A simple way to fine tune the redox potentials of cobalt ions encapsulated in nitrogen doped graphene molecular catalysts for the oxygen evolution reaction†

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Co²⁺ ions encapsulated in nitrogen doped graphene were applied as an oxygen evolution catalyst. Their redox potentials were tuned using different counter anions as liable ligands, and the redox potential related catalytic rates were explored. It was proposed that the electron density of Co²⁺ ions was a general descriptor for activity.

Combustion of fossil fuels dominates the global energy outputs, but causes the growth of fuel shortage and environmental pollution. One of the promising approaches to address these issues is the production of alternative chemical fuels via solar power and electrolysis driven water splitting or artificial photosynthesis.¹–⁴ Energy conversion in these devices is systematically engineered such that multiple physical and chemical processes, including mass diffusion, and interfacial electron transfer and transport, are integrated into compartmentalized spaces. Among them, electron transfer at heterogeneous interfaces is the rate-determining step. The high efficiency of energy conversion requires fast cathodic and anodic reactions with matching kinetics.⁵,⁶ In particular, the oxygen evolution reaction (OER) is a common anodic reaction, which is however kinetically sluggish.⁶,⁷ The potential required to drive the OER is greater than the standard value (1.23 V vs. SHE) for overcoming kinetic barriers. Furthermore, the OER pathways, which involve multiple elemental steps for coupled transfer of electrons and protons, and bonding a pair of oxygen atoms, are highly complicated. It has been reported that different intermediates, known as reactive oxygen species (ROS), are involved in enabling the OER to proceed. Identifying the nature of ROS is important, as they can determine the origin of the overpotential during oxygen conversion.⁸ However, to do so is challenging due to the short lifetimes of the intermediates.

First-row transition metal (Co, Ni, etc.) based materials have been widely examined as classical OER catalysts.⁹–¹⁴ It is well accepted that the metal cations exposed at materials’ surfaces are mostly responsible for the OER activity.¹⁵,¹⁶ Surface metal cations can exhibit different bond strengths with the oxygen intermediates during the OER to affect the overall rate of the catalytic reaction.¹⁷ The significance of metal cations as OER active sites can also be recognized by the type of natural OER catalyst, i.e., the oxygen evolving complex (OEC) of enzyme photosystem II.¹⁸ The geometry of the OEC is a cube framework sustained by a CaMn₄O₅ cluster. Catalysis is triggered by the redox active Mn²⁺ ions. Recent reports proposed that the redox properties of Mn²⁺ ions could be tuned by redox-inactive Ca²⁺ ions at the neighboring sites, which is closely related to the origin of the catalytic activity of the OEC.¹⁹,²⁰ These results suggest that high OER activity can be achieved by tuning the surrounding environments of active sites. Although much progress has been achieved, challenges still remain, especially in the aspect of gaining better fundamental principles of catalyst design. To explore the potential of metal cations for OER catalysis, we believe that it is important to further develop appropriate matrices with properties such as high surface area, electrical conductivity and chemical stability, in order to support metal cation based active sites. Furthermore, such catalysts can serve as a framework to probe the descriptor that governs the activity of metal cations.

In this work, we propose a novel and general strategy to synthesize OER electrocatalysts at room temperature simply by immobilizing Co²⁺ ions onto a nitrogen doped graphene (NG) matrix as driven by coordination. The direct connection of Co²⁺ ions to the graphene conductive basal plane combined with the electron tuning ability of conjugated π electrons of graphene is expected to facilitate the heterogeneous electron transfer and transport of redox processes. The resulting electrocatalyst
(NG–Co) shows a high turnover frequency (TOF) of 2.53 s⁻¹ at a relatively low overpotential of 0.40 V in 0.1 M KOH. To gain insight into the activity of NG–Co, we show that the counter anions of Co²⁺ ions have a certain impact on the coordination environments of Co²⁺ ions, leading to different electron donating/withdrawing strengths as reflected by the shift of the redox potentials of the Co²⁺/³⁺ couple. A volcano behavior is observed where the OER activities occur as a function of the electron densities of Co²⁺ ions. The results emphasize the importance of a moderate electron density of catalytic sites in achieving high OER activity.

The NG precursor was synthesized by pyrolysis of a graphene oxide (GO)/melamine scaffold shaped in an ice template. The obtained structure of NG has appropriate inner porosity at a mesoporous/microporous scale with a large surface area to facilitate mass transport. The N/O atoms within NG were assumed to have the ligand property due to their extra electrons compared to C atoms. Taking advantage of this feature, we tested the ability of NG to function as a potential support for various metal ions (M⁺), in order to generate electrocatalytic sites for the OER. Specific NG–M complexes were synthesized by mixing NG with Mₓ⁺ (Mₓ⁺ stands for Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ ions that originated from MClₓ in CH₂OH (Fig. 1a). Their electrocatalytic abilities toward the OER were characterized by current–potential polarization curves in 0.1 M KOH (Fig. 1a). The intrinsic OER activity of NG–Co within the overpotential range from 0.30 to 0.50 V was assessed in terms of TOFs (defined as the number of OER events completed per electrocatalytic site per second, Fig. 2c). Minimum TOFs were obtained when the

![Fig. 1](image)

**Fig. 1.** (a) Proposed interacting mechanism between Mₓ⁺ ions and NG. (b) OER potentials required at 2 mA cm⁻² as a function of d electron numbers of transition metal ions (all potentials in the text are referenced to the reversible hydrogen electrode, RHE, if not specified). (c) XPS Co 2p surveys of CoCl₂·6H₂O, NG and NG–Co. (d) Plot of the cathodic and anodic peak currents versus scan rates, the inset shows the CVs of NG–Co/GC, 0.1 M KOH, 50 mV s⁻¹.

![Fig. 2](image)

**Fig. 2.** (a) OER on NG–Co and NG in 0.1 M KOH, 10 mV s⁻¹, 1600 rpm. Ring current was recorded at 1.35 V. (b) CVs of NG–Co/GCE in CH₃CN with adding 0.1 M KOH (1/6 V/V), 50 mV s⁻¹. 0.1 M tetrabutylammonium perchlorate was applied as the electrolyte. (c) TOFs of the OER on NG–Co evaluated at overpotentials ranging from 0.30 to 0.50 V.
OER was assumed to occur on all the immobilized Co\textsuperscript{2+} ions of NG–Co/GC. The results showed that the TOFs became significant at overpotentials higher than 0.40 V (0.45 s\textsuperscript{-1}). In the electrocatalytic process, we believe that only Co\textsuperscript{2+} ions at the surface of NG–Co/GC actually are in contact with the electrolyte. The amount of Co\textsuperscript{2+} ions was therefore assessed by the charge for Co\textsuperscript{2+}/Co\textsuperscript{3+} redox in CVs, and the TOF significantly increased to 2.53 s\textsuperscript{-1}. This result surpasses those of many Co, Fe and Ni based catalysts reported recently (Table S1, ESI\textsuperscript{†}). OER electrocatalysis on the NG–Co/GC electrode was continuously tested at 1.75 V for 6000 s. The NG–Co/GC retained more than 86% of its original anodic current. The corresponding TEM images show that the graphene structure of NG–Co was maintained without the formation of Co oxides after the measurements (Fig. S4, ESI\textsuperscript{†}).

To demonstrate the contribution of Co\textsuperscript{2+} to the OER activity of NG–Co, vigorous acid treatment was performed to break the Co\textsuperscript{2−}/N/O connections by protonation of N/O atoms. As expected, the XPS survey revealed that Co\textsuperscript{3+} detached from NG upon acid treatment, accompanied by an increase of overpotential for the OER by more than 150 mV and a substantial drop of electrocatalytic current (Fig. S5, ESI\textsuperscript{†}). Besides, we found that the Co\textsuperscript{3+}/N sites may be more responsible for the OER activity. In another control experiment, graphene synthesized from pyrolysis of GO without melamine was used as a matrix to immobilize Co\textsuperscript{2+}. The GO derived graphene contained a certain amount of oxygen functional groups, such as carboxyl,\textsuperscript{28} which could be the coordination sites to Co\textsuperscript{2+} ions. Using the same synthesis strategy, graphene was mixed with CoCl\textsubscript{2}·6H\textsubscript{2}O to form graphene–Co. Although the Co 2p signals in the XPS survey of graphene–Co were relatively ambiguous, the Co 2p\textsubscript{3/2} peak could still be identified at a higher binding energy as compared to NG–Co. The electrochemical results showed that the graphene–Co also exhibited an improved activity toward the OER, although its catalytic activity was inferior to NG–Co as revealed by an onset potential difference of more than 100 mV (Fig. S6, ESI\textsuperscript{†}).

In the RRDE measurements, the Pt ring was set at 1.35 V to probe the possible intermediates of the OER on NG–Co/GC. When the potential was scanned to 1.58 V, the Pt ring started to show a small cathodic current, which nearly disappeared on the NG or NG–Co treated with acid (Fig. 2a and Fig. S5c (ESI\textsuperscript{†}), top graph). At such a high potential, the cathodic current most likely originated from the reduction of ROS intermediates, such as superoxide acid (\text{HO}_2^- + e^- \rightarrow \text{HO}_2, \text{E}^0 = 0.81 \text{ V vs. NHE})\textsuperscript{29} and hydroxyl radicals (\text{HO}^* + e^- \rightarrow \text{HO}^-, \text{E}^0 = 1.9 \text{ V vs. NHE}).\textsuperscript{30} The latter would not be unreasonable when the OER was initiated from HO\textsuperscript{−} ions.\textsuperscript{31} Our previous results have confirmed that the intermediate was HO\textsuperscript{*} by using a coumarin signal probe with an in situ fluorescence spectroelectrochemistry (Fig. 3a).\textsuperscript{21,32} In 60 \mu M coumarin contained KOH solution, the OER on NG–Co was continuously performed at 1.65 V for 50 min. A fluorescence emission of the KOH electrolyte appeared at 500 nm (Fig. 3b), demonstrating the formation of 7-hydroxyl-coumarin. If HOO\textsuperscript{−} was involved in the OER, its decomposition might lead to the formation of HO\textsuperscript{*}. This was not the case since addition of \text{H}_2\text{O}_2 to KOH electrolyte did not bring stronger fluorescence emission (Fig. S7, ESI\textsuperscript{†}). Based on these results, it can be concluded that

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\text{HO}^- \rightarrow \text{HO}^* + e^- \quad \text{(1)}
\]

Since HO\textsuperscript{*} is highly energetic, this step would require sufficient energy to improve the reaction kinetics, and thus be critical for the origin of the overpotential. On the other hand, it is worth pointing out that the NG–Co also exhibited an improved electrocatalytic activity toward the oxygen reduction reaction (ORR) as compared to that obtained from NG (Fig. S8, ESI\textsuperscript{†}). By the in situ fluorescence spectroelectrochemistry, the ORR was also intermediated by the generation of HO\textsuperscript{*} (Fig. S9, ESI\textsuperscript{†}). A faster reaction rate could be realized by lowering the activation energy barriers. Thus, the energy state of the highly energetic HO\textsuperscript{*} could affect both the overall pathways and kinetics of oxygen conversion.

Further centering on the Co\textsuperscript{2+} ions, their coordination states within NG–Co should be reasonably determined by the heteroatoms of NG as well as the nature of cobalt salt precursors. As seen in the energy dispersive X-ray spectroscopy images, both Co\textsuperscript{2+} and the Cl\textsuperscript{−} counter anions that originated from CoCl\textsubscript{2}·6H\textsubscript{2}O were identified to be distributed over carbon layers with close signal intensities (Fig. 4a). The Cl\textsuperscript{−} ions thus could be considered as liable ligands for Co\textsuperscript{2+} ions. Furthermore, by the
same synthesis method as for NG–Co but using different cobalt salt precursors, we obtained a series of analogous \( \text{Co}^{2+} \) ion based electrocatalysts (NG–Co–L) with different counter anions (\( \text{L} = \text{Ac}^-, \text{SCN}^-, \text{SO}_4^-, \text{NO}_3^-, \text{acac}^-, \text{NO}_3^-, \text{Br}^- \) and \( \Gamma^- \) ions). Since the coordination states are determined by various factors, such as net charges, charge donating/accepting ability and numbers of ligands, the exact natures of the ligands of NG–Co–L could be relatively complicated. To encompass all the possibilities for coordination results, we characterized the electron density of \( \text{Co}^{2+} \) ions to assess the impact from the nature of counter anions. This parameter was revealed by the redox potentials of \( \text{Co}^{2+} \) ions, which were obtained by differential pulse voltammetry (DPV) (Fig. S10, ESI†). The DPV curve of NG was featureless under the same conditions. The gradual increase of anodic peak potentials (\( E_{an} \)) indicates the stronger electron withdrawing effect occurring on \( \text{Co}^{2+} \) ions (Fig. 4b). The corresponding OER activities of NG–Co–L were then measured by the RRDE (Fig. S11, ESI†). It was found that the OER activities of NG–Co–L also varied with the counter anions. Optimum performance was observed on the electrocatalyst with median redox potentials of Co\textsuperscript{2+} ions, which were obtained by differential pulse voltammetry (DPV) (Fig. S10 (ESI†), the DPV curve of NG was featureless under the same conditions).\textsuperscript{34} The gradual increase of anodic peak potentials (\( E_{an} \)) values. Since the exact values of the onset potential of the OER can be somewhat ambiguous, we used the OER potential at 2 mA cm\textsuperscript{−2} as a parameter to evaluate the activities. As shown in Fig. 4c, a volcano trend like trend of the OER potential as a function of \( E_{an} \) of \( \text{Co}^{2+} \) ions appeared. If the OER potential was plotted at a lower current density of 1 mA cm\textsuperscript{−2} with respect to \( E_{an} \), the volcano trend remained but with larger standard deviations (Fig. S12, ESI†). This volcano graph demonstrates that the electron density of \( \text{Co}^{2+} \) ions can be a general descriptor for OER activity. Since OER electrocatalysis at the heterogeneous interface was triggered by substrate chemisorption on active sites, electron density was generally governed by the bonding energy of chemisorption and thus determined the thermodynamics of the OER.\textsuperscript{37} Besides, the influence of the coordination geometry of the active sites on the electrocatalytic activity of the NG–Co–L could not be a significant factor, as all these catalysts share a similar coordination geometry due to the rigid structure of NG.

We proposed and demonstrated a simple bottom up approach to the synthesis of heterogeneous \( \text{Co}^{2+} \) ion-nitrogen doped graphene complexes (NG–Co) under ambient environments. The as prepared NG–Co showed an excellent electrocatalytic activity toward the OER with a TOF of 2.53 s\textsuperscript{−1} at an overpotential of 0.40 V in 0.1 M KOH. Experimental results further demonstrated that the \( \text{Co}^{2+} \) ions encapsulated on NG could be fine tuned at the molecular level, e.g., their electron densities in coordination structures were changed by using different counter anions. The derived activity trends exhibited a volcano-like shape, from which we concluded that the electron density of \( \text{Co}^{2+} \) ions could be one general activity descriptor to determine the overall electrocatalytic reaction. This work opens up a facile bottom up approach to the synthesis of highly active electrocatalysts and provides insights into the general catalyst design strategies.

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Notes and references

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