

View Article Online View Journal

RSC Advances

This article can be cited before page numbers have been issued, to do this please use: Z. Zhang, S. Yang, M. Dou, H. Liu, L. Gu and F. Wang, *RSC Adv.*, 2016, DOI: 10.1039/C6RA12426G.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/advances

Published on 29 June 2016. Downloaded by University of Sussex on 05/07/2016 08:22:49

RSC Advances

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Systematic study of the transition-metal (Fe, Co, Ni, Cu) phthalocyanine as electrocatalyst for oxygen reduction and its evaluation by DFT

Zhengping Zhang,^a Shaoxuan Yang,^a Meiling Dou,^a Haijing Liu,^a Lin Gu^b and Feng Wang^a*

In this work, a facile approach is reported to prepare a series of transition-metal phthalocyanine (TMPc) supported on graphitized carbon black (TMPc/GCB, TM: Fe, Co, Ni and Cu) as oxygen reduction reaction (ORR) electrocatalyst, *via* the π - π interaction self-assembly. Through transmission electron microscopy (TEM), Raman spectra and UV spectra, it was found that TMPc coated on graphitized carbon black with non-aggregated morphology. The catalytic activity, both in terms of the onset potential (0.98 V to 0.76 V) and half-wave potential (0.90 V to 0.55 V) follows the trend of FePc/GCB > CoPc/GCB > CuPc/GCB > NiPc/GCB. However, the catalytic durability follows the decreasing order of NiPc/GCB > CoPc/GCB > FePc/GCB > CuPc/GCB. To better elucidate the ORR catalytic mechanism for TMPc/GCB, we employed density functional theory (DFT) calculations and drew the following results: (i) the -O₂ adsorption is the major step to determine the ORR catalytic activity; (ii) the way of O₂ adsorbed on TMPc is the key point to affect the Tafel slope; (iii) the -H₂O₂ desorption determine the transfer electron number; and (iv) the -OH desorption and the central metal atom removal leads to the damage for the catalytic durability.

Introduction

In the past decade, for satisfying the global energy demand and environmental protection, a tremendous number of the oxygen reduction reaction (ORR) studies have been undertaken to develop renewable-energy technologies, such as fuel cells and metal-air batteries.^{1, 2} Since the ORR is treated as a kind of multi-step electrochemical reactions with very sluggish kinetics, the electrocatalysts for ORR are the essential to overcome the major limiting factors of the above devices.³ In spite of high cost and scarce reserves, platinum (Pt) and Ptbased alloys are still applied as the most popular commercial electrocatalysts, due to their high catalytic activity and comparatively good durability for ORR.⁴ To break down the price barrier for large-scale commercialization of the fuel cell technologies, non-precious metal catalysts have attracted much attention in the development of low-cost and efficient electrocatalysts for ORR.^{5, 6} Since Jasinki's discovery that cobalt phthalocyanine exhibited the outstanding performance for the ORR in 1967,^{7, 8} similar metal macrocyclic compounds are widely studied as alternative ORR catalysts,^{9, 10} in virtue of their low price and abundant supply compared to Pt.¹¹

As one of the important transition-metal macrocyclic compounds, transition-metal phthalocyanine (TMPc) attracts increasing concern as significant electrocatalyst for ORR. The structure of TMPc strongly affects their ORR performance (*e.g.*, iron phthalocyanine can be modified with diphenylphenthioether functional groups to enhance catalytic stability.¹²). In addition, carbon carriers play an important role in improving the ORR performance (*e.g.*, carbon nanotubes and graphene can enhance cobalt phthalocyanine's ORR catalytic activity through forceful interaction).^{9, 10} Furthermore, the TMPc catalyst may be prepared either through *in-situ* of TMPc-functionalized carbon carriers or by post-treatment for incorporating carbon carriers to improve the ORR performance.^{13, 14}

Particularly, the type of the central transition-metal (TM) atom is the most determinant factor in influencing catalytic activity.¹⁵⁻¹⁸ It has been reported that iron or cobalt incorporated macrocycle exhibits high measurable levels of catalytic activity for ORR via an approximated 4-electron transfer or 2-electron pathway and the positive ORR onset potential by the experimental and theoretical methods. ¹⁹⁻²² Considering the ORR performance of metal macrocycle compounds is related with the highest occupied molecular orbital (HOMO) of metal macrocycle compounds.¹⁵ For FePc, CoPc and CuPc, the HOMO is determined by the 3d orbital of their central atom, whereas the HOMO of the NiPc and ZnPc is localized on the phthalocyanine ring.²³ For FePc, the HOMO level is higher than that of CoPc, which means the 3d electron of Fe atom is more easily transferred to oxygen.²⁴ In addition, other transition-metal phthalocyanine also exhibit unique



^a State Key Laboratory of Chemical Resource Engineering, Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing University of Chemical Technology, Beijing 100029, China. E-mail: <u>wanaf@mail.buct.edu.cn</u> ^b Institute of Physics Chinese Academy of Sciences, Beijing 100190, China

⁺ Electronic Supplementary Information (ESI) available: Detailed materials and experimental; FT-IR spectra, UV spectra, TG-DTA curves, XPS survey spectra and high resolution scans N 1s of TMPc/C. RDE tests of all catalysts in alkaline and acidic medium for ORR. See DOI: 10.1039/x0xx00000x

ARTICLE

catalytic traits for ORR (*e.g.*, copper phthalocyanine decreases the current efficiency for H_2O_2 formation²⁵). Despite these investigations are widely taken, our understanding of the ORR mechanism on TMPc compounds is far from consummation.

To comprehensively and systematically analyze the influence of the central metal atom in phthalocyanine macrocycle for ORR, we prepared a series of TMPc (TM: Fe, Co, Ni and Cu) supported on graphitized carbon black (TMPc/GCB) with similar N type and loading amount, *via* the π - π interaction self-assembly. The density functional theory (DFT) calculations were also employed to draw the correlation between the experimental catalytic activity and the theoretical models. This work comprehensively elucidates the effects of the central metal atom for TMPc and gain insights into the ORR mechanism.

Experimental

Published on 29 June 2016. Downloaded by University of Sussex on 05/07/2016 08:22:49

Preparation of the TMPc/GCB electrocatalysts

The FePc, CoPc, NiPc and CuPc (Fig. S1) were prepared by a solid-phase synthesis method in a muffle furnace,²⁶ and the graphitized carbon black (GCB) was derived from Vulcan XC-72 undergoing high-temperature graphitization (shown in ESI⁺). As shown in Scheme 1, a mixture of 30 mL isopropanol and 95 mg GCB were placed in a flask with stirring for 30 minutes, leading to a single homogeneous suspension. Then, it was mixed with a TMPc / tetrahydrofuran (5 mg / 20 mL) solution and sonicated for 2 hours to form a suspension of TMPc dispersed on GCB. Finally, the precipitates were rotary evaporated to dry at 60 °C rapidly, and turned into the TMPc supported on GCB (TMPc/GCB, TM: Fe, Co, Ni and Cu, respectively) electrocatalyst. For comparison, we also prepared another FePc electrocatalyst obtained from different loading amounts of FePc with GCB and a simple mixture of 5 mg FePc with 95 mg GCB termed FePc&C.

Physical characterization

Fourier Transform InfraRed (FT-IR) spectra were obtained with wavenumber from 2200 to 500 cm⁻¹ using a Perkin Elmer spectrum 100 FT-IR Spectrometer. The ultraviolet (UV) absorption spectroscopy was carried out using a Shimadzu UV-2450 with wavelength from 300 to 900 nm. The thermalgravemetric-differential thermal analysis (TG-DTA) was obtained on a Rigaku TG-8120 with under the atmosphere of air and the heating rate of 5 K min⁻¹. Transmission electron microscopy (TEM) images of the products were obtained by a JEOL JEM-2010. Scanning transmission electron microscopy (STEM) images of the products were obtained by a JEOL JEM-ARM200F. The X-ray diffraction profile (XRD) was obtained on a Rigaku D/Max 2500 VB2+/PC diffractometer with Cu Ka radiation (λ = 1.54056 Å) as the X-ray source. X-ray photoelectron spectroscopy (XPS) analysis were obtained using ThermoFisher Scientific ESCALAB 250 and ASAP 2020 analyzer charging referenced to the C 1s XPS peak (284.1 eV). Raman spectroscopy was obtained using a Horiba Jobin Yvon LabRam HR800 with an excitation wavelength of 532 nm.

Electrochemical measurements

Electrochemical measurements were conducted with Rotating Ring Disk Electrode Apparatus (RRDE-3A) been directly controlled by Model 2323, ALS (BAS INC, Tokyo, Japan)and CHI660E electrochemical workstation (CH Instruments Company, Austin, USA). All the electrochemical measurements were carried out in a single compartment glass cell. A potassium chloride (KCI) saturated calomel reference electrode (SCE), a platinum wire counter electrode and the TMPc/GCB modified glassy carbon (GC) working electrode were used together. 5 mg of the electrocatalyst was dispersed by ultrasonication with a mixture of 1 mL ethanol and 5 μ L Nafion solutions. 10 μ L of catalyst ink was transferred onto the polished GC electrode and dried for 20 min at room temperature.

Calculation methods

The DFT calculation optimization on TMPc and other molecules is carried out with the program Gaussian 09 with the B3LYP exchange correlation functional²⁴. The 6-31G²⁷ basis set for C, N, H, and O; the quasi-relativistic pseudopotential and basis set LANL2DZ²⁸ is used for iron, cobalt, nickel and copper. The use of the LANL2DZ has been successfully applied in the past for other transition metals.²⁹

In order to evaluate the reliability of calculation method, the structures of TMPc were all optimized, and the calculated properties of optimized TMPc are listed in Table S1. The calculated distances R_{TM-N} , which stands for bond length between the central metal atom and the nearest neighbouring N atom, are mainly investigated to prove the reliability of the calculation method.

Results and discussion

Physical characterization of the TMPc/GCB electrocatalysts

Multivariate characterization was employed to reveal the formation of TMPc. Shown in Fig. S2 is Fourier Transform InfraRed (FT-IR) of TMPc. The phthalocyanine frameworks metal ligand vibration can be preserved in the all the TMPc samples. The ultraviolet (UV) spectra showed the characteristic absorption *B* (300-400 nm) and *Q* (600-800 nm) bands of TMPc (Fig. S3). Similarly, differential thermal analysis (DTA) also reveals the successful formation of TMPc (Fig. S4).

Moreover physical characterization was carried out on the TMPc/GCB composites, typified by FePc/GCB. As shown in Fig. 1, we reproduced transmission electron microscopy (TEM) images of pure GCB and FePc/GCB. The TEM observation clearly reveals that both pure GCB and FePc/GCB exhibit similar interconnected and uniformly dispersed structure, with intensely graphitic lattice fringes. Such unique structure is not only beneficial for the facile diffusion of reactants on electrolyte, but also propitious to improve the electronic transmission capacity.³⁰ Notably, different from the smooth and intact surface morphology of GCB, the amorphous and irregular layer coats on surface of the FePc/GCB composite, probably owing to the adhesion of FePc onto the surface of

Published on 29 June 2016. Downloaded by University of Sussex on 05/07/2016 08:22:49

Journal Name

GCB via the possible π - π interaction.¹⁴ The high-magnification scanning transmission electron microscopy (STEM) images also confirmed this coating structure (Fig. S5). Furthermore, the digital photographs both of GCB and FePc/GCB (the inset image of Fig. 1a-b) were also taken after the sonication in ethanol 12 hours later. Thanks to the amorphous and irregular coating layer, the dispersion of the FePc/GCB composite in ethanol has been enhanced, which favours to fabricate a homogeneous electrode.³¹

To get insight into the chemical structure of the newlysynthesized materials, we investigated the powder X-ray diffraction (XRD) pattern of GCB and FePc/GCB (Fig. 2a). The XRD pattern for FePc/GCB only show a pronounced graphitic peaks at 25.7° and 43.1°, attributed to the (002) and (100) planes of graphitic carbon (JCPDS card: NO. 41-1487) similar to GCB. It infers that the formation of coating layer may be amorphous, attributed to that FePc cannot stack into a long range ordered state caused by the limitation of the number of FePc molecules on GCB.¹³ Besides, as shown in Fig. 2b, FePc/GCB exhibits lower proportion of the I_G/I_D (1.48) than GCB ($I_G/I_D = 2.04$) with relatively weaker single-peak 2D band in their Raman spectra. Combined with TEM images, it suggests that FePc has coated onto GCB successfully, *via* the π - π interaction.³²

To further understand the composite effect of TMPc/GCB, the UV spectrum of GCB and FePc/GCB is shown in Fig. 2c, including FePc for comparison. Different from GCB, the FePc/GCB composite exhibits the characteristic of FePc and a weak satellite band appears at ca. 730 nm, which has red-shift about ca. 60 nm compared with the Q band of FePc, attributed to the charge transfer of FePc to GCB. It indicates that the possible π - π interaction exists between FePc and the surface of GCB,³³ Besides, compared with the FT-IR spectrum of the GCB, the characteristic peaks of FePc obviously appear in the spectrum of FePc/GCB (Fig. S6). Of these bands, the most of vibrations FePc/GCB had slight shift compared with FePc, consistent with previous reports on TMPc-based materials for ORR, suggesting that the possible π - π interactions had formed between FePc and GCB.³⁴ In addition, the thermalgravemetric analysis (TGA) curve of FePc/GCB presents first weight-loss at ca. 380 °C, moving to higher temperature region than FePc (ca. 300 °C). Then, a greater weight loss of FePc/GCB appears at relatively high region (ca. 530 °C) compared with GCB (ca. 420 °C) (Fig. 2d). Other TMPc/GCB also exhibits the similar thermal stability, due probably to the possible π - π interaction between TMPc and GCB (Fig. S7).¹³

The surface composition of all the TMPc/GCB samples has been investigated by X-ray photoelectron spectra (XPS) methods. The XPS survey spectra (Fig. S8) of all the TMPc/GCB samples show the C, O, N, and Fe, Co, Ni and Cu contents, respectively. The results obtained that all the TMPc/GCB samples contain the similar amounts of each element. In additon, the high-resolution scans of Fe 2*p*, Co 2*p*, Ni 2*p* and Cu 2*p* are shown in Fig. 3, where deconvolution yielded two pairs of peaks for Fe²⁺ (723.4 and 712.0 eV), Co²⁺ (795.7 and 780.6 eV), Ni²⁺ (872.4 and 855.0eV) and Cu²⁺ (955.5 and 935.5 eV), respectively.³⁵⁻³⁸ Besides, nitrogen-bonding configurations of all the TMPc/GCB samples can be observed at the same region (399.6 eV), confirming as the convolution of phthalocyanine-N.³² Such binding energy of the peaks indicates that TM coordinates with N to form the TM-N₄ moieties. Through XPS measurements, we can confirm that all the TMPc/GCB electrocatalysts contain the similar loading amounts on the surface of GCB with the similar TM-N₄ moieties.

Electrochemical performance of the TMPc/GCB electrocatalyst

In this work, we also tried to prepare different loading amounts of FePc with GCB to confirm the best percentages of TMPc present. The 5%-FePc/GCB (5 mg FePc /95 mg GCB) exhibited better electrochemical performance than the 5% FePc&GCB and other loading amounts of FePc/GCB (1%, 10% and 20%-FePc/GCB) electrocatalysts. Consequently, we here only present the results for the TMPc/GCB electrocatalysts with 5% loading amounts (Fig. S10).

To evaluate the ORR performance for these TMPc/GCB electrocatalysts, the cyclic voltammetric (CV) measurements were first performed. As shown in Fig. 4, all of TMPc/GCB show well-defined catholic ORR peaks in O₂-saturated 0.1 M KOH solution, but not in N₂-saturated solution. Compared with the NiPc/GCB and CuPc/GCB electrocatalysts, FePc/GCB and CoPc/GCB exhibit positive peak potential with large cathodic current density. In particular, the FePc/GCB electrocatalyst showed the most positive ORR potentials (0.89 V vs. RHE, the same below) with the highest cathodic current density (1.36 mA cm⁻²) in the all the TMPc/GCB samples.

To further investigate the catalytic activity of these TMPc/GCB electrodes for ORR, rotating ring-disk electrode (RRDE) measurements (Fig. 5a) were employed in O₂-saturated 0.1 M KOH solution at 1600 rpm. The disk potential was scanned at 5 mV s⁻¹, and the ring potential was constant at 1.5 V. According to the RRDE measurements, the onset potential (E_{onset}) and the half-wave potential ($E_{1/2}$) of TMPc/GCB moves from *ca*. 0.98 V / 0.90 V (FePc/GCB) to *ca*. 0.76 V / 0.55 V (NiPc/GCB), respectively, following the trend of FePc/GCB > CoPc/GCB > CuPc/GCB > NiPc/GCB. Besides, NiPc/GCB and CuPc/GCB exhibit much poor catalytic activity with inconspicuous limiting diffusion current area, compared with FePc/GCB and CoPc/GCB. Specifically, the FePc/GCB electrocatalyst exhibits the superior catalytic activity, and even much better than the commercial Pt/C (Johnson Matthey, UK).

In order to get further insight into the ORR kinetics, the Tafel slopes of TMPc/GCB and the commercial Pt/C are shown in Fig. 5b and Table 1. The Tafel slopes for FePc/GCB, CoPc/GCB and commercial Pt/C catalysts can be divided into two parts: the low overpotential region ($b_1 = ca.$ 60 mV dec⁻¹), and the high overpotential region ($b_2 = ca.$ 120 mV dec⁻¹), but not for NiPc/GCB and CuPc/GCB. The smaller Tafel slope (b_1) does, the faster rate of ORR has. The FePc/GCB, CoPc/GCB and commercial Pt/C exhibits the similar Tafel slope (b_1), revealing that these three electrocatalysts share the similar rate-determining step at low over-potentials area.

DOI: 10.1039/C6RA12426G

ARTICLE

Subsequently, the electron transfer number per $O_2(n)$, was also measured by both of the $\rm H_2O_2/peroxide$ productivity and the Koutecky–Levich (K-L) equation (Fig. 5c-e and Fig. S11). The calculated peroxide percentage (% HO_2) at 0.40 V is following the trend: FePc/GCB (1.1 %) < Pt/C (3.1%) < CoPc/GCB (45.4 %) < CuPc/GCB (52.5 %) < NiPc/GCB (83.7%), and the electron transfer number shows FePc/GCB and Pt/C exhibiting the nearly 4-electron transfer pathway, CoPc/GCB and CuPc/GCB exhibiting between 4-electron and 2-electron transfer pathway, and NiPc/GCB showing almost 2e pathway. In addition, the K-L plots reconfirm the electron transfer number decreasing order follows: FePc (3.97), CoPc (3.67), CuPc (3.56) and NiPc (2.64). It is worth noting that for the CuPc/GCB electrode, in spite of the worse catalytic activity for ORR, the electron transfer number results infer that CuPc may be beneficial to decompose H₂O₂/peroxide.²⁵

Additionally, as shown in Fig. 5f, the current versus time (it) chronoamperometric measurements are carried out to evaluate the catalytic durability for the TMPc/GCB electrode. The current of CuPc/GCB declined much more rapidly than any other TMPc/GCB with holding at a constant potential. In contrast, the NiPc/GCB electrocatalyst exhibits the best catalytic durability, although NiPc/GCB shows the worst activity in the whole electrodes. According to the chronoamperometric measurements, the catalytic durability follows the decreasing order of NiPc/GCB > CoPc/GCB > FePc/GCB > CuPc/GCB. Finally, we also investigated the ORR performance of TMPc in a 0.1 M HClO₄ medium (Fig. S12). All the TMPc/GCB electrocatalysts show much worse activity in acid medium than alkaline medium. In particular, CuPc/GCB barely has the catalytic activity in acid medium, even worse than NiPc/GCB.

Catalyst evaluation by DFT

Published on 29 June 2016. Downloaded by University of Sussex on 05/07/2016 08:22:49

To comprehensively elucidate the influence of the central metal atom in phthalocyanine macrocycle for ORR, we carried out the DFT calculations to calculated the adsorption energy, combined with experimental results. The adsorption energy between catalyst and adsorbate molecule is one of the methods to evaluate whether the adsorbate is energetically favourable to be adducted to the surface of the molecular catalyst.¹⁶ Negative adsorption energy indicates that the adsorption reaction is energetically favourable to happen. Besides, lower adsorption energy means stronger bonding energy between catalyst and adsorbate. For desorption energy, the result is opposite.

For TMPc, many probable mechanisms for ORR had been reported.^{14, 19} It is widely believed that the catalytic site is the central transition-metal atom.¹⁶ Since TMPc molecules (Fig. 6a) only owe one catalytic site, the competing adsorption of TMPc with H₂O (Fig. 6b) and O₂ molecules is the key point to judge the catalytic activity (Equation 1-3). The outstanding ORR catalyst should be favourable to adsorb O₂ than H₂O. Since TMPc molecular only has one catalytic site for O₂ adsorption, the way of -O₂ adsorption is just calculated by the end-on (Fig. 6c) and side-on way (Fig. 6d). The calculation results in Table 2 indicate that only FePc and CoPc could adsorb O₂ molecule in

the stable structure by side-on way; meanwhile the end-on adsorption energy between O_2 and TMPc (ΔE_{TM-OO}) is lower than the side-on adsorption energy between O2 and TMPc $(\Delta E_{TM-0*0*})$, inferring that the end-on adsorption is the mainly way of TMPc adsorbing O_2 . Therefore, we compared ΔE_{TM-OO} and the adsorption energy of H_2O (ΔE_{TM-H_2O}) to evaluate the catalytic activity of TMPc. The ΔE_{TM-OO} of FePc and CoPc is more lower than ΔE_{TM-H_2O} , but NiPc and CuPc show the contrary results. It suggests that FePc and CoPc exhibit better catalytic activity than NiPc and CuPc. The results correlates well with our experimental results that NiPc/GCB and CuPc/GCB present much negative E_{onset} and $E_{1/2}$ with inconspicuous limiting diffusion current area. In addition, the results in Table 2 also show that the ΔE_{TM-OO} follow the increasing order of FePc, CoPc, CuPc and NiPc, which means the catalytic activity should follow the decreasing order of FePc > CoPc > CuPc > NiPc. The calculated results are in accord with the results from the CV and RRDE measurements.

In the state of TMPc-O*O*, the absorbed O₂ is completely cleaved, which means each oxygen atom in O₂ molecule is connected with the central metal. From the calculation results, just FePc and CoPc can provide the stable structure of TMPc-O*O*, but the side-on -O₂ adsorption of NiPc and CuPc barely happen. The results are according with the Tafel plots, that only NiPc/GCB and CuPc/GCB cannot be divided into two parts. Besides, FePc exhibits the lowest $\Delta E_{TM-O^*O^*}$ in the whole TMPc and the gap between $\Delta E_{TM-O^*O^*}$ and $\Delta E_{TM-O^*O^*}$ is much less ($\Delta E_{TM-O^*O^*}/\Delta E_{TM-O^*} = 0.70$) than that of CoPc ($\Delta E_{TM-O^*O^*}/\Delta E_{TM-O^*} = 0.15$). It indicates that the O₂ molecule can be adsorbed on FePc by both of the two ways.

$TMPc + H_2O \to TMPc \text{-} H_2O$	$\Delta E_{\mathrm{TM-H_2O}}$	(1)
$TMPc + O_2 \to TMPc\text{-}OO$	$\Delta E_{\mathrm{TM-OO}}$	(2)
$TMPc + O_2 \to TMPc \text{-} O^* O^*$	$\Delta \textit{E}_{_{\textit{TM-O}^{*}O^{*}}}$	(3)
$TMPc-H_2O_2 \to TMPc + H_2O_2$	$\Delta E_{des-H_2O_2}$	(4)
$TMPc\text{-}OH \to TMPc + OH$	$\Delta E_{\rm des-OH}$	(5)
$TMPc + 2H^{+} + 2e^{-} \rightarrow H_2Pc + TM^{2+}$	$\Delta E_{\textit{rem-TM}}$	(6)

In general, the ORR can be simply divided into the 4e pathway and the 2e pathway by the transfer electron number per O₂, which is a vital factor to evaluate the ability of catalyst to give O₂ molecule electron. The main reason for decreasing the transfer electron number is the H₂O₂ productivity. If the -O₂ adsorption end-on TMPc, after accepting 2e, the -O₂ adsorption probably transform into $-H_2O_2$ adsorption (Fig. 6e). Once the $-H_2O_2$ adsorption desperate from TMPc, the $-H_2O_2$ adsorption will generate H₂O₂ as by-product. Therefore, the $-H_2O_2$ productivity and the transfer electron number for ORR. As shown in Table 2, the $-H_2O_2$ desorption energy ($\Delta E_{des:H_2O_2}$) follow the increasing order of NiPc > CuPc > CoPc > FePc, which correlates well with our RRDE and K-L calculation results. In particular, FePc is able to adsorb O₂ by the side-on

Published on 29 June 2016. Downloaded by University of Sussex on 05/07/2016 08:22:49

Journal Name

way, in which the absorbed O_2 is completely cleaved and generates H_2O directly. It explains FePc/GCB exhibits tremendously low peroxide productivity.

According to literatures, there are two main processes damage catalytic durability for TMPc. The reversible processes is the generated -OH occupy the activity site on the surface of the catalysts (Fig. 6f), and the irreversible processes is the central transition metal atom removal (Fig. 6g). $^{\rm 18,\ 22}$ We calculated two of the processes (Equation 5, 6) and found the catalytic durability is basically in accord with the trend of -HO desorption energy (ΔE_{des-OH}), except CuPc. CuPc/GCB declined much more rapidly, because the removal energy of transitionmetal atom (ΔE_{rem-TM}) for CuPc is negative, inferring that the Cu atom removal is energetically favourable to happen. The calculated results are also in accord with the catalytic activity in acid medium. In addition, NiPc/GCB presents the most stable catalytic durability in the whole TMPc/GCB electrocatalysts, owing to high ΔE_{rem-TM} and the low ΔE_{des-OH} of NiPc.

Furthermore, our results are in agreement with other research works (Table S2). Different from CoPc, FePc exhibited ultra-high catalytic activity, but quite poor durability.^{16, 22} Considering the ORR performance of metal macrocycle compounds is related with the HOMO of metal macrocycle compounds.^{15, 24} For FePc, CoPc and CuPc, the HOMO is determined by the 3d orbital of their central atom, but the HOMO of NiPc is localized on the phthalocyanine ring, which leads the distinguishably higher ΔE_{TM-OO} of NiPc and poorer catalytic activity than other TMPc.^{15, 18, 23} Besides, the interaction between TMPc and supports also can affect the HOMO of TMPc, which probably improve the TMPc catalytic activity for ORR.^{29, 39} In common with other work, our results reveal that CuPc is beneficial to degradation of H₂O₂.²⁵ Combined with our theoretical analysis and other theoretical explanation, even if the high ΔE_{TM-OO} is detrimental to holding the two O atoms, the proper R_{TM-N} of CuPc could lead the linear N-Cu-N structure conveniently to drag the two H atoms away by the two N atoms.¹⁶

Considering both of the improvement in activity and the durability for ORR, the ideal TM-N₄ moieties not only be beneficial to the $-O_2$ adsorption, but also prevent the "poison" from occupying the active sites. He et al. predicted that decreasing the -OH adsorption energy on FePc (to enhance the catalytic activity) or increasing the $-O_2$ adsorption energy on CoPc (to enhance the catalytic durability) could be a good method to improve the ORR performance, both in catalytic activity and durability.¹⁶ In addition, based on our results and other works, the demetalation of TMPc should not be ignored for the unstable activity.^{12, 22, 32}

Conclusions

In this paper, we report a facile preparation of a series of TMPc/GCB electrocatalysts for ORR, *via* the π - π interaction self-assembly in isopropanol / tetrahydrofuran mixed solution. The composite electrocatalysts were verified by multivariate characterization analyses. Through transmission electron

microscopy (TEM), Raman spectra and UV spectra, it was found that TMPc was coated on graphitized carbon black with non-aggregated morphology. Furthermore, all the TMPc/GCB electrocatalysts underwent the electrochemical investigation to evaluate the ORR performance. According to the E_{onset} , $E_{1/2}$, Tafel slope, transfer electron number and durability measurement, the ORR catalytic activity follows the trend of FePc/GCB > CoPc/GCB > CuPc/GCB > NiPc/GCB, and the catalytic durability follows the decreasing order of NiPc/GCB > CoPc/GCB > FePc/GCB > CuPc/GCB. To better elucidate the ORR catalytic mechanism for TMPc/GCB, we employed DFT calculations and drew the following results: (i) the -O₂ adsorption is the major step to determine the ORR catalytic activity; (ii) the way of O₂ adsorbed on TMPc is the key point to affect the Tafel slope; (iii) the -H₂O₂ desorption determine the transfer electron number; and (iv) the -OH desorption and the central metal atom removal leads to the damage for the catalytic durability. Therefore, this work systematically elucidates the influence of the central metal atom in phthalocyanine macrocycle for ORR, and provides the basis to select proper transition-metal for non-precious metal catalysts in fuel cells and metal-air batteries.

Acknowledgements

This work was supported by the National Natural Science Funds of China (51432003, 51232003).

Notes and references

- E. Negro, A. H. A. M. Videla, V. Baglio, A. S. Aricò, S. Specchia and G. J. M. Koper, *Appl. Catal. B: Environ.*, 2015, **166-167**, 75-83.
- J. Zhang, Z. Zhao, Z. Xia and L. Dai, Nat. Nanotechnol., 2015, 10, 444-452.
- L. Dai, Y. Xue, L. Qu, H. J. Choi and J. B. Baek, *Chem. Rev.*, 2015, 115, 4823-4892.
- 4. C. Sealy, Mater. Today, 2008, 11, 65-68.
- R. Liu, C. von Malotki, L. Arnold, N. Koshino, H. Higashimura, M. Baumgarten and K. Mullen, J. Am. Chem. Soc., 2011, 133, 10372-10375.
- Y. Tan, C. Xu, G. Chen, X. Fang, N. Zheng and Q. Xie, *Adv. Funct. Mater.*, 2012, 22, 4584-4591.
- 7. R. Jasinski, Nature, 1964, 201, 1212-1213.
- 8. R. Jasinski, J. Electrochem. Soc., 1965, 112, 526-528.
- Y. Liu, Y.-Y. Wu, G.-J. Lv, T. Pu, X.-Q. He and L.-L. Cui, Electrochim. Acta, 2013, 112, 269-278.
- 10. C. Canales and G. Ramírez, *Electrochim. Acta*, 2015, **173**, 636-641.
- Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier and H. Dai, Nat. Mater., 2011, 10, 780-786.
- W. Li, A. Yu, C. H. Drew, G. L. Bernard and Z. Chen, J. Am. Chem. Soc., 2010, 132, 17056–17058.
- H. Li, Z. Xu, K. Li, X. Hou, G. Cao, Q. Zhang and Z. Cao, J. Mater. Chem., 2011, 21, 1181-1186.
- 14. L. Cui, G. Lv, Z. Dou and X. He, *Electrochim. Acta*, 2013, **106**, 272-278.
- 15. Z. Shi and J. Zhang, J. Phys. Chem. C, 2007, 111, 7084-7090.

DOI: 10.1039/C6RA12426G

Journal Name

- H. He, Y. Lei, C. Xiao, D. Chu, R. Chen and G. Wang, J. Phys. Chem. C 2012, 116, 16038-16046.
- C. Domínguez, F. J. Pérez-Alonso, M. Abdel Salam, J. L. Gómez de la Fuente, S. A. Al-Thabaiti, S. N. Basahel, M. A. Peña, J. L. G. Fierro and S. Rojas, *Int. J. Hydrogen Energ.*, 2014, **39**, 5309-5318.
- 18. J. Guo, H. He, D. Chu and R. Chen, *Electrocatalysis*, 2012, **3**, 252-264.
- 19. W. Orellana, Chem. Phys. Lett., 2012, 541, 81-84.

ARTICLE

- 20. H. Tang, H. Yin, J. Wang, N. Yang, D. Wang and Z. Tang, *Angew. Chem. Int. Ed.*, 2013, **52**, 5585-5589.
- 21. J. Zhu, N. Jia, L. Yang, D. Su, J. Park, Y. Choi and K. Gong, J. *Colloid Interface Sci.*, 2014, **419**, 61-67.
- R. Chen, H. Li, D. Chu and G. Wang, J. Phys. Chem. C, 2009, 113, 20689-20697.
- 23. M.-S. Liao and S. Scheiner, *The Journal of Chemical Physics*, 2001, **114**, 9780.
- 24. S. Sun, N. Jiang and D. Xia, J. Phys. Chem. C, 2011, 115, 9511-9517.
- R. M. Reis, R. B. Valim, R. S. Rocha, A. S. Lima, P. S. Castro, M. Bertotti and M. R. V. Lanza, *Electrochim. Acta*, 2014, **139**, 1-6.
- 26. Z. Weng, D. Liu, Z. Chen, H. Zou, S. Qin and F. Liang, *Cryst. Growth Des.*, 2009, **9**, 4163-4170.
- 27. H. W. J., R. Ditchfield and P. J. A., J. Chem. Phys., 1972, 56, 2257.
- 28. H. P. J. and W. W. R., J. Chem. Phys., 1985, 82, 299.

- 29. G. I. Cárdenas-Jirón, P. Leon-Plata, D. Cortes-Arriagada and J. M. Seminario, J. Phys. Chem. C, 2011, **115**, 16052-16062.
- B. Wu, Y. Kuang, X. Zhang and J. Chen, *Nano Today*, 2011, 6, 75-90.
- H. J. Choi, N. A. Kumar and J. B. Baek, *Nanoscale*, 2015, 7, 6991-6998.
- 32. R. Cao, R. Thapa, H. Kim, X. Xu, M. G. Kim, Q. Li, N. Park, M. Liu and J. Cho, *Nat. Commun.*, 2013, **4**, 2076.
- M. Shi, Z. Chen, L. Guo, X. Liang, J. Zhang, C. He, B. Wang and Y. Wu, J. Mater. Chem. B, 2014, 2, 4876-4882.
- 34. C. Zhang, R. Hao, H. Yin, F. Liu and Y. Hou, *Nanoscale*, 2012, **4**, 7326-7329.
- R. L. Arechederra, K. Artyushkova, P. Atanassov and S. D. Minteer, ACS Appl. Mater. Inter., 2010, 2, 3295-3302.
- M. Xing, L.-B. Kong, M.-C. Liu, L.-Y. Liu, L. Kang and Y.-C. Luo, J. Mater. Chem. A, 2014, 2, 18435-18443.
- X. Zhou, Z. Xia, Z. Zhang, Y. Ma and Y. Qu, J. Mater. Chem. A, 2014, 2, 11799.
- D. Zheng, Z. Gao, X. He, F. Zhang and L. Liu, *Appl. Surf. Sci.*, 2003, 211, 24-30.
- 39. J. Guo, H. Li, H. He, D. Chu and R. Chen, *The Journal of Physical Chemistry C*, 2011, **115**, 8494-8502.

RSC Advances

ARTICLE

 Table 1
 Tafel slopes (mV dec⁻¹) for FePc/GCB, CoPc/GCB, NiPc/GCB and CuPc/GCB at different voltages.

	b_1 (at low η)	b_2 (at high η)
FePc/GCB	52	122
CoPc/GCB	70	121
NiPc/GCB	-	111
CuPc/GCB	-	113
Pt/C	67	122

 Table 2
 Calculated properties of reaction energy of formulation 1) - 6) by using DFT method.

			$-O_2$ end-on		-O ₂ side-on			
	$\Delta E_{TM-H_2O}/eV$	<i>R_{тм-0} /</i> Å	<i>R₀₋₀ /Å</i>	ΔΕ _{тм-00} /eV	ΔE _{тм-0*0*} /eV	$\Delta E_{des \cdot H_2O_2} / eV$	$\Delta E_{des-OH}/eV$	$\Delta E_{rem-TM} / eV$
FePc	-1.404	1.733	1.324	-2.032	-1.420	1.286	3.292	0.898
CoPc	-0.698	1.888	1.269	-1.294	-0.197	0.641	1.595	0.465
NiPc	-0.278	2.273	1.296	-0.180	-	0.342	0.912	1.941
CuPc	-0.466	2.422	1.323	-0.271	-	0.449	-0.391	-0.665



Scheme 1 Schematic illustration of the preparation process of the TMPc/GCB electrocatalysts.

ARTICLE

Page 8 of 11

DOI: 10.1039/C6RA12426G



Fig. 1 Low-magnification TEM images of a) GCB and b) FePc/GCB, and the high-magnification TEM images of c) GCB and d) FePc/GCB. The inset of a) and b) showed the digital photographs of equivalent GCB and FePc/GCB dispersed in ethanol, respectively.



Fig. 2 a) XRD patterns and b) Raman spectra of GCB and FePc/GCB. c) UV spectra and d) TGA curves of GCB, FePc and FePc/GCB. Atmosphere: air, Rate: 5 °C min⁻¹.



Fig. 3 a) XPS high-resolution scans of a) Fe 2p, b) Co 2p, c) Ni 2p and d) Cu 2p of the TMPc/GCB electrocatalysts.

Published on 29 June 2016. Downloaded by University of Sussex on 05/07/2016 08:22:49.

View Article Online DOI: 10.1039/C6RA12426G ARTICLE



Fig. 4 Cyclic voltammetry curves of FePc/GCB, CoPc/GCB, NiPc/GCB and CuPc/GCB on glassy carbon electrodes in O₂-saturated (solid line) or N₂ saturated (dash line) in 0.1 M KOH at a scan rate 50 mV s⁻¹.



Fig. 5 a) RRDE measurements recorded with the TMPc/GCB and the commercial Pt/C in O_2 -saturated 0.1 M KOH at 1600 rpm. Disk current (l_d) is shown on the lower half and the ring current (l_r) is shown on the upper half of the graph. The disk potential was scanned at 5 mV s⁻¹, and the ring potential was constant at 1.5 V vs. RHE. b) Tafel plots of TMPc/GCB electrodes derived by the mass-transport correction of corresponding RDE data. c) The calculated electron transfer number (n) (shown on the upper half) and percentage of peroxide (shown on the lower half) for the TMPc/GCB catalysts at various potentials, derived from the corresponding RRDE data in Figure 3b. d) Linear polarization curves for FePc/GCB at a scan rate of 5 mV s⁻¹ at the different rotation rates (400, 625, 900, 1225, 1600 and 2025 rpm). The insets show K-L plots at 0.3 V. e) The electron transfer number (n) derived from the K-L equation at 0.3 V vs. RHE. e) Durability evaluation current versus time (*i*-*t*) chronoamperometric responses of the TMPc/GCB electrodes in O_2 -saturated 0.1 M KOH. See the ESIF for detailed calculations.

Published on 29 June 2016. Downloaded by University of Sussex on 05/07/2016 08:22:49.





Fig. 6 Optimized lowest energy structure of (a) isolated TMPc molecules, (b) -H₂O adsorption on TMPc, (c) -O₂ end-on adsorption on TMPc, (d) -O₂ side-on adsorption on TMPc, (d) -H₂O₂ adsorption on TMPc, (e) -OH adsorption on TMPc and (f) isolated H₂Pc molecules. The central light blue ball represents a TM (TM = Fe, Co, Ni or Cu) atom, blue balls represent N atoms, gray balls represent C atoms, and light white balls represent H atoms.

Published on 29 June 2016. Downloaded by University of Sussex on 05/07/2016 08:22:49.

Graphical abstracts



