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Unlocking the potential of graphene for water oxidation from orbital hybridization strategy

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Graphene-based electrocatalytic materials are potential low-cost electrocatalysts for the oxygen evolution reaction (OER). However, substantial overpotentials above thermodynamic requirements limit their efficiency and stability in OER-related energy conversion and storage technologies. Here, we embedded CrN crystals into graphene and in situ electrochemically oxidized them to construct graphene materials with encapsulated Cr6+ ions (Cr6+@G). These Cr6+@G exhibit the lowest OER overpotential of 197 mV at 10 mA cm−2 and excellent stability over 200 h at a high current density of about 120 mA cm−2 in alkaline electrolyte. Spectroscopic and computational studies confirm a stable ion coordination environment significantly benefiting to downshift of graphene Fermi level via C p orbitals hybridizing with d orbitals of Cr6+ ions that enhance the OER activity and stability.

Introduction

Developing highly active and stable electrocatalysts based on rational design principles is a critical knot along the renewable energy roadmap of converting electrical energy into fuels and chemicals. In particular, graphene-based electrocatalytic materials with inherently high surface area that offers a large number of active centers, are considered to be promising candidates for various energy conversion and storage systems1,2. However, underperformance in the oxygen evolution reaction (OER) hinders the graphene use in various energy processes, such as solar or electricity-driven water splitting (2 H2O → 2 H2 + O2)3,4, CO2 fixation (x CO2 + y/2 H2O → CxHyOz + (4x+y)/4 O2)5,6, and rechargeable metal-air batteries (MxO → xM + 1/2 O2)7,8.

It has been well recognized that OER from water splitting is mainly driven by the atom-scale interactions between the catalytic materials and OER intermediates (OH*, O*, OOH*)9. In particular, graphene-based catalysts function via the interactions between the valence band of the carbon active centers on graphene and the bonding orbital of the adsorbed OER intermediates to form C-O bonding (σ) and antibonding (σ*) states. And the OER activity over graphene is mainly determined by the energetic difference between the σ states and graphene Fermi level. With a high anode voltage, the Fermi level of graphene downshifts to the σ levels, which are fully occupied and dominated by O p orbital levels. O p orbital electrons accordingly start to transfer to graphene, causing electrically driven water oxidation. However, because of the...
inherently much higher Fermi level of graphene than $\sigma$ states, it inevitably requires a high applied voltage for graphene catalysts to activate oxygen intermediates, usually leading to a high OER overpotential of $\sim 0.35$ V for a current density of $10$ mA cm$^{-2}$.$^{10,11}$

Therefore, it is desired to propose a strategy to benefiting to tuning Fermi level of graphene for efficient OER. Enormous efforts go into the nonmetal doping method, with the major investigations on the chemical compositions$^{10,11}$, atomic configurations$^{12,13}$, and the construction of OER active centers$^{12,14}$. Systematically comparative studies have indicated that among the various nonmetal hetero-atoms such as N, B, P, S, and O, only B or N doping exhibits the reduction of OER activation energy$^{10,12-16}$, owing to the decreased energetic difference between C-O $\sigma$ level and Fermi level of graphene$^{10,12}$.  

Different to the nonmetal doping, theoretical investigations indicated that forming a stable ligand structure with 3d transition metal ions with strong electronegativity, such as Ni$^{4+}$ and Cr$^{6+}$, can highly promote electron transfer from graphene to the metal ions via $dp$ hybridization between C $p$ and transition metal $d$-orbitals, causing gap opening with drastic downshift of the Fermi level of graphene$^{17-19}$. As shown in Scheme 1, it should be predictable that the facile downshift of the Fermi level of graphene by the introduction of metal ions as strong electron acceptors can effectively decrease the energetic difference between the $\sigma$ state and the graphene Fermi levels, and thus the electron transfer barrier from OER intermediates to carbon active centers. Resultantly, low overpotentials are required. Here, we embedded the Cr$^{6+}$ ions, a strong electron acceptor, into graphene to narrow the energetic difference between the Fermi level of graphene and the $\sigma$ states. Validity of this strategy was first experimentally identified by embedding Cr$^{6+}$ ions into N-doped graphene (Cr$^{6+}$@G) as the catalysts, and then verified via density functional theory (DFT) calculations.

Results and Discussion

Synthesis and characterizations of Cr$^{6+}$@G
We firstly explored a controllable approach to encapsulate Cr species into N-graphene. We mixed D-glucose, NH$_4$Cl and CrCl$_3$ with certain amount of eutectic melting salts as the dispersing agent, followed by forming Cr-containing caramels at 150 °C via an amino-carbonyl reaction. We then pyrolyzed these caramels under N$_2$/Ar atmosphere to form Cr-containing graphene, and thoroughly rinsed the remnant powders by 1 M hot H$_2$SO$_4$ at 80 °C for 8 ~ 12 h to remove exposed Cr species and any other unstable impurities.

The acid-rinsed catalysts then underwent a second heat treatment under NH$_3$ for nitridation as the final step of the catalyst synthesis. A sp$^2$ hybridization characteristic in Raman spectra (1602 cm$^{-1}$) indicated the formation of graphene (Fig. S1). Deconvolution analysis on N 1s core-level X-ray photoelectron spectroscopy (XPS) revealed that N atoms were doped into graphene in the forms of pyridinic (398.6 eV) and graphitic N (401.1 eV) (Fig. S2$^{20}$). The scanning/transmission electron microscopy (SEM/TEM) and the atomic force microscopy (AFM) showed a nanosheet of N-graphene with the thickness of ~2 nm (Fig. 1A and Fig. S3-S5). X-ray diffraction (XRD) presented the single-phase patterns of CrN (JCPDS card No.11-0065) (Fig. S6). The high-resolution TEM (HRTEM) combined with atomic-resolution scanning transmission electron microscopy (STEM) performed in high-angle annular dark field (HAADF) mode (Fig. 1B-E and Fig. S7) revealed that CrN nanocrystals were embedded in compact and crystalline graphene shells (denoted as CrN@G). And the graphene shells could be well controlled with 2, 4, 7, and over 30 layers by adjusting the amount of molten salts. Noting that Fig. 1A shows the clear traveling track of CrN crystals, suggesting that the compact graphene shells originate from an encapsulating process by CrN rolling on the graphene nanosheet during nitridation. This confirms strong interactions between CrN and graphene, as observed by the XPS signal of Cr-C coordinate bond forming between CrN and graphene (Fig. 2A$^{21,22}$.

The as-synthesized CrN@G then underwent an electrochemical activation process by using cyclic voltammetry or chronopotentiometric holds at 10 mA cm$^{-2}$ to convert CrN@G to Cr$^{6+}$@G (Fig. S8$^{23}$). Cr 2p core-level XPS spectra in Fig. 2A obviously exhibited binding energy of Cr$^{6+}$ at 580.2 eV$^{24}$ and electron energy loss spectra (EELS) in Table S1 showed N leaching, indicating the electrochemical oxidation of CrN. Ongoing oxidation for over 24 h with further Cr$^{6+}$ generation and N leaching led to surface amorphization (XRD in Fig. S6, selected area electron diffraction in Fig. S9) and particle size shrinkage of CrN crystals (TEM in Fig. 2B-D). No Cr species were detected out of the graphene shells by HAADF-STEM (Fig. S7) or in the electrolyte by inductively coupled plasma mass spectrometry (ICP-MS), indicative of that Cr$^{6+}$ cations
Cr

Since the height of the pre-edge peak in XANES is sensitive to the

1.60 Å

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Fig. 2. Characterizations to identify Cr⁶⁺@G. (A) XPS spectra of Cr 2p before and after OER at 10 mA cm⁻² for over 24 h. (B) TEM view of Cr⁷⁺@G after OER operation. (C and D) TEM image and HRTEM lattice image for showing the encapsulating graphene layers and shrunk CrN after the lifetime test over 24 h. (E) Normalized XANES scans for the Cr K edge of Cr⁶⁺@G, referenced to K₂Cr₂O₇, CrN, and CrN@G. Inset in Fig. 2E shows the pre-edge features at 5993.5 eV. (F) The corresponding fast Fourier transformation in R space (phase shift not corrected). Experimental and fitting data are shown in solid lines and red circles, respectively.

were perfectly encapsulated in the graphene layers with no leakage.

X-ray absorption fine spectroscopy (XAFS) was further used to confirm the chemical structure of Cr⁶⁺@G after over 24 h lifetime test, referring to K₂Cr₂O₇, CrN, and CrN@G. As shown in Cr K-edge X-ray absorption near edge structure (XANES) spectra (Fig. 2E), an enhanced intensity of pre-edge peak at 5993.5 eV confirmed the transformation of Cr³⁺ in CrN to Cr⁶⁺, because the empty d-orbital (3d⁰) of Cr⁶⁺ increases the probability of the 1s to 3d transition. Since the height of the pre-edge peak in XANES is sensitive to the Cr⁶⁺-to-Cr³⁺ ratio, the percentage of Cr⁶⁺ in total Cr species was calculated to be 10.8 at.% according to the empirical formula proposed by Peterson et al.⁶. An electron paramagnetic resonance active Cr⁵⁺ signal at g = 1.98 shows another evidence of this transformation (Fig. S10). In addition, the Fourier transforms of Cr K-edge extended X-ray absorption fine structure (EXAFS) (Fig. 2F) showed a significant decrease in Cr-N bond distance from 2.06 Å for CrN@G to 1.72 Å for Cr⁶⁺@G (Table S2). The latter was consistent with previous study on the Cr⁵⁺-N with the bond length of around 1.60 Å.⁷ Therefore we believe that Cr⁶⁺-N ligands formed in Cr⁶⁺@G by Cr⁵⁺ coordinating with N on the surface of CrN crystals.

Evaluation of electrochemical activity and stability

We carried out the electrochemical measurements, and found that the OER activities of Cr⁶⁺@G dramatically faded with the thickening of outer graphene layers. This was because the electronic interactions between inner Cr⁶⁺ ions and the surfacial carbon atoms were buffered by increased graphene layers. As a result, Cr⁶⁺@G with averagely 2 graphene layers and Cr content of 0.27 at.% exhibits the best OER activity (Fig. 3A and Fig. S11, hereafter, Cr⁶⁺@G refers to this sample unless otherwise specified). The OER activity of Cr⁶⁺@G is far exceeding those of Cr(OH)₃, CrN, and CrN physically blended with N-graphene (CrN/G), and N-doped graphene (N-graphene) (Fig. 3B). Specifically, Cr(OH)₃ exhibits little OER activity, well consistent with prevailing viewpoint that most OER catalysts contain Cr³⁺ or Cr⁴⁺ instead of Cr⁵⁺ or Cr⁶⁺. In the case of Cr⁷⁺@G, the high OER activity of Cr⁶⁺@G suggests that other than CrN/G with Cr d-band as the catalytic center, the OER for Cr⁶⁺@G occurs on the C p band center at the surface of graphene. And compared with N-graphene, the embedded Cr⁶⁺ ions greatly contribute to activating the OER catalytic performance of the carbon surface.
Embedding Ni, Co, Fe, or Mn metal nanocrystals into N-graphene exhibited higher OER overpotentials compared to Cr$_6^+$@G (Fig. 3C, Fig. S3, S4, S6, S11, S13, S14 and Table S3), further demonstrating the efficacy of Cr$_6^+$ on modulating electronic structure of graphene. Cr$_6^+$@G only requires an overpotential $\eta = 255$ mV at $j = 10$ mA cm$^{-2}$.

The turnover frequency (TOF) at $\eta = 300$ mV are 0.92 s$^{-1}$ according to C mole number in the Cr$_6^+$-C ligand (Cr$_6^+$-C ligand number is determined by fitting EXAFS data to be about 3, Table S2), which is obviously higher than those of previously reported OER catalysts (Table S4). A three-dimensional (3D) electrode was constructed by loading Cr$_6^+$@G catalyst on a nickel foam to further check the potential for industrial applications. The 3D electrode shows a low overpotential of 197 mV at $j = 10$ mA cm$^{-2}$, which is comparable with the state-of-the-art gelled FeCoW oxyhydroxides electrolyt catalysts ($\eta = 192$ mV at $j = 10$ mA cm$^{-2}$) $^{35}$. And TOF value for Cr$_6^+$@G on 3D electrode was determined by referencing to C mole
Fig. 4. DFT calculations of OER. (A) A scheme showing the tetrahedral 4-coordinate structure for embedding Cr$^{6+}$ into pyridinic N-graphene. (B) Potential corrected free energy diagram for graphitic N-graphene and Cr$^{6+}$@pyridinic N-graphene models at 1.23 V$_{\text{RHE}}$ with calculated structures and rate-determining steps.

number in the Cr$^{6+}$-C ligand to be 5.8 s$^{-1}$ at $\eta = 286$ mV. Furthermore, the apparent current increase trend during the OER test shows great consistency with the generated oxygen concentration determined by in situ oxygen fluorescent probing (Fig. 3D and Fig. S15, S16), and the faradic efficiency determined by gas chromatography for $\text{O}_2$ production is 95.1% with H$_2$/$\text{O}_2$ molar ratio at ~2:1 (Fig. S17), suggesting high conversion efficiency from electric to chemical energy. A detectable change of oxygen concentration starts from $\eta = 0.14$ V, indicative of the onset potential at ~1.37 V vs. reversible hydrogen electrode (V$_{\text{RHE}}$), further exhibiting the excellent OER catalytic performance of Cr$^{6+}$@G. Obvious gas release on the 3D electrode was observed at the potential as low as 1.45 V$_{\text{RHE}}$, and even dramatic at 1.5 V$_{\text{RHE}}$ (Movie S1), representing promising candidate for electrochemical water splitting and artificial photosynthesis.

To check the OER stability of Cr$^{6+}$@G, we ran OER at constant current of 10 mA cm$^{-2}$ continuously for 24 h on RDE (Fig. 3E). An activation process of CrN@G to Cr$^{6+}$@G with a potential decrease of 18 mV was observed in the first ~6 h, following with a slight potential increase for the subsequent 18 h. After the stability test, few oxygen atoms could be detected on the graphene shells by EELS (Inset of Fig. 3E, Table S1), illustrating oxidative immunity on the graphene shells with good structural and chemical stability. The fine change in OER overpotential and surface oxygen content suggests exclusively good stability of Cr$^{6+}$@G. In contrast, N-graphene without modification of Cr$^{6+}$ exhibited over 150 mV potential increase in less than 2 h OER test. More importantly, under high current density of around 120 mA cm$^{-2}$ at 1.51 V$_{\text{RHE}}$, Cr$^{6+}$@G 3D electrode is stable for over 200 h (Fig. 3F), demonstrating the huge potential for large-scale applications.

**DFT simulations**

DFT calculations were carried out to confirm whether Cr$^{6+}$ is able to sufficiently influence the catalytic properties of graphene. According to the XPS results, we constructed pure, graphitic N-, and pyridinic N-graphene cluster models with or without Cr$^{6+}$, respectively. Based on the structural and energetic criteria, we found that one Cr$^{6+}$ ion coordinating to N-graphene with one dangling N atom (N$^0$) to form a tetrahedral 4 coordinate structure is the most structurally stable and energetic favorable (Fig. 4A), rather than Cr$^{6+}$ coordinating to N-graphene with or without N$_3^-$ ion (Fig. S18 and Table S5, details were described in the Supplementary Text). In our structure models, the N$^0$ is treated as the approximate description of the electroneutral CrN substrate to immobilize its surfacial Cr$^{6+}$ ions. The calculated Cr$^{6+}$-N$^0$ distance in the three proposed models is 1.44-1.77 Å (Table S5), well consistent with the measured Cr-N distance (1.72 Å) by EXAFS (Fig. 2F, Table S2), confirming that this approximate model is reasonable. The shortest atomic distances between Cr$^{6+}$ and its neighboring atoms are obtained on pyridinic N-graphene to be 1.98, 2.34, and 2.03 Å, meaning that pyridinic N-graphene cluster model with Cr$^{6+}$ is the most stable structure among the possible models. OER
intermediates, including ⋅OH, ⋅O, or ⋅OOH, and Cr⁶⁺ were then settled at the either side of the graphene nanosheet to simulate the chemical structure, in which Cr⁶⁺ ions were embedded inside the graphene, and OER intermediates at the outside. After fully structural relaxation, to check the catalytic activity for these graphene-based materials, the adsorbed free energy for OER intermediates was calculated at theoretical water oxidation equilibrium potential of 1.23 V (referencing to standard hydrogen electrode). As shown in Fig. 4B, Fig. S18 and S19, free energy calculations demonstrated that among graphene and N-graphene models without Cr⁶⁺, graphitic N-graphene exhibits the lowest overall reaction free energy change with the free energy uphill (1.02 eV) at the rate-determining step to form ⋅OOH, suggesting the graphitic N doping is beneficial to improve the catalytic activity of graphene, well consistent with the previous theoretical calculations. After introducing Cr⁶⁺, the Cr⁶⁺ embedded in pyridinic N-graphene (Cr⁶⁺@pyridinic N-graphene) exhibits the lowest overall reaction free energy change with reduced thermodynamic requirement (0.82 eV) at rate-determining step of the O₂ generation, and until the potential increased to 2.05 V, the free energies for all steps run downhill (Fig. S20). Obviously, the active center shifts from the graphitic-N bonding carbon of graphitic N-graphene to the carbon at the meta-position of pyridinic N of Cr⁶⁺@pyridinic N-graphene (Inset of Fig. 4B, Table S6). Furthermore, the ligand bond length between Cr⁶⁺ cation and the C active center during the 4-step reaction keeps around 2.36 Å, indicating the C active center nearby Cr⁶⁺, and the strong interaction between them. These results indicate that the Cr⁶⁺ ions significantly influence the adsorption energy of OER intermediates and the carbon active centers compared with N-graphene without embedded Cr⁶⁺.

Comparing the adsorbed free energy for OER intermediates on these constructed models (Fig. 4B and Fig. S21), we believe that the lower thermodynamic requirement on Cr⁶⁺@pyridinic N-graphene should result from a strong interaction between Cr⁶⁺ ions and N-graphene. The embedding of Cr⁶⁺ ions modulating the electronic structure of N-graphene was thus systematically investigated via natural bond orbital (NBO) analysis. For the Cr⁶⁺@pyridinic N-graphene after adsorption of OER intermediates (⋅OH, ⋅O, or ⋅OOH), charge population analysis indicates effective charge transfer of about 5.1-5.3 electrons from N-graphene to Cr. The nearly constant charge transfer that is almost independent to the absorption of OER intermediates, further demonstrates the strong hybridization between Cr⁶⁺ and N-graphene due to their stable ligand structures. Obviously, electron extraction from graphene by Cr⁶⁺ would downshift the Fermi level of graphene, hence narrow the energy difference between Fermi level of graphene and C-O bonding states. The calculated C-O bond lengths for ⋅OH, ⋅O, and ⋅OOH respectively adsorbed on carbon active centers are 1.37, 1.44, and 1.39 Å for with Cr⁶⁺@pyridinic N-graphene that makes the interfacial charge transfer more easily. The orbital component analysis reveals that for graphitic N-graphene the electron occupancy of OER intermediates is slightly higher than that of carbon active centers (Fig. 5A-C). However, for Cr⁶⁺@pyridinic N-graphene the electron occupancy of carbon active centers is evidently stronger than that of OER intermediates, demonstrating effective local electron transfer from OER intermediates to carbon active centers. These evidences from theoretical calculations clearly suggest that the introduction of Cr⁶⁺ would decrease the Fermi level of graphene, hence facilitates the electrons transfer from OER intermediates to carbon catalytic centers for catalyzing O₂ generation with much lower energetic requirement (Fig. 5D). The strong interaction between Cr⁶⁺ and N-graphene is mainly contributable to the high OER activity and stability of Cr⁶⁺@G material due to the embedded stable Cr⁶⁺ ligand structure and the strong electronic structure modulation by Cr⁶⁺.

Conclusion

We demonstrated an efficient and stable graphene-based OER catalytic material, Cr⁶⁺@G. The Cr⁶⁺@G electrode yielded a low OER overpotential of 197 mV at j = 10 mA cm⁻² and was stable at around 120 mA cm⁻² for over 200 h operation in alkaline media. To our knowledge, this is a record OER performance for carbon-based materials. Based on our experimental and theoretical findings, the modulation of Fermi level of graphene is of vital importance to the catalytic activity of graphene-based OER catalysts, while embedding metal ions with high electronegativity opens a strategic avenue to perfect the graphene-based electrocatalysts for clean and renewable energy future.
Fig. 5. The molecular orbital compositions for graphitic N-graphene and Cr$^{6+}$@pyridinic N-graphene after adsorption of OER intermediates. (A) Adsorption of $^*$OH. (B) Adsorption of $^*$O. (C) Adsorption of $^*$OOH. Fermi level $E_f$ refers to the highest valence orbital energy of the entire graphene clusters. (D) Schematic projected density of states (PDOS).

Materials and Methods

Materials. Analytical reagent D-Glucose, NH$_4$Cl, CrCl$_3$·6H$_2$O, CoCl$_2$·6H$_2$O, NiCl$_2$·6H$_2$O, FeCl$_3$·6H$_2$O, MnCl$_2$·4H$_2$O, NaCl and KCl were purchased from Shanghai Chemical Reagent Co. (China). KOH (99.999%) was purchased from Aladdin Industrial Inc. (China). All the above chemicals were used as received.

Material synthesis. Embedding CrN crystals into graphene (CrN@G) was achieved by following procedure (take the CrN@G with averagely 2 encapsulating graphene layers as a sample). Typically, 4 mmol D-glucose, 6 mmol NH$_4$Cl, 1.5 mmol CrCl$_3$·6H$_2$O and metal chloride salts (KCl/NaCl = 51/49 by weight) were thoroughly mixed with the weight ratio of 80:1 for salts to precursors, and heated at 150 °C for 12 h in an autoclave. Then the pre-reacted brown mixture was transferred to a porcelain crucible and pyrolyzed at 1050 °C under N$_2$ for 1 h. After natural cooling to ambient temperature, the blacked products were thoroughly ultrasonically rinsed with distilled water and ethanol for around 20 times. Acid leaching was then carried out ultrasonically in 0.5 M H$_2$SO$_4$ at 80 °C for 12 h to remove remnant salts and unencapsulated Cr species, and then rinsed with distilled water and ethanol for 20 times again. The resulting sample collected by filtration was dried in a vacuum at 60 °C for 24 h, then pyrolyzed at 900 °C under NH$_3$ to obtain CrN@G catalysts. CrN@G with 30, 7, 4, and 2 graphene encapsulating layers were controlled by varying the pyrolyzing time of 120, 60, 30, and 15 min. Increasing the content of CrCl$_3$·6H$_2$O, the CrN@G$_{3/4}$ (4 mmol D-glucose, 6 mmol NH$_4$Cl, 2 mmol CrCl$_3$·6H$_2$O) and CrN@G$_{5/3}$ (4 mmol D-glucose, 6 mmol NH$_4$Cl, 2.5 mmol
CrCl\textsubscript{2}·6H\textsubscript{2}O) were fabricated at the ratio of salts to precursors of 80:1, with pyrolyzing time under NH\textsubscript{3} of 15 min.

For comparison, embedding Co, Ni, Fe, and Mn metal nanocrystals into graphene was respectively fabricated by using the aforementioned procedure with a ratio of 80:1 for salts (KCl/NaCl = 51/49 by weight) to precursors (4 mmol D-glucose, 6 mmol NH\textsubscript{4}Cl, 1.5 mmol X (X = CoCl\textsubscript{2}·6H\textsubscript{2}O, NiCl\textsubscript{2}·6H\textsubscript{2}O, FeCl\textsubscript{2}·6H\textsubscript{2}O, or MnCl\textsubscript{2}·4H\textsubscript{2}O)). And pristine CrN powders were fabricated with pyrolysis of Cr(OH)\textsubscript{2} at 600 °C under NH\textsubscript{3} for 6 h. Physically-mixed CrN and N-graphene (CrN/G) was fabricated with precursors of 1.5 mmol CrN, 4 mmol D-glucose, and 6 mmol NH\textsubscript{4}Cl as precursors and the same synthesis procedure as CrN@G.

Converting CrN@G to embedding Cr\textsuperscript{6+} into N-graphene (Cr\textsuperscript{6+}@G) was carried out on a rotating disk electrode (RDE) in 1 M KOH by using at least 100 cyclic voltammetry scannings with a scan rate of 50 mV s\textsuperscript{-1} or chronopotentiometric holds at 10 mA cm\textsuperscript{-2} for 6 h.

**Material characterizations.** The morphology of as-prepared samples was characterized by the field emission scanning electron microscopy (FE-SEM, FEI NOVA NanoSEM230, USA), transmission electron microscopy (TEM, JEOL 3010, Japan), Double spherical aberration corrected scanning transmission electron microscope (Cs-corrected STEM, FEI Titan3 G2 60-300). The crystal structures of the samples were characterized by a powder X-ray diffractometer (XRD, Ultima III, Rigaku Corp., Japan) using Cu-K\textalpha\textsubscript{α} radiation (λ = 1.54178 Å, 40 kV, 40 mA). The surface composition of the samples was characterized by using X-ray photoelectron spectroscopy (XPS, ESCALAB 250) with the non-monochromatic Al K\textsubscript{α} X-ray as the X-ray source. Raman spectra were collected by a Jobin Yvon HR800 Raman scattering system with an excitation wavelength of 488 nm. Electron paramagnetic resonance (EPR) spectra were collected by a Bruker EMX-10/12 EPR Spectrometer. Inductively coupled plasma mass spectrometry (ICP-MS) were carried out with PE\textsuperscript{®} Optima 5300DV spectrometer. In situ fluorescence method to measure dissolved oxygen was carried out via a Mettler Toledo InPro 6870i optical oxygen sensor. The Cr K-edge EXAFS data collected on the BL14W1 beamline at the Shanghai Synchrotron Radiation facility (SSRF). Cr K-edge XAFS spectra were recorded from 5792 to 6786 eV in fluorescence mode with a step size of 0.25 eV at the near edge. Data processing was performed with the EXAFS data analysis program IFEFFIT\textsuperscript{38}.  

**Electrochemical measurements.** The electrochemical characterization was carried out with a CHI 760e electrochemical workstation, and rotating disk electrode (RDE, ALS RDRE-3A). The OER performance was measured with RDE technique in 1M KOH solution. All measurements were conducted in a thermostat-controlled, standard three-electrode cell at room temperature, in which a platinum foil, a Hg/HgO/1M KOH electrode and a RDE were used as the counter electrode, the reference electrode and the working electrode, respectively. And all the potentials were referenced to reversible hydrogen electrode (RHE) except as otherwise indicated. All the potential values measured were calibrated following the equation of

\[ E_{RHE} = E_{RE} + 0.095V + 0.0592 \times pH \]

where \( E_{RHE} \) and \( E_{RE} \) are reversible hydrogen electrode potential and Hg|HgO electrode potential, respectively. pH is the pH value of electrolyte.

The catalyst “ink” was prepared by ultrasonically mixing catalyst (10 mg), a 5 Wt% Nafion solution (Aldrich) (95 μL) and ethanol (350 μL) for 1 h. Then 4.5 μL ink was pipetted onto the RDE (Diameter = 4 mm), resulting in a material loading of around 716 μg cm\textsuperscript{-2}. The catalyst film was dried in air at room temperature. Steady-state cyclic voltammetry was performed in a potential range from 1 to 1.8 V\textsubscript{RHE} at a scan rate of 50 mV s\textsuperscript{-1} for 100 cycles.

For the OER measurements using RDE technique, the catalysts loaded glassy carbon electrode (GCE) was rotated at speed of 1600 rpm with a scan rate of 5 mV s\textsuperscript{-1}. The iR compensation was carried out by iR compensation procedure on the CHI660D electrochemical workstation, with the compensation rate set as 90% (Fig. S22). The turnover frequency (TOF) was calculated from the equation of

\[ TOF = \frac{j \times A}{4 \times F \times n} \]

where \( j \) is the current density at overpotential of 0.30 or 0.286 V in mA cm\textsuperscript{-2}, \( A \) is the area of the GCE, \( F \) is the Faraday constant with a value of 96485 C mol\textsuperscript{-1}, and \( n \) is the mole number of the active C atoms in Cr\textsuperscript{6+}-C ligand.

To obtain a three-dimensional electrode, the 70 μL catalyst ink was pipetted on the Ni foam with effective area of 1.4 cm\textsuperscript{2}, resulting in the catalyst loading at 1 mg cm\textsuperscript{-2}. To determine Faradaic efficiency of Cr\textsuperscript{6+}@G electrode, a gas chromatograph (Agilent 490 Micro GC, 5A zeolite column and Ar carrier) was used for the quantitative detection of \( \text{O}_2 \) and \( \text{H}_2 \). The experiment was performed in a gas-tight three-electrode electrochemical cell in 1 M KOH electrolyte. The cell was degassed by bubbling with high-purity Ar for 2 h to remove air. Electrolysis with gas detection was continued at a constant current density of 8 mA cm\textsuperscript{-2} for 3 h.

**DFT calculations.** A two dimensional 6 × 6 graphene supercell was used as the graphene cluster model. One central C atom was replaced by a N atom to construct graphitic N-doped graphene (N-graphene). The pyridinic N-graphene was built with the removal of the C atom neighboring to the N atom of N-graphene. An ionized cluster of Cr\textsuperscript{6+} bonded with 0 - 3 N atoms was located close to the center of the mentioned-above graphene clusters to construct the Cr\textsuperscript{6+} embedding into graphene, graphitic and pyridinic N-graphene models, respectively. Selecting nitrogen as a coordination atom is because nitridation treatment is one of the most common methods to improve the properties of graphene. Therefore, the N atom is introduced electroneutral that can offer the lone pair electrons to improve the properties of graphene. Therefore, the N atom is introduced electroneutral that can offer the lone pair electrons to improve the properties of graphene. Therefore, the N atom is introduced electroneutral that can offer the lone pair electrons to improve the properties of graphene. Therefore, the N atom is introduced electroneutral that can offer the lone pair electrons to improve the properties of graphene. Therefore, the N atom is introduced electroneutral that can offer the lone pair electrons.
bonding to Cr\textsuperscript{6+}. The peripheral carbon atoms of all the graphene clusters were saturated with terminal hydrogen atoms.

All calculations have been performed with Gaussian 09 software package \textsuperscript{39}. Geometry optimizations were carried out without constraints at the M06-2X \textsuperscript{40} level of theory in gas phase. The effective core potential (ECP) of Lanl2DZ \textsuperscript{41} was used to describe Cr, and the 6-31G(d) basis set was used for describing C, H, O, and N. Default convergence criteria were used. The vibrational frequency calculations were conducted at the same level of theory as geometry optimization to confirm whether each optimized structure is the minimum-energy one.

The free energies were determined assuming the conventional single site OER mechanism by the procedures proposed by Nørskov \textit{et al} \textsuperscript{42}. The computational hydrogen electrode model was used as a reference electrode for the expression of the chemical potentials of protons and electrons at any given pH and applied potential \textsuperscript{43}. Natural bond orbital (NBO) analysis was carried out to investigate molecular orbital (MO) compositions with C-squared population analysis (SCPA) method.

Acknowledgements

The authors thank Professor Xiaoshan Wu for experimental assistance in XAFS measurements. We are grateful to the High Performance Computing Center (HPCC) of Nanjing University for doing the numerical calculations in this paper on its IBM Blade cluster system. Funding: This work was supported primarily by the National Basic Research Program of China (2013CB632404), the National Natural Science Foundation of China (51572121, 21603098 and 21633004), the State Key Laboratory of NBC Protection for Civilian Universities (021314380084). This work has benefited from the program B for outstanding PhD candidate of Nanjing University (SKLNBC2014-09), the Natural Science Foundation of Jiangsu Province (BK20151265, BK20151383 and BK20150580), the program B for outstanding PhD candidate of Nanjing University and the Fundamental Research Funds for the Central Universities (021314380084). This work has benefited from the hard X-ray micro-analysis and spherical grating monochromator beamlines at CLS and the BL14W1 beamline at the Shanghai synchrotron radiation facility (SSRF).

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