant (Figure S1). Grafting the TADPy ligand onto GO was then accomplished through a “click” reaction between the as-prepared GO-pyridin-ethyl precursor and 2-azidopyridine. X-ray photoelectron spectroscopy (XPS) was used to verify the successful functionalization of GO with the TADPy ligand. The XPS survey spectrum of GO-TADPy revealed the signatures of carbon, nitrogen, oxygen, chlorine, and copper (Figure 3b). The high resolution N1s XP spectrum of GO-TADPy revealed two nitrogen signals, which were deconvoluted into three components with binding energy (BE) of 399.3, 400.0, and 401.7 eV (Figure 2c). The peak at 399.3 eV can be assigned to the pyridine-N, and the peaks at 400.0 and 401.7 eV were then attributed to the triazole-N.[7a, 17a] The FTIR spectrum of GO-TADPy showed additional signals at 1100 cm⁻¹ (Figure 2a), which shifted from 1141 cm⁻¹ in the GO-TADPy (red).

Incorporation of copper ions in the TADPy functionalized rGO afforded the final catalyst rGO-TADPyCu composite, whose morphology was examined by transmission electron microscopy (TEM, Figure 3a) and atomic force microscopy (AFM, Figure S2). The TEM image of the rGO-TADPyCu composite showed small pieces of functionalized rGO with dimensions less than 50 nm × 50 nm. The elemental composition of rGO-TADPyCu was analyzed by XPS. The survey spectrum of rGO-TADPyCu showed the signatures of carbon, nitrogen, oxygen, chloride, and copper (Figure 3b).
copper content was determined to be 0.56 at%. The Cu2p core–level XP spectrum displayed two major peaks at 930–938 eV and 950–958 eV, which were assigned to the BE values of Cu2p3/2 and Cu2p1/2, respectively.[12] Broad Cu(II) satellite peaks at 940–947 eV and 960–967 eV were noted (Figure 3c). The high resolution N1s XP spectrum of rGO-TADPyCu showed a broad nitrogen signal, which was deconvoluted into three components with binding energies of 399.0 eV, 400.0 eV and 401.0 eV (Figure 3d). After Cu incorporation, the binding energies assignable to the pyridine-N (399.0 eV) and the triazole-N (400.0, 401.0 eV) with the rGO-TADPyCu composite demonstrated up shifts when compared with those of the rGO-TADPy (pyridine-N: 398.3 eV; triazole-N: 399.3, 400.2 eV, Figure S3), suggesting the coordination of the TADPy ligand with Cu ions. The N-to-Cu ratio of 5.8 indicates the overall covalent attached TADPy ligands most probably coordinate with Cu ions in a 1:1 ratio as suggested in Figure 1b.

![Figure 3](image)

**Figure 3** (a) TEM image of rGO-TADPyCu. Inset shows the high resolution TEM image. (b) XPS survey spectrum of rGO-TADPyCu. (c) High resolution XP Cu2P spectrum of rGO-TADPyCu. (d) High resolution XP N1s spectrum of rGO-TADPyCu.

Electrochemical characterization of rGO-TADPyCu as an ORR catalyst was then evaluated in an O2-saturated 0.1M KOH solution using a rotating ring-disc electrode at room temperature. Cyclic voltammetry (CV) of rGO-TADPyCu in a 0.1M KOH solution revealed that in the absence of O2 only a clean capacitive CV background was observed; however, the introduction of O2 led to a large cathodic current with a peak at ~0.8 V vs. RHE (Figure 4a), indicating good O2 catalytic activity of rGO-TADPyCu. Linear sweep voltammetry (LSV) was used to further evaluate the catalyst ORR performance. Physisorbed rGO/TAPyCu (a simple mixture of rGO and a mononuclear triazole-pyridine TAPyCu complex, Figure S4), and rGO/TADPyCu (a simple mixture of rGO and a dinuclear triazole-dipyrnidine TADPyCu complex, Figure S5), were used as control samples. The ORR polarization curves of the rGO-TADPyCu catalyst demonstrates both of an enhanced limit current density as well as onset potential (Eonset) relative to those of control samples (Figure 4b). The rGO-TADPyCu catalyst showed half-wave potential (E1/2) value of 0.795 V vs. RHE at 1600 rpm. The Eonset (0.951 V, Figure 4e) with the rGO-TADPyCu catalyst showed significant positive shift compared with that of the metal-free rGO (Eonset = 0.887 V, Figure S6, S8), and it is also much more positive than that of the physisorbed mononuclear rGO/TAPyCu (Eonset = 0.917 V, Figure S6, S8) and dinuclear rGO/TADPyCu composite (Eonset = 0.937 V, Figure S7, S8). The onset potential is one of the important criteria used to evaluate the ORR activity of an electrocatalyst. These results indicated that a much lower ORR overpotential is observed with the rGO-TADPyCu catalyst when all the examined samples are compared. To the best of our knowledge, the E1/2 value of 0.795 V and the Eonset of 0.951 V are the most positive ones among the Cu complexes as ORR catalysts reported to date.[11, 12]

![Figure 4](image)

**Figure 4** (a) Cyclic voltammograms of rGO-TADPyCu in Ar (dotted black) and O2-saturated (red solid) 0.1 M KOH solution (b) Linear scanning voltammograms of rGO-TADPyCu (red), rGO/TADPyCu (blue), rGO/TAPyCu (black) and rGO (dashed black) catalysts in O2-saturated 0.1 M KOH. Electrode rotation speed 1600 rpm; scan rate, 10 mV s−1; loading, 0.6 mg cm−2. (c) Rotating-disk voltammograms of rGO-TADPyCu in O2-saturated 0.1 M KOH solution at the different rotation rates indicated. The dotted line indicates the background when scanned in Ar-saturated solution, loading 0.6 mg cm−2. (d) Koutecky–Levich plots at different potentials. Scan rate, 10 mV s−1. Theoretical 2e− and 4e− reduction processes are shown as dotted lines. (e) Peroxide yield for rGO-TADPyCu (red), rGO/TADPyCu (blue), rGO/TAPyCu (black) and rGO (dashed black) catalysts in O2-saturated 0.1.M KOH. (f) ORR polarization plots of rGO-TADPyCu after 0, 2000, 5000, 8000, and 10,000 potential cycles in an O2-saturated 0.1 M KOH solution, respectively. Inset shows ORR polarization plots of rGO/TADPyCu (blue) and rGO/TAPyCu (black) after 0 and 10,000 cycles, respectively. Potential was cycled between 0.575 and 0.975 V at a rate of 50 mV s−1. Electrode rotation speed 1600 rpm.

The rotating-disk voltammograms of the rGO-TADPyCu catalyst at different rotation rates are shown in Figure 4c, and its rotation-rate-dependent current−potential curves are depicted in Figure 4d, where linear Koutecky–Levich plots were observed. The electron transfer number (n) was calculated to be 3.85 from the slopes of Koutecky–Levich plots at 0.45–0.60 V, suggesting a principal 4e− oxygen reduction process. The amount of partially reduced product H2O2 detected from the ring electrode in the potential range from 0.6 V to 0.8 V was ~10%. However, within the same potential range, the amount of H2O2 increased to ~20%, ~40% and ≥60% with the rGO-TADPyCu, rGO/TADPyCu and rGO catalysts, respectively (Figure 4e). These results evidently suggested that the multinuclear Cu center within the rGO-TADPyCu catalyst is responsible for the high selectivity of 4e− vs. 2e− oxygen reduction. Furthermore, the rGO-TADPyCu catalyst catalyzes the ORR with less than 2% H2O2 generated in a phosphate buffer solution (pH 6.4, Figure S9).

Durability is also one of the major factors used to measure ORR performance in fuel cell technology. The stability of the rGO-TADPyCu catalyst was evaluated by an accelerated durability test protocol, in which the potential was cycled between 0.575 and 0.975 V at 50 mV s−1 in a 0.1M KOH solution saturated with O2. A subtle negative shift of E1/2 (~−41 mV) samples, an obvious negative shift (~−80 mV) and ≥60% with the rGO-TADPyCu, rGO/TADPyCu and rGO catalysts, respectively (Figure 4f). The catalyst stability was also verified by repeated CV cycles (Figure S10). The high stability of this bio-inspired rGO-
TADPyCu catalyst probably comes from the low overpotential for the ORR and the high selectivity of 4e⁻ reduction process. Moreover, the covalent immobilization of the catalyst onto rGO also contributed beneficial effects. All these catalyst stability test results clearly confirm that the covalent grafted multinuclear Cu catalyst has excellent stability in alkaline media, which outperformed the other Cu ORR catalysts reported, and is also superior to the Pt/C catalyst under similar conditions (Figure S11).

A methanol cross-over test on the rGO-TADPyCu catalyst was also performed. As is usual for non-precious-metal catalysts, the catalyst under similar conditions (Figure S11). ErGO-TADPyCu catalyst showed excellent stability and high ORR activity compared with that of the physisorbed mononuclear rGO/TAPyCu as well as the dinuclear rGO/TADPyCu catalysts. This bio-inspired rGO-TADPyCu catalyst has a good tolerance to the methanol cross-over effect and may be used as a methanol-tolerant cathode catalyst in direct methanol fuel cells.

In summary, taking inspiration from the multicopper centers in the active site of laccase, we prepared a novel multicopper–graphene composite rGO-TADPyCu as an ORR catalyst, in which a dinuclear Cu complex was immobilized on the surface of rGO via the covalent grafted TADPy dinucleating ligand. This bio-inspired rGO-TADPyCu catalyst displayed a high selectivity of 4e⁻ reduction process compared with that of the physisorbed mononuclear rGO-TAPyCu as well as the dinuclear rGO/TADPyCu catalysts. The rGO-TADPyCu catalyst showed excellent stability and high ORR activity in alkaline media ($E_{\text{onset}} = 0.951 \text{V vs. RHE}$), rendering it the hitherto most efficient Cu ORR catalyst reported. This work demonstrated that a covalent immobilization of bio-inspired multicopper model complex on carbon–based material is a promising approach for preparing a robust Cu ORR catalyst while mimicking the laccase catalytic ORR activity. This biomimetic rGO-TADPyCu catalyst may provide a hopeful alternative to noble metal catalysts in alkaline fuel cells.

This study was financially supported by the NSF of China (11872174), the Program for Professor of Special Appointment (Eastern Scholar) at the Shanghai Institutions of Higher Learning, and sponsored by the Shanghai Pujiang Program (13PJ1401900).

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†Electronic Supplementary Information (ESI) available: Experimental details and additional figures. See DOI: 10.1039/c000000x/