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ARTICLE



CHEMICAL SOCIETY

Accelerating the oxygen reduction reaction via a bioinspired carbon-supported zinc electrocatalyst

Faezeh Nahavandi | Behnam Seyyedi 🗅

Nanotechnology Research Centre, Urmia University, Urmia, Iran

Correspondence

Behnam Seyyedi, Nanotechnology Research Centre, Urmia University, Shahid Beheshti Avenue, Urmia 5715944931-165, Iran. Email: b.seyyedi@urmia.ac.ir

Oxygen utilization in electrochemical energy generation systems requires to overcome the slow kinetics of oxygen reduction reaction (ORR). Herein, we have outstretched an efficient strategy in order for developing a bioinspired Zn (N_4)/sulfur/graphitic carbon composite (Zn-S-Gc) with an effective performance for the ORR at low temperature. The catalyst composite was created by attaching the Zn (N_4) centers in the form of zinc phthalocyanine on the sulfur-linked graphitic carbon surface. The most positive ORR onset potential of about 1.00 V versus a reversible hydrogen electrode (RHE) was obtained due to the unique structure of a new catalyst in KOH solution (pH = 13) at low temperature (T = 298 K). The catalyst was evaluated using the rotating-disk electrode method in the potential range of -0.02-1.18 V versus RHE. The number of transferred electrons as one of the most important parameters (n > 3.70) is almost constant in a wide range of low overpotentials (0.1-0.6 V), which indicates a more efficient four-electron pathway from O₂ to H₂O on the catalyst surface. The estimated Tafel slope in an appropriate range is about ≈ -133.3 mV/dec at a low current density and E1/2 of the electrocatalyst displays a negative shift of only 11 mV after 10,000 cycles. The mean size of the catalyst centers is on the nanoscale (<50 nm).

KEYWORDS

electrocatalyst, fuel cell, nanomaterials, nonprecious metal catalysts, oxygen reduction reaction, zinc phthalocyanine

1 | INTRODUCTION

Oxygen is an abundant element in the Earth's crust and its reactions play the most important role in electrochemical energy generation and storage systems such as fuel cells. The fuel cells, as a next generation of energy systems, supply electricity by the conversion of chemical energy and their performance strongly depends on sluggish kinetics of oxygen reduction reaction (ORR).^[1–5] Enhancing of the ORR kinetics is inconceivable without the use of efficient electrocatalysts. Widespread research studies were carried out for design and production of suitable catalysts. The platinum-based compounds are a well-known accelerator for the ORR, which have considerable limits.^[6–9] Thus, many attempts have been made to develop an efficient alternative

during the past 25 years. Nonprecious metal catalysts (NPMCs) supported by nitrogen-doped or sulfur-doped carbon allotropes are serious possible alternatives for the platinum-based catalysts.^[10–14] As different electrocatalysts lead ORR in aqueous solutions by two pathways, many precursors have been introduced with different performance: either through an efficient two-step, two-electron pathway from O_2 to hydrogen peroxide or more efficient fourelectron way from O_2 to H_2O or less efficient.^[15–17] The researchers have indicated that the M-N₄-C structure is the closer catalyst for the 4-electron pathway. Here, M is various transition metals, such as: iron, copper, cobalt, zinc etc.^[18–23] On the other hand, Nature uses cytochrome enzymes to catalyze the ORR. The MN₄ centers in the complex cytochrome structure as NPMCs are the active sites for

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the ORR.^[24] In this work, M (N₄) centers were created on the sulfur-linked graphitic carbon, where M is the zinc atom. The Zn (N₄) centers are stabilized by the zinc phthalocyanine structure and graphitic carbon, crystalline allotrope of carbon and the most stable form of carbon under standard conditions, is used as a carbon substrate. Phthalocyanines and their derivatives have been widely used as pigments in industry. Metal phthalocyanines as a two dimensional (2D) metal organics form M (N₄) centers with most transition metals, moreover, they have been investigated as catalysts for various reactions including ORR and redox systems. Although metal phthalocyanines have been never commercialized as catalysts, due to their chemical and thermal stability and specific properties, they have often been investigated for several applications.^[25–28]

The findings of this study demonstrate a highly performing bioinspired zinc-based catalyst for the ORR in alkaline media (KOH, 0.1 mol/L) at low temperature (T = 298 K). Zn-S-Gc is found to offer a much higher ORR activity than metal-free organic N-C and Pt-based catalysts in an alkaline electrolyte, and is especially considerable in terms of E_{Onset}, E_{1/2}, *n* (the number of electrons transferred), the Tafel slope, and the catalyst durability. Elemental microanalysis, thermogravimetric analysis, inductively coupled plasma (ICP), Fourier-transform infrared (FT-IR) spectroscopy, X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and Scanning electron microscopy (*SEM*) methods were employed to evaluate the catalyst structure.

2 | EXPERIMENTAL

2.1 | Reagents and materials

All initial chemicals were of guaranteed reagent (GR) grade from Sigma-Aldrich, Merck, and Alfa Aesar. Deionized water was used to prepare the aqueous solutions.

2.2 | Synthesis of zinc phthalocyanine $(ZnN_8H_xCl_{16-x})$

ZnPc was synthesized using a simple microwave oven under atmosphere pressure. Water used in the synthesis was distilled before use. A mixture of zinc (II) chloride, high purity urea, and phthalic anhydride with a weight ratio of 1:4:4 was dissolved in saturated solution of NaCl (50 mL). Next, 100 mg ammonium molybdate as a catalyst and 0.5 mmol lauric acid as a capping agent to suppress the flocculation of nanoparticles were added to the solution. Dissolved chemicals in a beaker were reacted using a microwave oven (Samsung-900 W) at low temperature (100–125°C) for 10 min. The ZnPc powders were filtered, washed, and dried in air oven at 80°C overnight. Elemental Microanalysis (flash EA112 automatic elemental analyzer) was used for synthesizing ZnPc (Table 1).

 TABLE 1
 Elemental analysis of ZnC₃₂N₈H_xCl_{16-x}

Elements (%)	Cu	С	Ν	Cl	Н
Calculated for CuPc	6.17	36.26	10.57	46.81	0.19
Found for CuPc	6.20	36.20	10.51	46.91	0.18

The elemental mass percentages of Zinc (Zn%), Carbon (C%), Nitrogen (N%), Chlorine (Cl%), and Hydrogen (H%) in ZnPc (ZnC₃₂N₈H_xCl_{16-x}) were calculated by the following equations, respectively:

$$Zn\% = \frac{M_{Zn}}{M_{ZnPc}} \times 100$$
 (1)

$$C\% = \frac{32M_C}{M_{ZnPc}} \times 100$$
 (2)

$$N\% = \frac{8M_N}{M_{ZnPc}} \times 100 \tag{3}$$

$$Cl\% = \frac{(16 - x)M_{Cl}}{M_{ZnPc}} \times 100$$
 (4)

$$\mathrm{H\%} = \frac{x\mathrm{M}_{\mathrm{H}}}{\mathrm{M}_{\mathrm{ZnPc}}} \times 100 \tag{5}$$

where, M_{Zn} , M_C , M_N , M_{Cl} , and M_H are molar mass of zinc, carbon, nitrogen, chlorine, and hydrogen, respectively. and *n* is the number of chlorine atoms in the ZnPc structure. Comparison of the results (experimental and theoretical data) of the elemental microanalysis of prepared ZnPc shows the value of *x* about 2.

2.3 | Preparation of Zn-S-Gc

Catalyst synthesis included the following steps. First, about 3.9 g (50 mmol) of Na₂S was added to 50 mL of dimethylformamide (DMF) to obtain a solution and after that temperature was decreased to -5° C using an ice bath. Then, about 0.6 g (50 mmol) of dried graphitic carbon was mixed in the solution and the mixture was reacted at -5° C for 12 hr. The obtained sample was filtered, washed, and dried in an air oven at 80°C overnight. To prepare Zn-S-Gc, 50 mg of dried powder and 50 mg ZnPc were dispersed in 50 mL DMF and then cooled to -5° C. The mixture was reacted for 24 hr. The Zn-S-Gc powders were filtered, washed, and dried in an air oven at 80°C overnight.

2.4 | Physical characterization

The FT-IR spectra of the Graphitic carbon, Zn-S-Gc, and ZnPc were recorded using a ThermoNicolet model NEXUS FT-IR 670 spectrometer between 4,000–400 cm⁻¹ with the standard KBr pellet method. XRD of ZnPc, Graphitic Carbon, and Zn-S-Gc was carried out using X' Pert Pro-Panalytical with Cu-K α radiation with a wavelength of 1.54 A° at room temperature. The 2 θ angular data were collected between 2° and 80° at a scan rate of 1° per step. To determine the Zn loading weight to the final ORR zinc-based catalyst, the amounts of zinc and sulfur in the obtained Zn-S-Gc sample

were analyzed by ICP-optical emission spectrometry (ICP-OES) using an ICP-MS 7900 (Agilent) (Zn: 9014 ppm and S: 4359 ppm). The weight ratio (\approx 2.07) is approximately equal to the molecular mass ratios of zinc and sulfur (\approx 2.04). The catalyst particle size and morphology were analyzed by *SEM* and TEM using an FESEM-MIRA III (TESCAN) and EM10C-100 KV (Zeiss), respectively.

2.5 | Electrochemical measurements

The catalytic performance of the obtained samples for ORR were evaluated by liner sweep voltammetry (LSV) and cyclic voltammetry (CV) using an Autolab PGSTAT302N potentiostat/galvanostat. The measurements were completed with employing a conventional three electrode cell. Next, a glassy carbon rod (2 mm diameter) was used as a counter electrode^[29] and the Ag/AgCl electrode was employed as a reference electrode. Afterward, a catalyst film-coated glassy carbon rotatingdisk electrode (RDE) with a surface area of 0.19625 cm^{-2} was used as a beneficial electrode. Then, the catalyst ink was produced by adding 2 mg of obtained powder to a solution containing 50 µL Nafion (5 wt %) and 450 µL deionized water, moreover, the suspension was sonicated for 30 min. At the next step, 20 µL of the catalyst ink was placed onto the RDE surface and was dried slowly to form a dry catalyst film (catalyst loading $\approx 0.4 \text{ mg/cm}^2$). Additionally, CVs and LSVs were performed in O₂-saturated KOH (0.1 mol/L) solution by varying the potential from -0.02 to 1.18 V versus reversible hydrogen electrode (RHE) at scan rates of 50 mV/s and 10 mV/s. Also, the electrolyte temperature was sustained at $25 \pm 1^{\circ}$ C and the background CV and LSV measurements were performed in the N2-saturated KOH (0.1 mol/L) solution.

3 | RESULTS AND DISCUSSION

The ZnPc and Zn-S-Gc catalysts were synthesized via a low temperature method as shown in Scheme 1. The first step involved synthesis of chlorinated ZnPc with microwave irradiation in saturated sodium chloride solution. The initial materials were Phthalic anhydride, Urea, and Zinc (II) chloride. Next, disodium sulfide, zinc phthalocyanine, and graphitic carbon precursors were reacted in the DMF solution at -5° C. Following the linking of zinc phthalocyanine and sulfur atoms on the graphitic carbon under natural conditions at -5° C, the as-synthesized Zn-S-Gc catalyst was obtained.

3.1 | Powder XRD analysis

The powder XRD technique was used to study the crystal phase structures of ZnPc, Graphitic carbon, and Zn-S-Gc and is illustrated in Figure 1. In general, ZnPc has different crystal phases and according to the two peaks in the low 20 range (5–10°) at room temperature, it is in the α -ZnPc phase and a monoclinic crystal system.^[30,31] The ZnPc and Zn-S-



SCHEME 1 Fabrication of Zn-S-Gc catalyst through a low temperature process



FIGURE 1 XRD pattern of graphitic carbon, Zn-S-Gc, and ZnPc

Gc diffraction patterns represent the peaks at 7.79° , 9.41° , 13.94° , 15.51° , 16.50° , and 23.81° with different intensities identical to the α -phase of the phthalocyanine structure.

The average size of the ZnPc and Zn-S-Gc (crystalline) domains, D, along the (100), (102), (200), (302), (204), (400), and (414) directions were estimated from the Debye–Scherrer equation:^[32,33]

$$D = \frac{K \cdot \lambda}{\beta \cdot Cos\theta} \tag{6}$$

where *D* is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size; *K* is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite; λ is the X-ray wavelength; β is the line broadening at half the maximum intensity full width at half maximum (FWHM), after subtracting the instrumental line broadening, in radians; and θ is the Bragg angle. The difference of mean size of crystalline domains for α -ZnPc and Zn-S-Gc could be due to the sulfur bridge between α -CuPc and graphitic carbon substrates (Table 2).

3.2 | FT-IR analysis

To find the functional group structures of ZnPc, Figure 2 displays the FTIR spectral measurement for ZnPc, Graphitic

TABLE 2 The calculated crystalline domain size for ZnPc and Zn-S-Gc

Directions	Calculated for ZnPc (nm)	Calculated for Zn-S-Gc (nm)
(100)	0.66	0.80
(102)	0.66	0.80
(200)	0.57	0.57
(302)	0.67	1.00
(204)	0.67	0.67
(400)	0.62	1.01
(414)	0.74	1.01



FIGURE 2 FTIR spectra of ZnPc, graphitic carbon, and Zn-S-Gc

carbon, and Zn-S-Gc with a resolution of 2 cm^{-1} in the region of fundamental frequencies from 400 to $4,000 \text{ cm}^{-1}$. It is quite clear that the IR spectra matching cannot be achieved due to the strong couplings.^[34] The NH stretching and bending vibrations were not observed at about 3,289 and 1,006 cm⁻¹, respectively, in ZnPc and Zn-S-Gc. The absence of these bands is due to the replacement of hydrogen by zinc cations. The C-H stretching vibrations of benzene rings are observed at about 3,186 cm⁻¹ (ZnPc and Zn-S-Gc). The C-C stretching vibrations of pyrrole and isoindole structures in phthalocyanine skeletal are observed at about 1,734, 1,458, 1,310, 1,183, 1,131, 1,079, 885, 715, and 655 cm^{-1} . The C—H bending in plane vibration and aryl structure has appeared at 1470 and 1,536 cm^{-1} . The peaks at 1440 and 1,291 cm⁻¹ determine the =N-C bond and the stretching vibration of the aromatic phenyl ring. The complex bands appearing at 700-1400 cm⁻¹ were assigned to the C-N in isoindole and C-Cl and C-S stretching vibration and the C-H in-plane bending vibrations and C-H outof-plane bending vibrations.^[35–37]

3.3 | TEM and SEM characterization

Figure 3a,b shows the microstructure images of the Zn-S-Gc catalyst that was characterized by field emission *SEM*. A network structure of Zn-S-Gc consists of randomly crumpled sheets observed in the form of multilayer solid, which might



FIGURE 3 SEM and TEM images of synthesized Zn-S-Gc

be attributed to the presence of foreign sulfur atoms. The TEM images indicate the homogeneous amorphous texture of graphitized carbon that the Zn (N_4) centers with diameter less than 50 nm are deposited on the surface of the carbon particles (Figure 3c,d).

3.4 | Electrochemical evaluation for ORR

The CVs of ZnPc and Zn-S-Gc in O_2 saturated KOH solution were measured at a scan rate of 50 mV/s (Figure 4). ZnPc shows a weak peak in the O_2 -saturated solution due to ORR activity at about 0.67 V, while for Zn-S-Gc, a well-defined cathodic peak appears, which indicates the excellent catalyst performance for ORR.

To further investigate the ORR performance, the RDE curves were obtained for Zn-S-Gc at various rotating rates



FIGURE 4 Cyclic voltammograms of the synthesized ZnPc and Zn-S-Gc



FIGURE 5 Polarization curves for catalyst performance at various rotating rates

(200–2000 rpm). Figure 5 shows the onset potential of the catalyst for the ORR about 1.0 V (vs. RHE) after correcting background current at $i_{ORR} = -0.02 \text{ mA/cm}^2$.

The amounts of transferred electrons (n) of the Zn-S-Gc catalyst were calculated using the Koutecky-Levich (K-L) equations:^[38]

$$J^{-1} = J_L^{-1} + J_K^{-1} = \frac{1}{B\omega^{0.5}} + \frac{1}{J_K}$$
(7)

$$B = (0.201) \cdot n \cdot F \cdot C_{O_2} \cdot \sqrt[3]{D_{O_2}^2} \cdot \frac{1}{\sqrt[6]{\nu}}$$

where J is the measured current density, J_k is the kinetic current density, and ω is the rotation rate of the electrode $(F = 96,485 \text{ C/mol}, C_{O_2} = 1.2 \times 10^{-6} \text{ moL/mL}, D_{O_2} = 1.9 \times 10^{-5} \text{ cm}^2/\text{s}$, and $v = 0.01 \text{ cm}^2/\text{s}$). The K-L plots of the synthesized sample for the ORR are obtained as shown in Figure 6.

Using Equation (1), the slopes remain approximately constant over the potential range from 0.1 to 0.6 V. The amount of transferred electrons (n) for Zn-S-Gc is close to 4 (Table 3).

Figure 7 shows calculated Tafel slopes for Zn-S-Gc. The electrocatalytic activity of the sample for ORR is reflected by its Tafel slope of diffusion-corrected kinetic current density. A Tafel slope of -40 mV/dec was observed at a low current density (high potential) and a value of -133.3 mV/dec was obtained in a high current density range (low potential). To be clear, the Tafel slope of commercial Pt/C is ~ 60 and 120 mV/dec, which would be used as a reference. Principally, the range of the Tafel slope for ORR has been reported between 30 and 130 mV/dec in alkaline solution.^[36] This value allows the catalyst to determine the rate-controlling reaction, when, the four electrons pathway and two electrons pathway compete together. On a metal/metal-oxide surface, the rate determining step is a pseudo 2-electron pathway,



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FIGURE 6 The K-L plots for Zn-S-Gc

TABLE 3 The electron transfer number of Zn-S-Gc

<i>E</i> (V)	n
$0.1 V (\mathcal{J}^{-1} = 7,513.6x + 478.55, R^2 = 0.9947)$	3.73
$0.2 V (\mathcal{J}^{-1} = 7,433.4x + 507.15, R^2 = 0.9942)$	3.77
0.3 V ($\mathcal{J}^{-1} = 7,489.8x + 550.20, R^2 = 0.9968$)	3.74
$0.4 V (J^{-1} = 7,861.4x + 614.47, R^2 = 0.9983)$	3.57
$0.5 V (\mathcal{J}^{-1} = 8,353.4x + 697.72, R^2 = 0.9996)$	3.36
$0.6 V (J^{-1} = 8,511.8x + 832.43, R^2 = 0.9993)$	3.30



FIGURE 7 Calculated Tafel slope for Zn-S-Gc

which gives a Tafel slope of $\approx 60 \text{ mV/dec}$ at high potential. However, on a pure metal surface, the first electron transfer is the rate-determining step, resulting in a Tafel slope of $\approx 120 \text{ mV/dec}$. Such a high Tafel slope for Zn-S-Gc indicates that the protonation of O^{2-} is smoother than the Pt-based electrocatalyst; however, the protonation of O^{2-} is a rate-limiting step on the active sites. The difference in the Tafel slope of Zn-S-Gc indicates that the zinc oxide is formed on the catalyst surface at high potential. Therefore, the ORR occurs by the 4-electron pathway at the surface of Zn-S-Gc.^[38]



FIGURE 8 ORR polarization plots of the Zn-S-Gc electrocatalyst before and after 10,000 potential cycles between 0.5 V and 1.0 V (vs. RHE) in O_2 saturated KOH solution

Catalyst durability was checked by cycling the potentials between 0.2 and 1.0 V (vs. RHE) at 50 mV/s in O₂-saturated KOH (0.1 mol/L) solution to evaluate the electrochemical stability of the Zn-S-Gc catalysts. According to the literature, more than 4,000 cycles are now routinely used, after 10,000 cycles, $E_{1/2}$ of Zn-S-Gc displays a negative shift of only 11 mV (Figure 8), which is lower than the most reported values.^[39]

4 | CONCLUSIONS

This work demonstrates a new nonprecious metal electrocatalyst for the ORR. The results reflect the intrinsic activity and selectivity of the prepared catalyst. The catalyst exhibited limiting current density and half-wave potential as compared with the platinum-based electrocatalyst due to the good mass transportation on the catalyst. The ORR occurs on the surface of the Zn-S-Gc catalyst and aqueous solution by multi step reactions. The particles sizes of the obtained powders are on the nanoscale (<50 nm). The catalytic activity of the prepared zinc-based catalyst is comparable with the Pt/C electrocatalyst as a reference. The Tafel slope of diffusion-corrected kinetic current density is ~ -133.3 mV per decade at a low overpotential. The Zn-S-Gc nanostructure exhibits a superior durability performance using NPMCs in the system.

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ORCID

Behnam Seyyedi D https://orcid.org/0000-0001-8084-9108

REFERENCES

- W. Yahui, Y. Fuli, Y. Hongwei, Z. Chunbao, C. Yanli, D. Keqiang, J. Chin. Chem. Soc. 2013, 60, 73.
- [2] M. Pang, C. Li, L. Ding, J. Zhang, D. Su, W. Li, C. Liang, *Ind. Eng. Chem. Res.* 2010, 49, 4169.
- [3] B. Seyyedi, J. Chin. Chem. Soc. 2017, 64, 1503.
- [4] Z. Liu, X. Y. Ling, X. Su, J. Y. Lee, J. Phys. Chem. B 2004, 108, 8234.
- [5] B. Seyyedi, Pigm. Resin Technol. 2017, 46, 267.
- [6] B. Men, Y. Sun, Y. Tang, L. Zhang, Y. Chen, P. Wan, J. Pan, Ind. Eng. Chem. Res. 2015, 54, 7415.
- [7] D. Ke-Qiang, J. Chin. Chem. Soc. 2010, 57, 1309.
- [8] Z. Liu, X. Lin, J. Y. Lee, W. Zhang, M. Han, L. M. Gan, *Langmuir* 2002, 18, 4054.
- [9] G. Liu, H. M. Zhang, M. R. Wang, H. X. Zhong, J. Chen, J. Power Sources 2007, 172, 503.
- [10] M. H. Lee, P. S. Wang, J. S. Do, J. Solid State Electrochem. 2008, 12, 879.
- [11] M. Lefèvre, E. Proietti, F. Jaouen, J. P. Dodelet, Science 2009, 324, 71.
- [12] S. Ma, G. A. Goenaga, A. V. Call, D. Liu, Chem. A Eur. J. 2011, 17, 2063.
- [13] G. Wu, D. Y. Li, C. S. Dai, D. L. Wang, N. Li, Langmuir 2008, 24, 3566.
- [14] D. Wang, D. Su, Energ. Environ. Sci. 2014, 7, 576.
- [15] J. Park, Y. Nabae, T. Hayakawa, M. Kakimoto, *ACS Catal.* 2014, *4*, 3749.
 [16] N. M. Cantillo, G. A. Goenag, W. Gao, K. Williams, C. A. Neal, S. Ma,
- K. L. Morec, T. A. Zawodzinski, J. Mater. Chem. A 2016, 4, 15621.
- [17] H. A. Gasteiger, S. S. Kocha, S. Sompalli, F. T. Wagner, *Appl. Catal. Environ.* 2005, 56, 9.
- [18] C. Choi, H. Lim, M. Chung, J. Park, H. Shin, H. Kim, S. Woo, J. Am. Chem. Soc. 2014, 136, 9070.
- [19] B. Seyyedi, Pigm. Resin Technol. 2017, 46, 156.
- [20] B. Meunier, S. P. D. Visser, S. Shaik, Chem. Rev. 2004, 104, 3947.
- [21] M. Szybowicz, J. Mol. Struct. 2004, 704, 107.
- [22] M. Wojdyla, B. Derkowska, W. Bala, Opt. Appl. 2005, 35, 561.
- [23] W. Bala, M. Wojdyla, M. Rebarz, M. Szybowic, M. Drozdowski, A. Grodzicki, P. Piszczek, J. Optoelectron. Adv. Mater. 2009, 11, 264.
- [24] T. R. Walton, J. R. Griffith, J. G. O'Rear, J. Adhes. Sci. Technol. 1975, 23, 665.
- [25] M. Laskoski, M. B. Schear, A. Neal, D. D. Dominguez, H. L. Ricks-Laskoski, J. Hervey, T. M. Keller, *Polymer* 2015, 67, 185.
- [26] M. Laskoski, A. Neal, T. M. Keller, D. D. Dominguez, C. A. Klug, A. P. Saab, J. Polym. Sci. A: Polym. Chem. 2014, 52, 166.
- [27] T. J. Marks, Science 1985, 227, 881.
- [28] G. A. Attard, A. Brew, J. Ye, D. Morgan, S. Sun, *ChemPhysChem* 2014, 15, 2044.
- [29] J. Chen, C. Jones, S. Linic, V. Stamenkovic, ACS Catal. 2017, 7, 6392.
- [30] L. Yu, Y. Zhang, B. Zhang, J. Liu, Sci. Rep. 2014, 4, 1.
- [31] J. Mack, M. J. Stillman, Coord. Chem. Rev. 2001, 219, 993.
- [32] A. De Lorenzi, S. Giorgianni, R. Bini, Mol. Phys. 1999, 96, 101.
- [33] H. Ding, J. Wei, H. M. Xiong, Nanoscale 2014, 6, 13817.
- [34] D. Li, S. Ge, T. Yuan, J. Gong, B. Huang, W. Tie, W. He, *CrstEngComm* **2018**, *20*, 2749.
- [35] F. Iwatsu, T. Kobayashi, N. Uyeda, J. Phys. Chem. 1980, 84, 322.
- [36] D. Roy, N. M. Das, N. Shakti, P. S. Gupta, RSC Adv. 2014, 4, 42514.
- [37] X. Liu, K. Zhu, J. Tian, O. Tang, Z. Shan, J. Solid State Electrochem. 2014, 18, 2077.
- [38] T. V. Basova, E. K. Kol'tsov, I. K. Igumenov, Sens. Actuators B Chem. 2005, 105, 259.
- [39] H. Liang, W. Wei, Z. Wu, X. Feng, K. Müllen, J. Am. Chem. Soc. 2013, 135, 16002.

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