

Two-dimensional Nitrogen-doped Mesoporous Carbon/Graphene Nanocomposites from the Self-assembly of Block Copolymer Micelles in Solution

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Electronic Supplementary Information

Abstract The self-assembly of block copolymer in solution has proven to be an effective strategy for building up a wide range of nanomaterials with diverse structures and applications. This paper reports a facile self-assembly approach towards two-dimensional (2D) sandwich-like mesoporous nitrogen-doped carbon/reduced graphene oxide nanocomposites (denoted as mNC/rGO) with well-defined large mesopores. The strategy involves the synergistic self-assembly of polystyrene-block-poly(ethylene oxide) (PS-*b*-PEO) spherical micelles, *m*-phenylenediamine (mPD) monomers and GO in solution and the subsequent carbonization at 900 °C. The resultant mNC/rGO nanosheets have an average pore size of 19 nm, a high specific surface of 812 m²·g⁻¹ and a nitrogen content of 2.2 wt%. As an oxygen reduction reaction (ORR) catalyst, the unique structural features render the metal-free nanosheets excellent electrocatalytic performance. In a 0.1 mol·L⁻¹ KOH alkaline medium, mNC/rGO exhibits a four-electron transfer pathway with a high half-wave-potential ($E_{1/2}$) of +0.77 V versus reversible hydrogen electrode (RHE) and a limiting current density (J_L) of 5.2 mA·cm⁻², which are well comparable with those of the commercial Pt/C catalysts.

Keywords Block copolymer; Self-assembly; 2D materials; Mesoporous carbon; ORR

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The catalytic oxygen reduction reaction (ORR) at the cathode is a critical step in industrial electrocatalytic processes for fuel cells^[1]. However, the sluggish kinetics of ORR significantly limits the efficiency of electrochemical energy conversion. Although precious Pt metal has been adopted as an effective ORR electrocatalyst, large-scale commercial production has been hampered by its high cost and poor durability^[2, 3]. In this regard, extensive efforts have been devoted to the development of cost-effective and durable alternatives, such as nonprecious metal catalysts or metal-free heteroatom-enriched (e.g. N, B, and S) carbonaceous catalysts^[4]. Incorporation of heteroatoms into a carbonaceous skeleton can induce the uneven charge distribution of carbon atoms, modulate the catalytic sites and consequently improve the O₂ adsorption and ORR performance^[4]. So far, a number of N-doped carbon materials have been fabricated by employing various nitrogen-containing precursors including melamine^[5], polypyrrole^[6] and polyaniline^[7], etc. However, most of the obtained materials show insufficient catalytic activity and poor stability due to the poor electrical

conductivity, low specific surface area and limited catalytic sites.

Graphene, a two-dimensional (2D) monolayer nanosheet of hexagonal carbon with intriguing properties such as high surface area and superior electrical conductivity, has emerged as an ideal substrate for the fabrication of nanocomposites containing numerous catalytic sites^[8, 9]. It is believed that rational growth of mesoporous catalytic-active materials on graphene may provide abundant catalytic sites, facilitate the ions diffusion and improve the electrical conductivity, thus enhancing the ORR performance of the resulting materials. Furthermore, large mesopores of > 10 nm diameter can fasten ion diffusion^[10], and thus offer better ORR performance compared with < 10 nm mesopores^[11–13]. To this end, hard templates, such as silica nanoparticles, have been used to construct 2D graphene-based mesoporous materials with large pores (> 10 nm)^[11]. However, the complicated and time-consuming multistep procedures as well as the use of toxic or corrosive chemicals in the hard-template method impede its extensive use^[14–16]. In contrast, the soft-template method based on the self-assembly of block copolymer in solution, which provides a versatile strategy for constructing various ordered nanostructures of tunable dimensions^[17–22], shows great advantages in pore structure control and easy

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template removal and has proven to be efficient for the fabrication of mesoporous materials^[15, 23, 24]. Nevertheless, the fabrication of graphene-based 2D N-doped mesoporous carbon materials with large pores by the soft-template method has not yet been documented due to the lack of suitable template and the difficulty in patterning mesoporous substances on graphene surfaces.

Here, we demonstrate a facile approach towards 2D mesoporous N-doped carbon/reduced graphene oxide nanosheets (denoted as mNC/rGO) *via* the self-assembly of polystyrene-block-poly(ethylene oxide) (PS-*b*-PEO) block copolymer in solution with *m*-phenylenediamine (*m*PD) as the nitrogen-containing carbon source. As illustrated in Fig. 1, the PS-*b*-PEO diblocks first self-assemble into spherical micelles when a mixture of ethanol and H₂O (*V/V*, 1/2) is added slowly into their tetrahydrofuran (THF) solution. After the addition of aqueous solutions of *m*-phenylenediamine (*m*PD) and graphene oxide (GO), the synergistic self-assembly of the spherical micelles, GO, and *m*PD monomers leads to the close-arrangement of spherical micelles on both GO surfaces as well as the adsorption of *m*PD molecules in the PEO coronae *via* H-bonding. Triggered by ammonium persulfate (APS), the *m*PD monomers are converted to a poly-*m*-phenylenediamine (PmPD) network after 24-h polymerization at 0 °C. Subsequently, the PS-*b*-PEO micelles are removed by the pyrolysis at 900 °C under argon atmosphere, generating 2D sandwich-like N-doped mesoporous carbon/rGO nanocomposites (mNC/rGO) with large pores. After the treatment with NH₃, the resultant mNC/rGO nanosheets possess a mean pore size of 19 nm, an average thickness of 35 nm, a high specific surface area of 812 m²·g⁻¹, and a nitrogen doping content of 2.2 wt%. Benefiting from the unique structures, the mNC/rGO nanocomposites show excellent catalytic performance as a metal-free catalyst for ORR in an alkaline medium, with a half-wave-potential ($E_{1/2}$) of +0.77 V versus

reversible hydrogen electrode (RHE) and a limiting current density (J_L) of 5.2 mA·cm⁻², which is well comparable with that of the commercial Pt/C catalyst and is also better than those of many reported N-doped carbon materials, such as 3D N-doped porous carbon^[25, 26], N-doped porous carbon nanosheets^[27, 28], N-doped porous carbon/rGO nanosheets with pore sizes of < 10 nm^[25, 29, 30] and N-doped graphene^[31–33]. To our knowledge, this study represents the first case of making 2D mesoporous carbon nanomaterials with well-defined pore structure for electrocatalytic applications, by taking advantage of block copolymer self-assembly in solution.

The PS-*b*-PEO diblock copolymer was synthesized by employing a PEO₁₁₄ initiator (the subscript number denotes the degree of polymerization) *via* atom transfer radical polymerization (ATRP)^[34, 35]. The detail procedures are given in the electronic supplementary information (ESI). Gel permeation chromatography (GPC, Fig. S1, in ESI) and nuclear magnetic resonance (NMR, Fig. S2, in ESI) analyses reveal the successful synthesis of the copolymer. The number average molecular weight (M_n) of the diblocks and the degree of polymerization (DP) of the PS block are determined to be 1.38×10^4 and 89, respectively. The polydispersity index (PDI) of 1.1 indicates a narrow molecular-weight distribution of the copolymer (Fig. S1, in ESI). The self-assembly of PS₈₉-*b*-PEO₁₁₄ was performed by a simple one-step cosolvent method^[24, 34, 35], which involved the slow addition of ethanol/H₂O (*V/V*, 1/2) mixed solvent into a tetrahydrofuran (THF) solution (2.5 mg·mL⁻¹) of the copolymer under mild stirring at room temperature. The resulting spherical micelles possess a mean diameter of (17 ± 2) nm (Fig. S3, in ESI). Then, the addition of GO (synthesized by the Hummer's method^[36]) and *m*PD monomers led to a close packing and single-layered arrangement of the micelles on the GO surfaces, driven by H-bonding and electrostatic interaction between the PEO chains in the micelles and the oxygen-

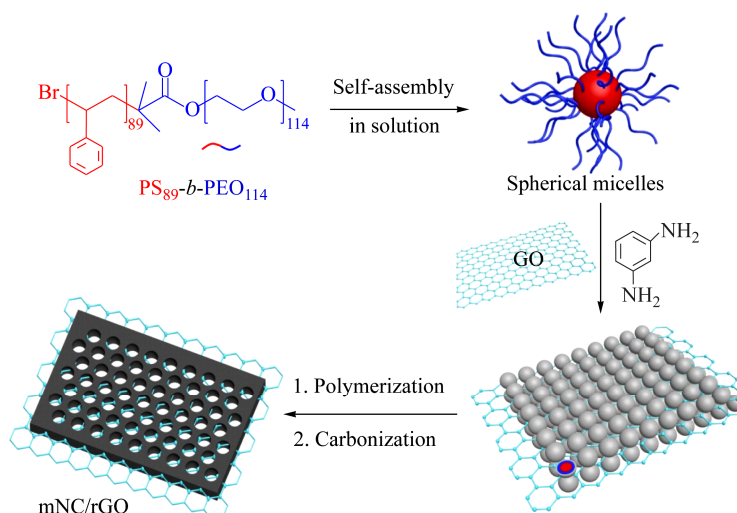


Fig. 1 Schematic illustration of the fabrication of 2D mNC/rGO with well-defined large mesopores through the self-assembly of PS-*b*-PEO block copolymer in solution. The spherical micelles consist of a core (red color) formed by hydrophobic PS blocks and the coronae (blue color) constructed by hydrophilic PEO chains around the core; the coronae can adsorb *m*PD molecules that will be polymerized into a PmPD network.

bearing groups on GO (such as $-\text{COOH}$ and $-\text{OH}$)^[24, 37]. Meanwhile, *m*PD monomers were adsorbed in the PEO domains through H-bonding. TEM images in Fig. S4 (ESI) demonstrate the effective adsorption and tight packing of the block copolymer (BCP) micelles on the GO surfaces. Triggered by APS at 0 °C, *m*PD monomers polymerized into a *Pm*PD polymeric network around the micelles. Fourier transform infrared spectra (FTIR) confirmed the polymerization of *m*PD to *Pm*PD (Fig. S5, in ESI). Similar to the Ostwald ripening, a strong force from polymerization could lead to the migration of the *m*PD monomers in the PEO phase from the top of the micelles into the voids of adjacent micelles, leaving the top of the micelles void of *Pm*PD moiety^[24]. After several cycles of centrifugation and washing with pure water to remove the residual *m*PD monomers and APS, the dried black powder was carbonized at a high temperature of 900 °C under Ar atmosphere for 2 h and then treated with NH_3 for 1 h, yielding the 2D mNC/rGO nanocomposites. Thermal gravimetric analysis (TGA) gave a carbon yield of ~42 wt% after carbonization under Ar atmosphere at 900 °C (Fig. S6, in ESI).

The structural characterizations of mNC/rGO are presented in Fig. 2. Scanning electron microscopy (SEM, Fig. 2a and Fig. S7 in ESI) and transmission electron microscopy (TEM, Fig. 2b) images reveal the closely packing mesopores on the nanosheets. According to SEM images, mNC/rGO possesses an average pore size of approximately 18 nm, in agreement with the TEM result. Meanwhile, a partial overlap of the mesopores shown in TEM images suggests that mesoporous *Pm*PD grows on both sides of the rGO sheets. Atomic force microscopy (AFM) height profile indicates a uniform thickness of 35 nm for the nanosheets (Fig. 2c), which is close to twice the average diameter of the $\text{PS}_{89}\text{-}b\text{-PEO}_{114}$ spherical

micelles, confirming the growth of mesoporous *Pm*PD monolayers on both sides of GO sheets. Nitrogen adsorption-desorption isotherm shows a typical type IV curve, which is a characteristic of mesoporous structures (Fig. 2d). From the isotherm, the specific Brunauer-Emmett-Teller (BET) surface area and pore volume of mNC/rGO are calculated to be $812 \text{ m}^2\cdot\text{g}^{-1}$ and $0.69 \text{ cm}^3\cdot\text{g}^{-1}$, respectively. Based on the Barrett-Joyner-Halenda (BJH) method, the average pore size is calculated to be 19 nm, which is in good accordance with the SEM and TEM results.

X-ray photoelectron spectroscopy (XPS) was performed to analyze the element composition of mNC/rGO. The XPS spectrum in Fig. 3(a) shows the presence of C1s, O1s, and N1s signals distinctly, which gives carbon and nitrogen contents of 90.7 wt% and 2.2 wt%, respectively. The N1s peak can be further deconvoluted into three signals with binding energies of 398.5, 401.0, and 402.5 eV, which correspond to pyridinic N (14.6%), graphitic N (59%) and pyridine-N-oxide atoms (26.4%), respectively (Fig. 3b)^[11]. The Raman spectrum shows two prominent peaks at 1594 and 1333 cm^{-1} , which can be assigned to the G (graphitic carbon) and D (disordered carbon) bands, respectively (Fig. 3c)^[38]. Based on the intensity (*I*) of the two peaks, the large I_G/I_D ratio (~0.8) indicates a high degree of graphitization for mNC/rGO, which favors the electrical conductivity of the resulting materials. Electrochemical impedance spectroscopy (EIS) measurement reveals a low electrical resistance of ~250 Ω for mNC/rGO, confirming its good conductivity (Fig. S8, in ESI).

N-doped carbon materials are commonly applied as ORR electrocatalysts since the doping-induced uneven charge distribution of C atoms can modulate the catalytic sites, and thus improve the O_2 adsorption and facilitate the oxygen

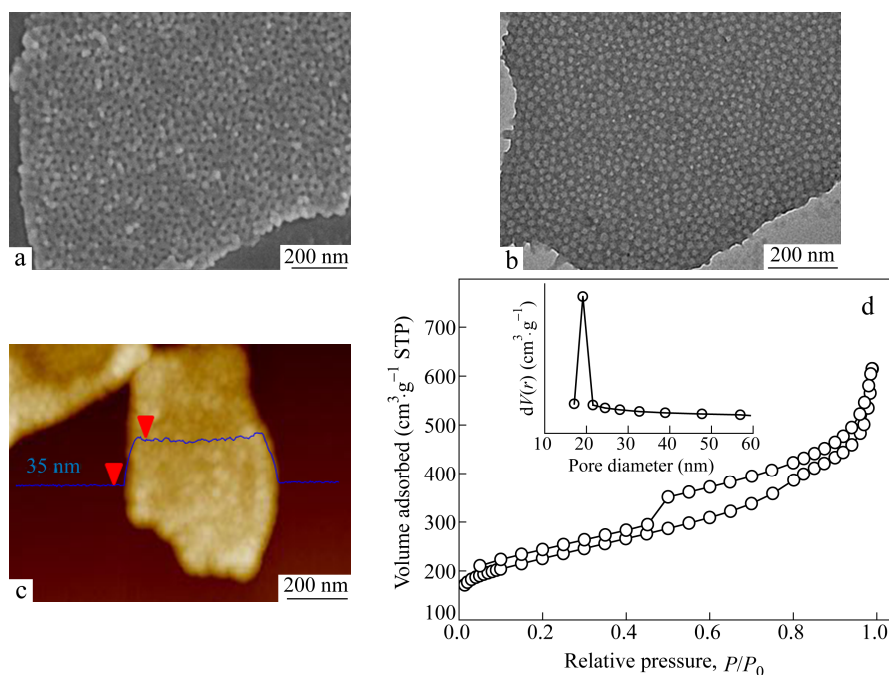


Fig. 2 Structural characterizations of the mNC/rGO nanosheets: (a) SEM image, (b) TEM image, (c) AFM height profile, (d) nitrogen adsorption-desorption isotherm and pore size distribution (inset) (The isotherm is vertically offset by $100 \text{ cm}^3\cdot\text{g}^{-1}$ STP.)

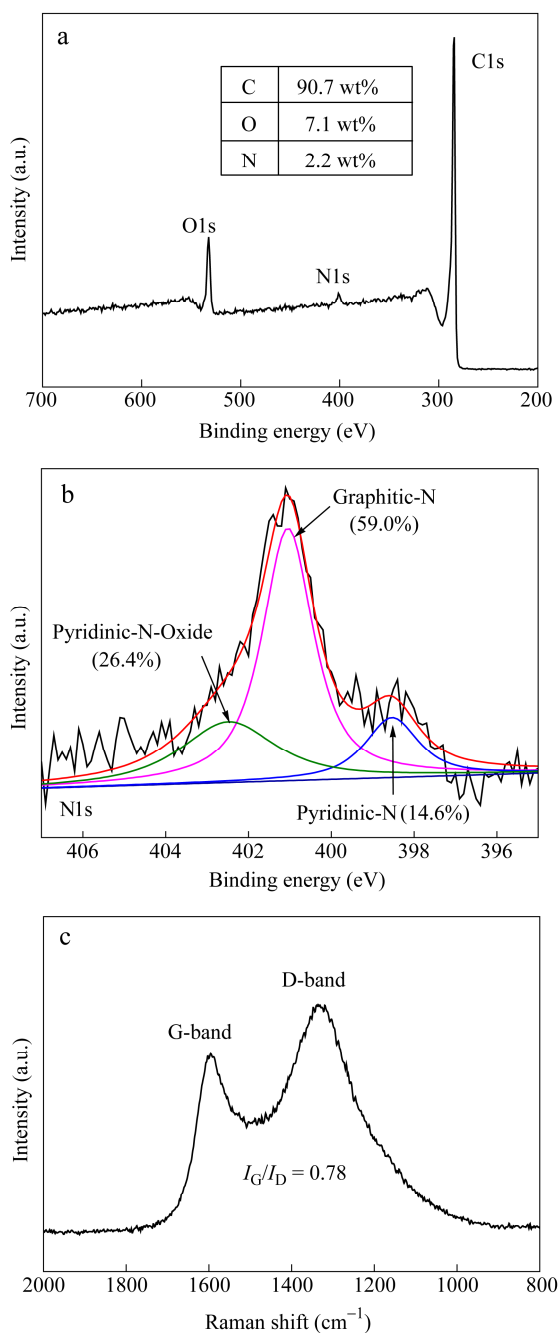


Fig. 3 (a) XPS survey spectrum, (b) N1s XPS spectrum and (c) Raman spectrum of mNC/rGO (The inset table in (a) shows the contents of C, O, N elements, respectively.)

reduction process^[39]. In the present work, the electrocatalytic performance of mNC/rGO as a metal-free ORR catalyst was examined in a three-electrode cell system under alkaline conditions (0.1 mol·L⁻¹ KOH). First, the ORR catalytic activity of mNC/rGO was evaluated by cyclic voltammetry (CV) measurements in N₂ or O₂-saturated electrolyte at a scan rate of 100 mV·s⁻¹. As shown in Fig. 4(a), no obvious redox peak is observed in the N₂-saturated solution; on the contrary, a well-defined cathodic ORR peak centered at ~0.65 V versus RHE appears in O₂-saturated solution, which reveals a pronounced electrocatalytic activity of mNC/rGO for oxygen reduction. The rotating disk electrode (RDE) voltammograms

of mNC/rGO and commercially available Pt/C catalyst at a rotation rate of 1600 r·min⁻¹ are compared in Fig. 4(b). The onset potential of mNC/rGO is as high as ~0.92 V versus RHE. Meanwhile, mNC/rGO possesses a half-wave-potential of +0.77 V versus RHE, which is very close to that of Pt/C (+0.78 V), as well as a limiting current density of 5.2 mA·cm⁻² that is higher than that of Pt/C (4.99 mA·cm⁻²). Such performance is better than those of many reported N-doped carbon materials, such as 3D N-doped porous carbon^[25, 26], N-doped porous carbon nanosheets^[27, 28], N-doped porous carbon/rGO nanosheets (pore size below 10 nm)^[25, 29, 30] and N-doped graphene^[31–33] (see comparison in Table S1, in ESI). Figure 4(c) shows the linear sweep voltammetry (LSV) curves of mNC/rGO in an O₂-saturated 0.1 mol·L⁻¹ KOH solution at different rotation rates from 400 r·min⁻¹ to 2025 r·min⁻¹. Apparently, the limiting current density increases with increasing the rotation rate. Based on ring current (*I_R*) and disk current (*I_D*) from the rotating ring disk electrode (RRDE) curves (Fig. S9, in ESI) and the following equations^[30]:

$$n = \frac{4I_D}{I_D + I_R/N} \quad (1)$$

$$\text{HO}_2^- \% = 200 \times \frac{I_R/N}{I_D + I_R/N} \quad (2)$$

where *N* represents the current collection efficiency of the Pt ring (0.37, according to the manufacturer), the electron transfer number (*n*) and H₂O₂ yield (HO₂⁻%) of mNC/rGO are calculated to be 3.6–3.9 and 6.9%–22.4% at the potential range from 0 V to 0.7 V, respectively. This result manifests that mNC/rGO exhibits a primary four-electron ORR pathway with a low H₂O₂ yield (Fig. 4d). Tafel slope of mNC/rGO (146 mV·dec⁻¹) is slightly higher than that of Pt/C (127 mV·dec⁻¹), suggesting a similar ORR mechanism on the surface of these catalysts (Fig. 4e).

The stability of mNC/rGO was studied at a constant voltage of 0.4 V for 2 × 10⁴ s in 0.1 mol·L⁻¹ KOH solution at a rotation rate of 1600 r·min⁻¹ (Fig. 4f). The corresponding current-time curve shows a slow current attenuation and a high relative current of 87.3% after 2 × 10⁴ s for mNC/rGO. In sharp contrast, Pt/C exhibits a fast current loss of 15% within the first 1500 s and obtains a lower relative current of 82.3% after 2 × 10⁴ s. As methanol fuel in the anode sometimes permeates through the polymer membrane into the cathode and then seriously affects the performance of the catalysts, the catalytic selectivity of mNC/rGO against the electro-oxidation of methanol molecules was also tested. The ORR current of mNC/rGO loses only 5% after adding 2% (V/V) methanol, much more stable than that of Pt/C, which exhibits a sharp decrease to negative current (the inset of Fig. 4f). Obviously, mNC/rGO possesses a high selectivity for methanol and a remarkable resistance to electro-oxidation, which is much better than that of the commercial Pt/C catalyst.

In conclusion, we prepared 2D sandwich-like mesoporous nitrogen-doped carbon/rGO nanocomposites through the self-assembly of PS-*b*-PEO block copolymer in solution.

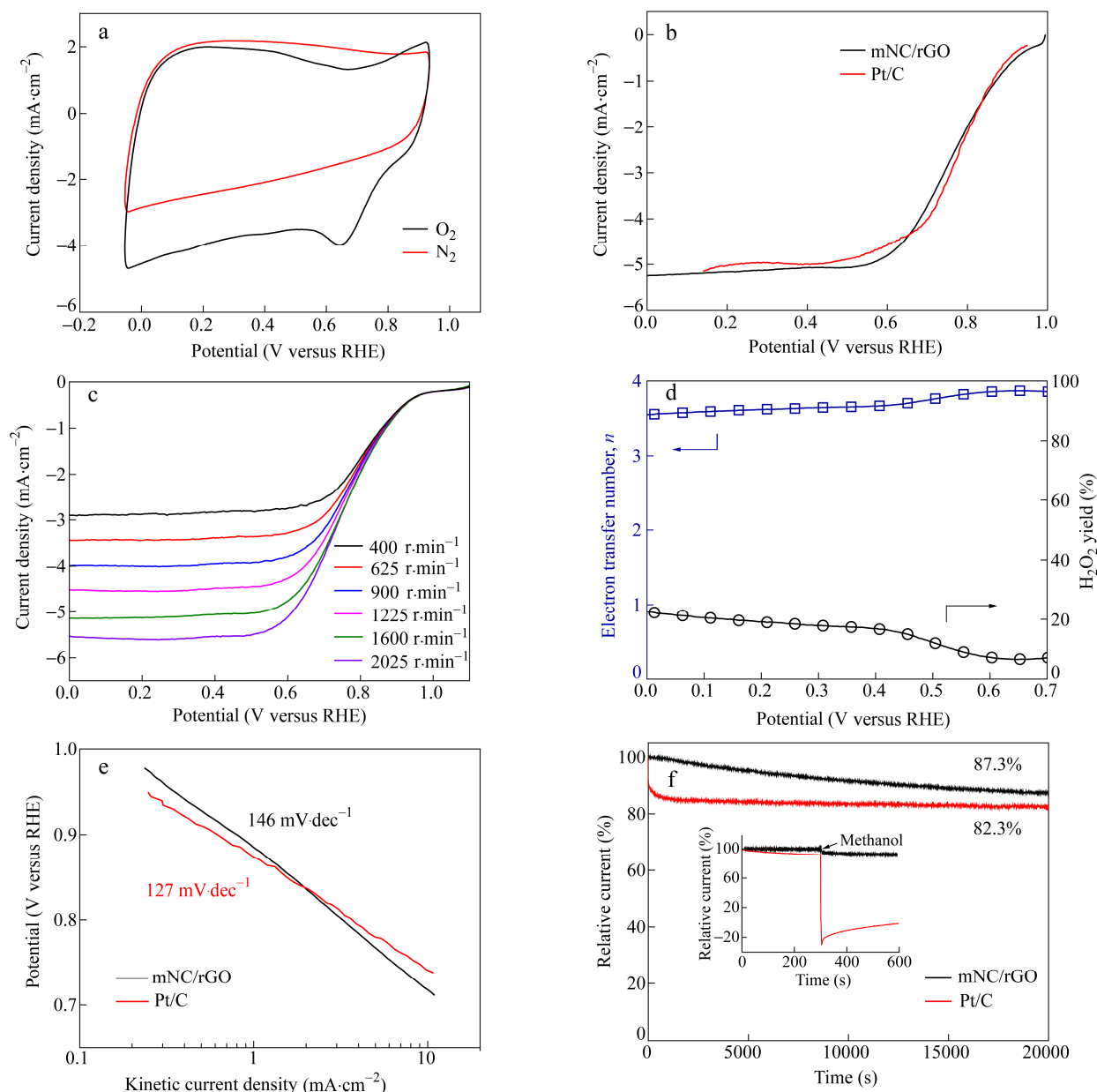


Fig. 4 ORR catalytic performance of the as-prepared mNC/rGO in 0.1 mol·L⁻¹ KOH electrolyte: (a) CV curves of mNC/rGO in N₂ or O₂-saturated 0.1 mol·L⁻¹ KOH solution at a scan rate of 100 mV·s⁻¹; (b) RDE plots of mNC/rGO and a commercially available Pt/C catalyst at a scan rate of 10 mV·s⁻¹ and a rotation rate of 1600 r·min⁻¹; (c) LSV curves of mNC/rGO at a scan rate of 10 mV·s⁻¹ with different rotation rates from 400 r·min⁻¹ to 2025 r·min⁻¹; (d) Electron transfer number (n) and H₂O₂ yield of mNC/rGO, which are calculated from the RRDE data (Fig. S9, in ESI); (e) Tafel plots of mNC/rGO and the commercial Pt/C; (f) Durability comparison of mNC/rGO and the commercial Pt/C catalysts at 0.40 V in O₂-saturated 0.1 mol·L⁻¹ KOH with a rotation speed of 1600 r·min⁻¹ (The inset shows the chronoamperometric responses of mNC/rGO and the commercial Pt/C at 0.40 V and a rotation rate of 1600 r·min⁻¹, the arrow stresses the addition of 2% (V/V) methanol at 300 s.)

The obtained mNC/rGO nanosheets with a uniform thickness of 35 nm exhibit a high specific surface area up to 812 m²·g⁻¹, an average pore size of 19 nm, and a nitrogen content of 2.2 wt%, which offer abundant catalytic sites and facilitate oxygen adsorption and reduction in the ORR process. The mNC/rGO composites exhibit superb electrocatalytic performance as metal-free catalyst for ORR in a 0.1 mol·L⁻¹ KOH solution, with a half-wave-potential of +0.77 V versus RHE, a limiting current density of 5.2 mA·cm⁻² and an

excellent long-term stability, which is well comparable with the catalytic performance of the commercial Pt/C catalyst. The self-assembly strategy developed in this study holds promise in the construction of a wide range of 2D mesoporous nanomaterials with well-defined pore structures for energy-related applications.

Electronic Supplementary Information

Electronic supplementary information (ESI) including experiment details, supporting figures and tables, etc., is available free of

charge in the online version of this article at <https://doi.org/10.1007/s10118-018-2091-1>.

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