A robust design of Ru quantum dot/N-doped holey graphene for efficient LiO2 batteries†

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Herein, we report a simple, versatile, defect-engineered method to fabricate Ru quantum dots (Ru QDs) uniformly anchored on a nitrogen-doped holey graphene (NHG) monolith. It uses in situ pyrolysis of mixed glucose, dicyandiamide (DCDA), and RuCl3, followed by an acid treatment, and a final heat treatment to introduce in-plane holes of various sizes. A novel transmission method in scanning electron microscopy was successfully implemented to directly visualize the holes with color contrast. A low accelerating voltage of 5 kV enabled prolonged observation without significant electron beam damage. The mechanisms of hole creation were examined in detail using various characterization techniques as well as control experiments. The Ru QDs had significant catalytic activity and resulted in larger in-plane holes through the graphene sheets. The mechanical strain and the chemical reactivity of Ru QDs significantly diminished the activation energy barrier for the oxidation of C=C bonds in the graphene structure. The Ru QD/NHG hybrid material was utilized as an electrocatalyst for the oxygen evolution reaction in LiO2 batteries, showing much lower charge overpotentials compared to the bare NHG counterpart. The defect-laden holey graphene counterpart can be highly functionalized for multiple applications, leading to a new method of nanoengineering based on atomic scale defects.

Introduction

Non-aqueous rechargeable lithium–oxygen (Li–O2) batteries are being developed for high-density electrical energy storage because of their ultrahigh theoretical energy density (approximately 5–10 times higher than that of conventional Li-ion batteries).1,2 In these batteries, the electrochemical energy storage is based on the reversible redox reaction 2Li0 + O2 + 2e− ↔ Li2O2, which involves the oxygen reduction reaction (ORR) during discharging (Li2O2 formation) and the oxygen evolution reaction (OER) during charging (Li2O2 decomposition).3,4 On the other hand, a few challenges still exist and need to be unraveled before developing these batteries for practical purposes, such as electrolyte decomposition at high potentials, poor cycling stability, and inadequate energy efficiency.5,6,7 These drawbacks primarily originate from high charge overpotentials. Therefore, tremendous efforts have been made to reduce the high overpotentials by various approaches, among which the insertion of active catalysts into the cathode materials is a successful strategy to solve or at least reasonably control this problem.8 In addition, to accommodate the non-conductive solid discharge product (Li2O2) in the cathode materials of these batteries, porous carbon electrodes with large surface areas have been predominantly used.9–10 Among the many carbon materials, graphene is considered an ideal candidate because of its large specific surface area, high electrochemical stability, and excellent electric conductivity.11–13 However, the 2D structure of graphene is barely able to provide sufficient electrolyte impregnation throughout the electrode. This hinders the diffusion of Li ions and oxygen gas to the inner spaces, and the limited diffusion pathway can also induce charge polarization.14,15 Besides, the sheets are prone to adhere to each other during cathode preparation. Therefore, graphene-based cathode...
materials with more porous structures are desirable for Li–O2 batteries with enhanced energy efficiency, because these porous counterparts can more effectively store Li2O2 during discharge and release oxygen during the subsequent charge process.

One interesting approach to the diffusion problem is introducing in-plane holes onto the basal plane of graphene sheets, thereby retaining their 2D-related properties but with improved molecular transport to ensure easy diffusion pathways for reaction products, Li ions, and oxygen. During the past few years, holey graphene (also known as graphene nanomesh\textsuperscript{16,17} or graphene antidote\textsuperscript{18,19}) has attracted widespread attention as a new type of graphene-based material. Due to their enhanced electronic properties\textsuperscript{16,20} and high charge/discharge rates\textsuperscript{21,22} as well as high volumetric performance,\textsuperscript{23,24} holey graphene materials have various applications, especially in energy storage.\textsuperscript{25–27} The holes provide easy pathways for reactants, and therefore effectively decrease the charge polarization. The edges around the holes also affect the properties of graphene sheets, delivering better electrode performance than the intact counterpart.

Recently, a few research groups have conducted excellent investigations on the electrochemical performance of porous graphene materials as cathode electrodes for Li–O2 batteries.\textsuperscript{13–15,28,29} However, the effects of existing functional groups of 2D perforations on the Li–O2 battery performance remain poorly understood. Hence, this study aims to systematically evaluate these perforations, and to examine their physical and chemical effects in the material in detail.

Differently from the various conventional bottom-up (e.g. chemical vapor deposition)\textsuperscript{30} and top-down (e.g., chemical reduction of graphene oxide and liquid exfoliation of pristine graphite)\textsuperscript{31,32} synthesis strategies of graphene, we used another simple yet versatile single-step method to produce a highly conductive freestanding N-doped graphene (NG) monolith with Ru QDs grown through the plane of graphene.

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The Ru QDs were embedded in the graphene material by design for two purposes: tune the morphology of the graphene sheets by creating in-plane holes, and serve as an efficient catalyst to facilitate Li2O2 decomposition during charging. While Ru-based metals and metal oxides are known as effective catalysts for decreasing charge polarization,\textsuperscript{14,29,33–37} the weak bonding between the catalyst particles and graphene often leads to coarsened and agglomerated Ru nanoparticles, thereby rapidly reducing the catalytic activity.\textsuperscript{38} In contrast, the direct insertion of nanoparticles through the plane of graphene, as depicted in Scheme 1, can ensure a very strong contact between the two components. The result is more dispersed and stable Ru nanoparticles.

A subsequent acid treatment produces the corresponding NHG. Since the surface energy of graphene is quite low, the Ru QDs remain well embedded in the graphene sheets. The resulting Ru QD/NHG composite presents excellent metal distribution, remarkable thermal and chemical stability, and enhanced electrochemical performance as a cathode material in Li–O2 batteries.

We also used an innovative transmission method in scanning electron microscopy (SEM) to directly evaluate the in-plane holes.\textsuperscript{39} This technique provides a higher spatial resolution compared to conventional SEM methods, since a transmission beam is used for imaging. The low accelerating voltage also avoids electron beam damage. To the best of our knowledge, this is the first report on imaging holes through graphene sheets utilizing a low-kV transmission electron beam in SEM.

Results and discussion

1. Synthesis of the Ru QD/NHG composite

The complete synthesis process of the Ru QD/NHG composite is depicted in Scheme 1. First, a homogeneous mixture of DCDA, glucose, and RuCl3 was directly transformed into the Ru QD/NG

![Scheme 1 Schematic of the fabrication of the Ru QD/NG and Ru QD/NHG composites.](image)
composite by heating to 1000 °C, under a continuous N₂ flow in order to remove the oxygen gas from the synthesis atmosphere. The decomposition of DCDA and glucose at high temperature created strongly reducing, nitrogen-rich carbon compounds, which reduced RuCl₃ to Ru QDs. It is known that between 350 and 750 °C, a layered g-C₃N₄ intermediate could be formed from DCDA, and both the Ru species and carbon intermediates can be confined in its interlayer gaps.⁴⁸–⁵¹ This g-C₃N₄ template was subjected to complete thermolysis up to around 750 °C, and further heating to 1000 °C eliminated the template to produce graphene layers with Ru QDs formed in situ. While the bare NG monolith contained 13.56 at% nitrogen (Fig. S1†), the Ru QD/NG had only 6.45 at% nitrogen doping, likely due to the presence of the Ru QDs. The Ru percentage can be easily controlled by changing the content of the metal salt in the precursor. The as-synthesized graphene had a mostly layered structure with subunits including the Ru QDs.

In the next step, the Ru QD/NG composite was treated with an acid to introduce holes into the basal planes of the graphene monolith. The wet chemical method using combined ultrasonic vibration and acid oxidation is depicted in Scheme 1, step 2. A few recent studies have used a mild acid treatment to fine tune the creation of in-plane holes through graphene sheets.²¹,⁴³–⁴⁶ However, in these studies the high content of oxygen-containing functional groups in graphene oxide greatly facilitated hole creation.²¹,⁴³–⁴⁶ Since our NG monolith had a much lower content of oxygen functional groups, we instead employed concentrated nitric acid (HNO₃, 60%) in addition to continuous high-power bath sonication at 70 °C to fabricate holes on the graphene sheets in the Ru QD/NG composite. The optimum sonication duration was found to be 5 h. Finally, the acid-treated samples were heat-treated under a high purity Ar atmosphere at 900 °C in order to stabilize the graphitic domains and diminish the content of oxygen-containing functional groups. The released oxygen reacted with nearby in-plane carbons with vacancy defects (holes) to produce CO and/or CO₂ gases,⁴⁷–⁴⁹ and this further enlarged the holes.

2. Morphology and structure

Systematic experiments were conducted to characterize the produced Ru QD/NHG composite. For SEM analysis, it turned out that the spatial resolution of conventional reflective techniques is inadequate to reveal the anchored Ru QDs as well as the in-plane holes (Fig. 1a and b). However, the low-kV transmission electron beam in SEM offers a sufficient spatial resolution to observe the holes and Ru QDs, as well as graphene wrinkles. The obtained low- and high-magnification color-coded images are presented in Fig. 1c and d, respectively. The wrinkled and crumpled planes (pink colored in Fig. 1d) suggest that the graphene monolith is transparent and flexible. Due to their electron transparency, graphene single layers appear as light pink/green as indicated by three squares A, B and C in this figure. Uniformly distributed Ru QDs and holes appear as obvious fine spots in dark pink and light green, respectively. This novel SEM imaging technique can quickly identify monolayers and flat areas, as they exhibit a contrast with the wrinkled areas or holes. Unlike the high energy beam used in transmission electron microscopy (TEM), the low energy of the transmission beam in the current SEM configuration provides damage-free observations.⁵⁹ Consequently, observations could be carried out for extended time periods to locate the area of interest for high resolution TEM (HRTEM) analysis.

The high-angle annular dark-field imaging-scanning transmission electron microscopy (HAADF-STEM) image of the composite (Fig. 1e) and its corresponding HRTEM micrograph (Fig. 1e, inset on the top right) reveal the presence of graphene with one or a few layers, and anchored Ru QDs of a clear polycrystalline nature. The HAADF-STEM image also showed no apparent agglomeration of the as-formed Ru QDs, even at the high synthesis temperature of 1000 °C, suggesting that the composite had a very strong resistance to grain coarsening. The particle size distribution of the Ru QDs determined from the HRTEM analysis is presented in the top left inset of Fig. 1e. Most particles fall within the size range of 1–5 nm, with an average size of 2.63 nm. The chemical mappings by means of energy-dispersive spectroscopy (EDS) again confirmed that the Ru QDs are uniformly distributed on the NG monolith, as elucidated in Fig. S2.† Fig. 1g and h are the HRTEM images of the acid-treated and the subsequent Ar-treated Ru QD/NHG composite, respectively. Holes with the size range of 2–6 nm were seen in the acid-treated sample, and they were significantly enlarged by annealing in Ar. The irregular hole shapes probably correlate with the shapes of the intrinsic oxidation-vulnerable areas on the initial NG monolith. The HRTEM images also reveal continuous, flexible, and wrinkled sheets after acid treatment, and a uniform graphene framework with in-plane holes and Ru QDs. Very small graphene domains, a few nanometers in size, were also observed.⁵⁰,⁵¹ The polycrystalline nature of the Ru QDs and their elemental conditions after severe acid treatment were further verified by means of the selected area electron diffraction (SAED) pattern (inset of Fig. 1g). The Ru QDs retained their small sizes after annealing at up to 900 °C, thereby confirming their strong bonding to the graphene structure. As depicted in Fig. S3,† the average Ru QD size after Ar treatment was around 4.27 nm, comparable to that of the as-synthesized material. Atomic force microscopy (AFM) was also utilized to accurately measure the size and thickness of the Ru QD/NG and Ru QD/NHG composite sheets. It was found that the size of the sheets varied from 5 µm to around 20 µm in Ru QD/NG. However, further bath sonication plus acid treatment diminished the sheet size to less than 10 µm, and we also observed a few sheets as small as hundreds of nanometers in size. Fig. S4† presents a typical AFM image of the final Ar-treated Ru QD/NHG composite, along with the height profile along the selected line. Larger holes irregular in shape and size could be clearly seen over the whole graphene sheet. The sheet thickness was generally below 2 nm. Assuming that each graphene layer is about 1 nm thick,⁴⁶,⁵² the number of graphene layers is then estimated as one or two.

The presence of completely crystalline Ru QDs anchored through the NG monolith was also revealed by X-ray diffraction (XRD) analysis. The pattern in Fig. 2a is completely consistent with JCPDS card number 00-006-0663 (hexagonal Ru). The
Fig. 1  (a, b) Typical SEM images of Ru QD/NG, and (c, d) color contrast transmission electron beam images of Ar-treated Ru QD/NHG in SEM at low and high magnifications. A low electron beam energy of 5 kV and a beam current of 800 pA were selected to avoid beam damage. In (d), the large holes in the graphene sheets are marked, and uniformly distributed Ru QDs appear as small dark pink spots. Graphene single layers are indicated in a light pink/green color, with three selected square areas A, B, and C. (e) HAADF-STEM image of Ru QD/NG. Top right inset: the corresponding bright field image; top left inset: size distribution of Ru QDs. (f) HRTEM image of Ru QD/NG, clearly showing its polycrystalline nature, as well as both the monolayer and the few-layer structure of graphene with small domains. (g) HRTEM image of acid-treated Ru QD/NHG, showing the uniform distribution of in-plane holes through the graphene monolith. Inset: the SAED pattern of Ru QDs, confirming the polycrystalline characteristics of Ru after the severe acid treatment. (h) HRTEM image of Ar-treated Ru QD/NHG with larger holes.
The strongest peak appeared at $2\theta = 43.92^\circ$, suggesting that the Ru QDs were anchored into the graphene sheets in the dominant (101)-oriented plane. The Ru species remained crystalline even after severe acid treatment and were not oxidized to RuO$_2$. In the Ar-treated sample, the Ru peaks were more intense than those of the as-synthesized and acid-treated samples, partially on account of the increased grain size after heating. The broad hump in the range of $2\theta \equiv 25$–26$^\circ$ in all three samples is attributed to the graphene (002) peak, indicating the co-existence of crystalline graphitic and disordered graphene structures. The broad XRD peaks of the synthesized Ru QD/NG showed only restricted stacking along the c-axis. On the basis of the broad (002) peak, the lamellar stacking distance of graphene was estimated to be 0.334 nm, which is smaller than that of ideal graphite (0.340 nm) due to the nitrogen doping through the graphene planes. The (002) peak shifted slightly to a lower angle after acid treatment. This is attributed to the expansion of the interlayer spacing from 0.334 to 0.357 nm, a result of the reduced van der Waals attraction between the NHG layers.

The Raman spectra confirm the strong graphitization in all three samples, as highlighted by the intensive G band in 1578–1595 cm$^{-1}$ (Fig. 2b). This is consistent with the previous results for NG monoliths. The samples also displayed a broad D-band centered at around 1348–1366 cm$^{-1}$, reflecting the disordered edges and boundaries of the graphene domains, which are in agreement with the HRTEM observations. Although the Ru QD/NHG composite after severe acid treatment contained graphitic structures, the degree of graphitization was

![Fig. 2](https://example.com/fig2)

(a) XRD patterns, (b) Raman spectra, (c) EELS measurements, and (d–f) high-resolution C 1s XPS spectrum of (1) Ru QD/NG, (2) acid-treated Ru QD/NHG, and (3) Ar-treated Ru QD/NHG. (g) N$_2$ adsorption/desorption isotherm of Ru QD/NG and Ar-treated Ru QD/NHG, clearly confirming the presence of large mesopores in the latter. (h) The BJH pore distribution and (i) cumulative pore volume for N$_2$ adsorption in the same materials as in (g).
sloightly diminished in comparison with that of the Ru QD/NG on account of the defects and oxygen-containing functional groups. Accordingly, the D to G intensity ratios \(I_D/I_G\) were 1.01 and 1.08 for the as-synthesized Ru QD/NG and the acid-treated Ru QD/NHG, respectively. Interestingly, the Raman spectrum profile of the Ar-treated Ru QD/NHG is almost identical to that of the acid-treated one, but its \(I_D/I_G\) ratio was slightly reduced to 1.07. The annealing process increased the stability of sp\(^2\)-type carbons in the graphitic region of the graphene sheets. Since these carbons contribute to the G peak, the \(I_D/I_G\) ratio is lowered.

The sp\(^2\) bonding in the three graphene counterparts after each fabrication step was confirmed by electron energy loss spectroscopy (EELS) of the carbon K near-edge structure (Fig. 2c). The sharp edge at around 286 eV corresponds to the 1s → \(\pi^*\) transition and is only detected in carbon materials with sp\(^2\) bonding.\(^{28,29}\) There is another intense peak at around 293 eV, which is attributed to 1s → \(\sigma^*\) transition in the graphene structure and has been observed in all carbon allotropes.\(^{29}\) The \(\pi^*\) peak at 286 eV is not as sharp as that in graphite (which is considered as 100% sp\(^2\) carbon), as shown in Fig. 2c and S5.\(^\dagger\) However, the ratio between the integrated intensities of the \(\pi^*\) edge and \(\sigma^*\) edge in the Ru QD/NG, i.e., the fraction of sp\(^2\) graphene domains as discussed in detail in the ESI,\(^\dagger\) is 90% the value of graphite with an equivalent thickness. This percentage decreased to 86% after acid treatment for 5 h. The percentage increased to 91% after subsequent Ar treatment for 1 h at 900 °C, demonstrating that most of the graphene-like regions contained sp\(^2\) domains. It should also be mentioned that this percentage may be underestimated, since the abundant small graphene domains can provide more edge defects to the electron beam and diminish the calculated fraction of sp\(^2\) carbon.

X-ray photoelectron spectroscopy (XPS) measurements of the carbon (C 1s), nitrogen (N 1s) and Ru (Ru 3d) regions were conducted to investigate the binding energies in the electronic structures, and confirm the presence of structural defects and oxygen-containing groups. The spectra are shown in Fig. 2d–f, and S6.\(^\dagger\) The sharp and asymmetrical C 1s peak (Fig. 2d–f) at 284.6 eV confirms the significant contribution of sp\(^2\)-type carbon atoms after various steps. Five different peaks centered at 284.6, 285.7, 286, 287.8, and 289 eV are attributed to the sp\(^2\) type carbon (C=C/C=C), C=N, epoxy/alcoxy (C=O), carbonyl (C=O), and carboxylate (O=C=O) groups, respectively.\(^{21,46}\) In all three samples, the Ru 3d region had two strong peaks: Ru 3d5 at 280.0 eV and Ru 3d3 at 284.1 eV.\(^{46}\) One oxidation state of Ru\(^{4+}\) (RuO\(_2\)) was also seen at 280.7 and 284.7 eV, consistent with RuO\(_2\) 3d5 and RuO\(_2\) 3d3, respectively, and these peaks were weak in the as-synthesized Ru QD/NG sample. After the acid treatment to form in-plane holes, the intensity of Ru\(^{4+}\) 3d5 and Ru\(^{4+}\) 3d3 peaks increased. This change is very clear in the RuO\(_2\) 3d3 peak at 284.7 eV. Meanwhile, the contributions of Ru 3d5 and Ru 3d3 peaks decreased, and the Ru 3d5 peak became broader than that of the Ru QD/NG sample. Following the acid treatment, all the intensities of oxygen-containing functional groups in C 1s peaks also increased, and the peak intensity of C=O=C/C=C bonds was diminished. Finally, the C=O functionalities almost vanished after Ar treatment, and the contribution from the C=O and O=C=O groups was reduced.

The N\(_2\) adsorption–desorption isotherms at 77 K, the pore size distributions, and the pore volume of the Ru QD/NG and Ru/NHG samples after acid treatment and subsequent Ar annealing are presented in Fig. 2g–i, respectively. The pore size distribution was obtained from the isotherm adsorption branches based on the Barrett–Joyner–Halenda (BJH) model. All the adsorption/desorption isotherms have very similar characteristic type IV shapes according to the IUPAC classification, with an H\(_2\) hysteresis loop.\(^{61}\) The hysteresis, common in the high pressure region, suggests the presence of slit-shaped capillaries with very wide bodies and narrow short necks, and meso- or micro pores from the aggregation of plate-shaped particles. The hysteresis in the Ru QD/NG sample was almost negligible, while the two treated Ru QD/NHG samples displayed more significant hysteresis. The size of the hysteresis loop is generally related to the mesopore volume and the connectivity of the pores. In all three samples, the significant N\(_2\) adsorption at low relative pressures indicates the existence of micro pores. The average pore size, pore volume and surface area of the three samples are presented in Table S1.\(^\dagger\) The specific surface area of acid-treated Ru/NHG is less than that of the Ru QD/NG. Although the creation of in-plane holes over the whole graphene sheets could increase their surface area, as already demonstrated by the AFM results (Fig. S4\(\dagger\), the high acoustic pressure produced by the high-power, prolonged bath sonication provides too many frictional forces in the cavitation bubbles, thereby disrupting/breaking the graphene framework on the carbonaceous surface. The result is smaller graphene sheets with a smaller specific surface area. The Ar treatment increased the specific surface area slightly to 397.8 m\(^2\) g\(^{-1}\). As illustrated in Fig. 2h, the measured pore size distribution of the Ru QD/NG showed an average pore diameter of 3.8 nm, while that of the Ar-treated Ru/NHG ranged from 0 to 160 nm. Two pore distribution peaks at 19 and 35 nm in the Ar-treated Ru/NHG counterpart are due to the creation of larger holes through the graphene monolith, demonstrating the presence of mesopores in this sample. In Fig. 2i, the pore volume was 2.675 cm\(^3\) g\(^{-1}\) for Ru QD/NG and was reduced to 1.487 cm\(^3\) g\(^{-1}\) by the acid treatment, while Ar annealing produced no change.

3. Hole creation mechanisms

Previous research suggests that oxygen functionalities are the main factor for the creation of in-plane holes through graphene oxide sheets. And, further chemical or thermal reduction lowered the content of oxygen functionalities in the resulting holey reduced graphene oxide for various applications.\(^{21,43–46}\) In our work, a similar trend was observed after acid treatment for the N-doped graphene. However, the C–O, C=O and O=C=O groups were only effective for creating micro pores smaller than 1–2 nm, as indicated by the arrows in Fig. S7a.\(^\dagger\) A closer examination shows a holey structure with small micro pores (Fig. S7b\(\dagger\)). These results suggest that the Ru QDs have a pronounced effect on the creation of large in-plane holes. The Ru QDs can diminish the reaction energy barrier for the creation of large holes, either by acting as an efficient catalyst or by
the strain-induced sp²–sp³ bond character variations. First, the catalytic oxidation of NG by Ru QDs during the acid treatment (step 2) most likely started from the above-mentioned surface defects. Oxygen molecules in the environment assisted in creating large in-plane holes through the graphene monolith, by removing the carbon atoms near the Ru QDs. In addition, the presence of Ru QDs on the graphene monolith generated highly localized compressive strain, which further enhanced the chemical reactivity and reduced the activation energy barrier for the oxidation of C≡C bonds.

Fig. 3a compares the Raman G band position in the as-synthesized NG (without Ru) and Ru QD/NG followed by acid treatment of various durations. The frequency conspicuously increased from 1548.85 ± 2 to 1587.51 ± 2 cm⁻¹ after the addition of Ru QDs, clearly confirming that larger local compressive strain was created in the latter. The bath sonication plus acid treatment had the same effect, as the frequency of the G band after 5 h of acid treatment increased from 1548.85 ± 2 and 1587.51 ± 2 cm⁻¹ to 1566.35 ± 2 and 1595.12 ± 3 cm⁻¹ for NHG and Ru QD/NHG, respectively. Further acid washing of the Ru QD/NHG, however, had no significant effect on the G band position, as the frequencies after 7 and 12 h of acid washing were almost identical (1596.49 ± 3 and 1596.38 ± 3 cm⁻¹, respectively). This trend suggests that after 5 h of treatment the strain is relieved by the creation of in-plane holes through graphene sheets. This microscopic change is demonstrated by the full width at half maximum (FWHM) of the G band, as illustrated in Fig. 3b. This band broadened during the first 5 hours of acid washing, which supports the existence of mechanical strain in Ru QD/NG. Beyond 5 h, the FWHM decreased instead, indicating that the introduction of holes by Ru QDs gradually released the compressive strain in the graphene monolith. The \( \frac{I_D}{I_G} \) ratio also continued to change during acid treatment, confirming the increased content of oxygen functionalities, which reduced the content of sp²-type carbon in the Ru QD/NHG sample as the acid treatment time was increased. Increased compressive strain is another cause of the reduction of sp² carbons, since it facilitates the sp² → sp³ bonding transformation which leads to a higher integrated intensity of the D band.

Fig. 3 (a) Phonon frequency of the Raman G mode in the bare NHG and Ru QD/NHG composites as a function of acid treatment time. (b) FWHM of the G mode, the \( \frac{I_D}{I_G} \) ratio, and the sp² content derived from EELS measurements in Ru QD/NHG as a function of acid treatment time. (c) Phonon frequency of the G mode, its FWHM variation, and sp² content of Ar-treated Ru QD/NHG as a function of annealing time. Dozens of random points on each sample were measured in order to examine the correlation between strain induced by the Ru QDs and G band variations. (d) \(^{13}\)C MAS-NMR spectra of Ru QD/NHG after Ar treatment for 1 and 2 h at 900 °C. The content of oxygen functional groups obviously decreased with the annealing time.
Finally, during the Ar annealing at 900 °C (step 3), the difference in thermal expansion coefficients between the graphene structure and Ru QDs created additional compressive strain and led to enhanced chemical reactivity and the oxidation of C=C bonds. These local defective areas offer sp³-like reactive positions. These positions can easily adsorb O₂ and decompose carbon into CO or CO₂ gases, thereby enlarging the localized catalytic perforations.⁷⁰–⁷² As shown in Fig. 3c, the frequency of the G band decreased continuously with the annealing time, reaching a constant value after 20 min. The sharpening of the G band suggests lessened mechanical strain. Besides, the calculated content of sp² carbon rapidly increased to 95 ± 1% after 5 min of annealing, and stayed constant up to 20 min. Beyond 20 min, however, the sp² bonds started to break, which increased the fraction of larger in-plane holes.

The evolution of the oxygen-containing functional groups during heat treatment was also evaluated by solid state magic-angle-spinning nuclear magnetic resonance (MAS-NMR) spectroscopy. As illustrated in Fig. 3d, the major peaks at ~117 and ~125 ppm observed in both 1- and 2 h Ar-treated Ru QD/NHG samples are attributed to sp² carbon.⁷³ The upward change in the ¹³C shift for the sp³ species with the annealing time corresponds to the diminished sp² network and is consistent with the EELS results (Fig. 3e). The peak of the 1 h Ar-treated sample at ~160 ppm which vanished after 2 h Ar treatment is assigned to ¹³C=O.⁷⁴ These results are in excellent agreement with the above discussions: increasing the annealing time creates larger holes.

We have performed several control experiments to support our hypothesis about the catalytic role of Ru QDs. The result of removing Ru (i.e., bare N-doped graphene) presented above confirms that the Ru QDs are crucial for the fabrication of well-designed holey graphene (Fig. S7 and S8†). As mentioned earlier, the decomposition of the g-C₃N₄ intermediate product at around 750 °C can also produce some small holes over the graphene sheets, principally by the elimination of inherent C–N structures. While Fig. S8† demonstrates that the acid treatment further enhanced the content of pores in the NHG, there is no considerable change in the hole size between the NG and NHG samples. Additionally, the hysteresis in the high-pressure region of the isotherm is much smaller for NHG than for the Ru QD/NHG composites, further demonstrating the crucial role of Ru QDs in the creation of large in-plane holes.

We also changed the RuCl₃ salt to CoCl₂, NiCl₂, FeCl₃, AgCl, and PdCl₂ to check the catalytic effect of other metals in creating large mesopores. The corresponding M/NNG (M = Co, Ni, Fe, Pd, Ag) composites were all successfully synthesized according to step 1 in Scheme 1, and Fig. S9† presents the XRD patterns and XPS measurements of these as-synthesized composites. However, Co, Ni, and Fe clearly had a very low catalytic effect on the hole creation compared to Ru under the same acid treatment conditions, as the resulting holes were barely visible. Pd and Ag had relatively higher catalytic effects but were still not comparable to that of the Ru QDs, as neither reduced the charge polarization when tested in Li–O₂ batteries (Fig. S10†). Thus, we believe that the Ru QDs have the highest ability to reduce the activation energy barrier for the perforation, while the other metal nanoparticles require more chemical/thermal energy to introduce holes through the graphene sheets.

4. Electrochemical characterization in Li–O₂ batteries

As a proof of concept, the synthesized samples were utilized as cathode materials in Li–O₂ batteries, and the results are presented in Fig. 4. The intrinsically non-conductive Li₂O₂ is well-known to decompose to create large polarization during the charge process. The bare NHG electrode had high polarization and poor cyclability, as shown in Fig. 4a. The poor cyclability is explained by the electrolyte deterioration and carbon contamination induced by the high overpotential.⁷⁵,⁷⁶ Hence, an appropriate catalyst is indispensable for decreasing the charge polarization and enhancing the charge efficiency of the Li–O₂ battery. Considering that the formed discharge product (Li₂O₂) is a solid, the catalyst particles should be uniformly distributed on the graphene monolith for maximum catalytic activity. In this respect, the synthesized graphene with the anchored Ru QD catalyst has the ideal structure. Furthermore, Ru and RuO₂ are already known as promising OER catalysts for Li–O₂ batteries.¹⁴,³³,³⁴

The electrochemical properties of the bare NHG and Ru QD/NHG, as well as the acid-treated and Ar-treated Ru QD/NHG electrodes are compared and presented in Fig. 4b. Compared to the bare NHG, the Ru QDs are shown to effectively decrease the charge polarization. The addition of holes through the graphene monolith after acid treatment further reduces the charge polarization (red line), as highlighted by the two areas outlined by the dotted green lines. The initial oxidation range below 3.6 V is derived from the oxidation of the surface Li₂O₂·O₂ product, and that above 3.6 V is from the oxidation of crystalline Li₂O₂.⁷⁷,⁷⁸ Both processes were well activated with the addition of in-plane holes, because these holes facilitate the movement of oxygen and Li ions. As mentioned in the Introduction section, while Li–O₂ batteries require an especially porous electrode structure for the transport of reaction products (Li ions and O₂), the 2D morphology of graphene unfortunately does not provide it. Furthermore, during the slurry casting and heating steps of electrode preparation, graphene sheets are easily stacked and stuck together to form a denser electrode, further hindering the diffusion of reaction products. In this respect, additional spaces and holes are of great importance for providing sufficient diffusion pathways of oxygen and Li ions. We believe that the acid-treated Ru QD/NHG electrode satisfies these requirements for an efficient air electrode, by virtue of the additional decrease in charge polarization. The 1 h Ar-treated Ru QD/NHG electrode (orange line) also has high polarization in the initial oxidation range, most likely due to the reduced oxygen functional groups on its surface by Ar treatment, as well as the reduced integrity of graphitic carbon. The oxygen functional groups on the surface catalyze the formation of defective Li₂O₂,³³,⁷⁹ causing decreased polarization in the initial oxidation range below 3.6 V. For this purpose, some amount of functional groups on the surface is preferable. Therefore, in this study the acid-treated Ru QD/NHG electrode, not the Ar-treated one, appears to be the most efficient for lowering charge polarization in Li–O₂ batteries.
It is notable that the lowered initial charge polarization of the acid-treated Ru QD/NHG composite was sustained during subsequent cycles (Fig. 4c). The cyclability was relatively poor because the TEGDME electrolyte is not stable with Li metal. However, switching to an amide-based electrolyte (LiNO₃ in N,N-dimethylacetamide, DMA) which has been reported to be relatively stable with Li metal, more than 20 stable cycles could be achieved (Fig. S11–S13†). This enhancement originates from the high solvation ability of the electrolyte, which induces the solution-mediated growth mechanism instead of the surface-based mechanism during the discharge process. Although this improved cyclability still falls short of practical applications, it is clear that the combination of the Ru QDs and the in-plane holes effectively suppressed the charge polarization (Table S2†). However, more work is needed to further enhance the cyclability of the acid-treated Ru QD/NHG composite.

Cyclic voltammetry (CV) was further applied to examine the catalytic activity of the acid-treated Ru QD/NHG counterpart toward the OER in the potential window of 2.0–4.5 V (vs. Li/Li⁺). Fig. S14† compares the converted dQ/dV charge curve with CV results. The CV tests were conducted using a three-electrode system, in order to exclude other factors such as the Li metal or separator that could disturb the charge curve. In the three-electrode system, the working electrode was the acid-treated Ru QD/NHG sample, and the counter electrode was Pt with Ag/Ag⁺ in acetonitrile solution as the reference electrode. The dQ/dV curve showed three dominant peaks during the reversible anodic scan, which were related to the OER, and highlighted with dashed-line squares (Fig. S14b†), and are well matched with those in CV curves (Fig. S14d†). These results clearly demonstrated the effect of acid-treated Ru QD/NHG counterpart on the decomposition of Li₂O₂ during the charging of the Li–O₂ cell.

The inner reaction of the acid-treated Ru QD/NHG electrode was analyzed using the galvanostatic intermittent titration technique (GITT). In Fig. 4d, the relaxation potential at each step is almost close to the theoretical formation voltage of Li₂O₂ (2.96 V), implying the reversible formation and decomposition of Li₂O₂. The time vs. voltage graph (Fig. 4e) demonstrates that the relaxation time is fully enough. However, at the end of charge the relaxation potential still could not reach 2.96 V, indicating that some side reactions occurred. In carbon-based electrode materials, some of the carbon always undergoes side reactions with Li₂O₂ to form Li₂CO₃. Successful strategies to inhibit or at least control such side reactions would further enhance the cyclability of Li–O₂ batteries. Nevertheless, the unique structure presented here (graphene with well-controlled holes) represents an innovative step for enhancing the energy efficiency of Li–O₂ batteries.

To further evaluate the reaction products in the Li–O₂ batteries with the acid-treated Ru QD/NHG electrode, we disassembled the batteries at the end of the first full discharge to 2.0 V and after final cycling. XPS analysis, SEM and TEM observations, and SAED measurements were conducted to identify the discharge products on the electrodes. First, SEM was utilized to directly observe the electrodes after full discharge in the two electrolytes of TEGDME and DMA. The
electrodes were washed with acetonitrile solvent to eliminate residual electrolytes and salts, and dried in a vacuum oven overnight. As shown in Fig. S15,† the SEM images clearly show that the electrodes were fully covered with solid toroidal Li2O2 particles. Therefore, Li2O2 was formed in both electrolyte systems as a final discharge product, which is thoroughly consistent with previous reports.4,5 The toroidal Li2O2 particles formed with DMA were larger than those formed with TEGDME due to the high solvation ability of the former, which is also in good accordance with a previous report using the same electrolyte.6 The formation of Li2O2 in the discharge process was further monitored by using the TEM micrograph and SAED pattern (Fig. S16†), which elucidate the coexistence of Ru QDs and Li2O2 nanoflakes on the holey graphene monolith. Typical electron diffraction spots corresponding to (100), (103), and (112) of Li2O2 were found in the SAED pattern. Further, high-resolution Li 1s XPS spectra confirmed that the major phase in the discharge product was Li2O2 with a binding energy of 54.8 eV (Fig. S17†).

Additionally, we investigated the oxygen evolution during charging using in situ gas analysis (differential electrochemical mass spectroscopy, DEMS) to confirm the formation of Li2O2 during discharging. Fig. S18a† shows the charge profile of the acid-treated Ru QD/NHG electrode, after first discharge to 0.5 mA h. Then, the electrode was transferred to a DEMS cell to measure the gas evolution during charging, and the amounts of oxygen and carbon dioxide gases as functions of time are presented in Fig. S18b.† The evolution of the oxygen gas at the beginning of the charge clearly demonstrates the decomposition of Li2O2. However, carbon dioxide, which is supposed to be formed from the Li2CO3 by-product, was also detected in the high voltage ranges during charging. A small amount of Li2CO3 was already confirmed by the Li 1s XPS spectra after discharge (Fig. S17†). Li2CO3 and other interfering phases such as LiOH·H2O were also found in the samples after full cycling, as presented in Fig. S19 and S20.† The accumulated by-products, which do not decompose well during charging and therefore are gradually stacked on the electrode surface, are the major cause of the cycle decay.7 According, reducing the formation of these by-products during discharging would be most important to further increase the cyclability of Li–O2 batteries.

Conclusions

In summary, we developed a facile, low-cost, and scalable approach to fabricate highly integrated Ru QDs uniformly anchored through the plane of NHG and used this composite material as a promising OER electrocatalyst for Li–O2 batteries for reducing charge overpotentials. The underlying mechanisms of hole creation during acid and subsequent heat treatments were investigated in detail. The Ru QDs serve two purposes: as an effective catalyst to decrease the activation energy barrier for the oxidation of carbon atoms, and for the introduction of small and large in-plane holes in the graphene plane. The mechanical strain due to the presence of these nanostructures also greatly facilitates the creation of holes. The method of acid treatment is scalable and can be applied to mass produce holey graphene without using expensive equipment or complicated steps. The electrochemical Li–O2 performance especially the cycle stability and the optimal design of the holes should be further improved by optimizing the other components and catalysts, in order to achieve a long lifetime for energy-related applications. This report points to a new direction for the continued optimization of holey graphene in this type of battery. In addition, we successfully applied a novel transmission method in SEM to directly observe the holes with color contrast in a large scale for the first time. This method will certainly provide critical insights for future research.

Experimental

1. Materials

DCDA, v(+)glucose, CoCl2, AgCl, PdCl2, FeCl3, NiCl2, and RuCl3 all from Sigma-Aldrich, and HNO3 (60%, Samchun, extra pure) were used as received without further purification.

2. Fabrication of Ru QD/NHG nanocomposites

DCDA, v(+)glucose, and a metal chloride at a mass ratio of 40.0 : 1.0 : 0.3 were homogeneously mixed, added to 200 mL deionized water in a beaker, and heated to 90 °C with continuous stirring for water evaporation. The resulting white powder was then transferred into an alumina crucible, heated at a constant rate of 3.3 °C min–1 to 1000 °C under flowing nitrogen gas, maintained at that temperature for 1 h, and subsequently cooled in the furnace. The as-obtained Ru QD/NG composite was then sonicated in 60% HNO3 at 70 °C in a sonication bath for different times up to 12 h. Finally, the acid-treated Ru QD/NHG sample was heat-treated under a high purity Ar atmosphere at 900 °C for various times (5 min to 2 h) to produce the Ar-treated Ru QD/NHG composite.

3. Chemical and microstructural characterization

Powder XRD patterns were recorded on a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 0.154059 nm) in an argon atmosphere. XPS measurements were conducted on an ESCA 2000 spectrometer (VG Microtech) using monochromated Al Kα radiation. The main C 1s peak was calibrated to carbon black (284.6 eV) for the high-resolution scans. The spectral peaks were deconvoluted using Lorentzian line shapes and Shirley background subtractions. Raman spectra were acquired on a Jobin-Yvon LabRAM HR instrument with an Ar laser source of 532 nm in a macroscopic configuration. Lorentzian fitting was carried out to obtain the exact positions and widths of the D and G bands in the Raman shift. The results presented in Fig. 3 are the averages of 15–50 individual spectra taken from different locations on the samples, together with the error bars. The increased errors are thus attributed to the increasing inhomogeneity of the results. Solid-state 13C MAS-NMR spectra were recorded using a Bruker Avance II 500 spectrometer (125.7 MHz) equipped with a 4 mm diameter solid-state probe head. ZrO2 rotors were used with approximately 50 mg of Ru QD/NHG samples rotating at a 10 kHz speed. Elemental analysis (EA) (Thermo EA1112, Thermo Electron Corp.) was performed to
determine the chemical composition of the samples. The BET surface area, pore size and volume distribution were acquired by using a Quantachrome® ASiQwin™ system with nitrogen adsorption at 77 K using the BJH method. Field emission SEM (FESEM) results were obtained on a JEOL-7800F instrument. TEM analyses were carried out with a JEOL (JEM-ARM 200F) spherical aberration correction scanning transmission electron microscope (Cs-corrected-STEM) operated at an acceleration voltage of 200 kV, coupled with EDS analysis. EELS measurements were performed by using an FEI Titan™ HRTEM with an acceleration voltage of 80–300 kV. The thickness and size of the sheets in the composites were measured with an AFM instrument (Nanowizard I, JPK).

Furthermore, a novel method using an electron beam with a low accelerating voltage (5 kV, 800 pA) was utilized in a Zeiss Merlin FESEM instrument to image the graphene layers in the transmission mode. An Optimus horizontal TKD unit with an Argus™ detector (Bruker) was used. This detector, composed of three separate diodes and a phosphorescent screen, is situated beneath the graphene sample. The working and detector distances were 6 mm and 10 mm, respectively. The diodes convert the intensity of the transmission beam at each scan point to RGB values, which are then constructed into color-coded images. Sufficient color contrast was produced by the Argus™ detector to enable hole detection in highly transparent graphene monolayers. Since green represents the lowest number of received electrons, the holes on the graphene appear in green. The curved or folded surfaces appear pink due to more significant electron scattering, and graphene single layers appear as light pink to green due to their electron transparency. The Ru QDs can also be easily seen as dark pink spots. More details regarding the sample and the detector configuration can be found in a previous study.19

4. Electrochemical characterization

The air cathode was prepared with the graphene material using a wet casting process. The synthesized graphene and polytetrafluoroethylene (PTFE, 60 wt% dispersion in H2O) as a binder were mixed at a weight ratio of 8:2, and dispersed in isopropanol solution. The slurry was cast on a Ni mesh current collector (Nilaco Corp., 1/2 inch diameter) and the residual solvent was dried overnight at 60 °C. The prepared electrode was assembled with a Li metal anode and a glass fiber separator (GE/D microfiber filter paper, Whatman) into a Swagelok-type cell. All the cells were assembled in a glovebox with an Ar atmosphere. The electrolyte was 1 M lithium bis(trifluoromethane) sulfonamide (LiTFSI) in tetraethylene glycol dimethylether (TEGDME). A potenti-galvanostat (WBCS 3000, WonA Tech, Korea) was used to measure the electrochemical properties of the Li–O2 cells. Each cell was pressurized with pure oxygen to 770 Torr using an automated throttle valve, and tested at different current rates of 100, 300, 500, and 700 mA g−1 between 2.0 and 4.5 V (vs. Li/Li+). The in situ DEMS system was composed of a mass spectrometer (MS; HPR-20, Hiden Analytical, U.K.) and a potenti-galvanostat. The cells were first discharged and then transferred to the DEMS system to detect the gas evolution during charging. Prior to charging, the DEMS cell was fully relaxed in an Ar gas flow (10 cm³ min⁻¹) for 10 h. The MS was calibrated for O₂, CO₂, and Ar using a mixed gas of 0.22% O₂, 0.20% CO₂, and 99.58% Ar (v/v). For CV tests in the three-electrode system, the working electrode was the acid-treated Ru QD/NHG sample, Pt was the counter electrode, and Ag/Ag⁺ in acetonitrile solution was the reference electrode.

Author contributions

MNS, HDL, SFKB, and KBK conceived the original idea. MNS synthesized and characterized the samples, participated in all other steps in this work, and wrote the manuscript. SHS, HKK, MSK, SWL, and KCR participated in the structural analyses. HDL and YK performed the electrochemical tests. MNS, MA, HUG, and DIK applied the novel SEM imaging technique. SFKB, KK, and KBK supervised the work and commented on the manuscript. All the authors discussed the results and have given approval to its current, final edition.

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