Ultrasonic-assisted hydrothermal synthesis of cobalt oxide/nitrogen-doped graphene oxide hybrid as oxygen reduction reaction catalyst for Al-air battery

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**ABSTRACT**

A persistent ultrasound-assisted hydrothermal method has been developed to prepare cobalt oxide incorporated nitrogen-doped graphene (Co$_3$O$_4$/N-GO) hybrids. The electrochemical behaviors and catalytic activity of the prepared hybrids have been systematically investigated as cathode materials for Al-air battery. The results show that ultrasonication can promote the yield ratio of Co$_3$O$_4$ from 63.1% to 70.6%. The prepared Co$_3$O$_4$/N-GO hybrid with ultrasonication exhibits better ORR activity over that without ultrasonication. The assembled Al-air battery using the ultrasonicated Co$_3$O$_4$/N-GO hybrid exhibited an average working voltage of 1.02 V in 4 M KOH electrolyte at 60 mA cm$^{-2}$, approximately 60 mV higher than that using hybrid without ultrasonication. This should be attributed to large number density of fine Co$_3$O$_4$ particles growing on the dispersed GO sheets under the persistent ultrasonication. The related ultrasonic mechanism has been discussed in details.

1. Introduction

Storage and conversion of renewable resources are promising to meet the most urgent goals for clean energy production and environmental remediation [1,2]. Aluminum-air battery is one of the promising and efficient energy storage and supply systems, delivering renewable energy with metals and the inexhaustible O$_2$ in air [3–5]. However, there are many technical and scientific issues that hinder the large-scale development and application of Al-air batteries.

The oxygen reduction reaction (ORR) activity is one of the most important concerns for the Al-air battery with high energy efficiency [5]. Precious metal catalysts (e.g. Pt, Au, Ag) have superior ORR catalytic performance [6,7]. However, their scarcity, high cost and poor tolerance limit the large-scale application. Thus, it is crucial to develop low-cost and efficient ORR catalysts for Al-air battery. Transition metal oxides have been reported to be cheap and effective ORR catalysts [8,9], and among them, Co$_3$O$_4$ has attracted great interests [10–12]. However, careful adjustment should be done to promote the electrical conductivity and stability of the Co$_3$O$_4$-containing ORR catalysts.

One of the effective strategies is using highly stable and conductive catalyst carriers or supporters, for instance, the widely employed graphene oxide (GO) [13–16]. Furthermore, additional nitrogen doping could greatly increase the electron mobility and introduce chemically active sites for catalyst deposition [17,18]. Thus, hybrid air-breathing cathodes consisting of cobalt oxide and nitrogen doped graphene oxide, exhibit high ORR activity in alkaline solutions [19–23]. However, cobalt oxide nanoparticles are easy to aggregate into random bundles among the graphene layers [24]. Such agglomeration gives rise to the reduction of ORR activity for the air-breathing cathodes, due to the decreased number density of active sites.

Many efforts have been made to avoid the agglomeration of catalyst particles. Ultrasound is the prevailing approach to disperse the particles [25–27]. In general, an ultrasonication for 0.5 ~ 1.5 h can yield dispersive and fine nano particles [28–31]. Similar ultrasonication treatment for precursors prior to hydrothermal synthesis has been applied to prepare hybrid catalysts nanoparticles [32,33]. However, the agglomeration of reacting precursors or nanoparticles and catalyst carriers possibly reappears during the long-time hydrothermal synthesis process [34]. Thus, an ultrasonication upon hydrothermal synthesis is proposed to achieve a sufficient dispersion of hybrid catalyst particles.
and carriers, which has been scantily investigated.

In this work, a persistently ultrasound-assisted hydrothermal process (HU) is developed to prepare a hybrid catalyst incorporating cobalt oxide with nitrogen-doped graphene oxide (HU-CoO4/N-GO). This hybrid is characterized using XPS, FESEM, TEM and electrochemical measurement. In addition, a full Al-air battery is constructed to evaluate the ORR activity of the as-prepared hybrid catalyst.

2. Experimental section

2.1. Material synthesis

Graphene oxide used was commercial product (Tu ling Co., Ltd). Analytical grade CaH2CoO4·4H2O, NH4OH, Na2SO4, KOH, and activated carbon and acetylene black were supplied from Sinopharm Chemical Reagent Co., Ltd. De-ionized (DI) water was used as a solvent in the synthesis process.

The schematic diagram for the synthesis route of HU-CoO4/N-GO hybrid is shown in Fig. 1. Firstly, graphene oxide (450 mg) was dispersed in Co(CH3COO)2 aqueous solution (0.2 mol L\(^{-1}\), 225 ml) at room temperature, then added NH4OH (4.2 ml, 30% solution) for nitration under ultrasonication. Then, the dispersed precursors were transferred to a Teflon-lined and sealed autoclave with a capacity of 300 ml. A persistently ultrasound-assisted hydrothermal synthesis was carried out at 150 °C for 10 h in a self-designed apparatus, where a 40 kHz ultrasound with a fixed power of 600 W was transmitted into a stainless reactor with periodically repeated switch on for 30 min and off for 5 min via silicone fluid media. The underlying synthesis process for CoO4/N-GO hybrid is considered as follow: Co\(^{2+}\) cations can homogeneously coat onto GO sheets due to the electrostatic interaction. During the ultrasound-assisted hydrothermal process, N atoms from NH\(_4\)OH are doped into the graphene oxide. The precursor covered on the surface of nitrogen can be doped on the graphene oxide surface and finally transformed into CoO4/N-GO hybrid via the following reaction:

\[
6\text{Co}^{2+} + 12\text{OH}^- + O_2 \xrightarrow{\text{150°C}} 2\text{Co}_3\text{O}_4 + 6\text{H}_2\text{O}
\]  

Finally, the HU-CoO4/N-GO hybrid was collected after centrifugation, washed with ethanol and DI water and lyophilization on the reaction products. Similar synthesis was also conducted without ultrasound assistance to prepare H-CoO4/N-GO hybrid. HU-CoO4 and HU-N-GO were also prepared without the addition of GO and Co (CH3COO)2, respectively. A blank H-N-GO was also prepared for a direct comparison.

2.2. Material characterizations

Powder XRD (X-ray diffraction) patterns for the synthesized samples were performed using an Ultima IV X-ray diffractometer with Cu Kr (\(\lambda = 1.54 \AA\)) radiation. The chemical states of C, N, O, and Co elements in the samples were detected by XPS (X-ray photoelectron spectroscopy measurements, AXISULTRA-DLD, Al Kr X-ray radiation source at 150 W). The yield of CoO4 synthesized by hydrothermal reaction was determined by ICP (inductively coupled plasma emission spectrometer, Optima-7000DV). The morphology observation was conducted using a Zeiss Auriga scanning electron microscope (FESEM) coupled with energy dispersive spectra (EDS) and a JEM-2100 transmission electron microscope (TEM).

2.3. Electrochemical measurements

The electrochemical measurements were performed in a three-electrode system using a CHI660E electrochemical workstation. Catalyst powders coated on the glassy carbon electrode (geometric diameter: 3 mm) were used as the working electrode in the aqueous solution of 0.1 M KOH saturated with O2. Hg/HgO electrode and platinum foil served as the reference electrode and the counter electrode, respectively. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were carried out at a scan rate of 50 mV s\(^{-1}\) and 5 mV s\(^{-1}\), respectively. Electrochemical impedance spectroscopy (EIS) was conducted in the scanning range from 0.1 Hz and 100 kHz at 1.023 V.

2.4. Al-air battery tests

Al-air batteries were assembled with the commercial pure Al anode and self-made air-breathing cathodes loaded with the as-prepared hybrid catalysts. The surface area of electrodes was 1 cm\(^2\), and 4 M KOH aqueous solution was used as electrolyte. The discharge tests were conducted using a LANHE battery testing system at the current densities of 20, 40 and 60 mA cm\(^{-2}\), respectively.

3. Results and discussion

3.1. Production of synthesized CoO4

Table 1 lists the calculated production of the CoO4 after hydrothermal synthesis with or without ultrasonication based on ICP measurement. The total amount of Co was 2.652 g in each trial for hydrothermal synthesis. The residual Co in the collected filtrates was 0.857 g, 1.065 g, 0.780 g and 0.979 g in HU-CoO4, H-CoO4, HU-N-GO.

| Item (g) | HU-CoO4 | H-CoO4 | HU-CoO4/N-GO | H-CoO4/N-GO |
|---------|---------|--------|-------------|-------------|
| Total amount of Co | 2.625 \(\pm 0.034\) | 2.017 \(\pm 0.029\) | 0.780 | 0.979 |
| Residual Co in filtrate | 0.857 | 1.065 | 0.780 | 0.979 |
| Production | \(\pm 0.012\) | \(\pm 0.018\) | \(\pm 0.022\) | \(\pm 0.017\) |
| Co production | 1.768 | 1.560 | 1.845 | 1.646 |
| Theoretical CoO4 | 3.576 \(\pm 0.034\) | 3.517 \(\pm 0.032\) | 3.498 \(\pm 0.031\) | 3.489 \(\pm 0.032\) |
| Actual CoO4 production | 2.408 | 2.125 | 2.514 | 2.242 |
| Yield ratio | 67.3% | 59.4% | 70.3% | 62.7% |

| Item (g) | HU-CoO4 | H-CoO4 | HU-CoO4/N-GO | H-CoO4/N-GO |
|---------|---------|--------|-------------|-------------|
| Total amount of Co | 2.625 \(\pm 0.034\) | 2.017 \(\pm 0.029\) | 0.780 | 0.979 |
| Residual Co in filtrate | 0.857 | 1.065 | 0.780 | 0.979 |
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Table 1 The calculated production of the CoO4 after hydrothermal synthesis with or without ultrasonication via ICP measurement.

Fig. 1. Schematic synthetic procedure of HU-CoO4/N-GO hybrid.
Co$_3$O$_4$/N-GO hybrid and H-Co$_3$O$_4$/N-GO hybrid, respectively. Consequently, the Co$_3$O$_4$ production in HU-Co$_3$O$_4$, H$_4$N-GO, H-Co$_3$O$_4$/N-GO and H-Co$_3$O$_4$/N-GO hybrid were 2.445 g (67.7%), 2.161 g (59.8%), 2.5502 g (70.6%) and 2.2785 g (63.1%), respectively. It suggests that the ultrasonication can promote the hydrothermal reaction for Co$_3$O$_4$ production. Furthermore, the catalyst carrier N-GO also has a slight promotion on the Co$_3$O$_4$ production.

3.2. XRD and XPS analysis

Fig. 2(a) shows the XRD pattern of the prepared HU-Co$_3$O$_4$/N-GO hybrid. The diffraction peaks at 31.2°, 36.7°, 59.2° and 65.1° can be readily indexed to the (220), (311), (511) and (440) planes of face centered cubic Co$_3$O$_4$, respectively [13]. It indicates a successful synthesis of cubic Co$_3$O$_4$ in the ultrasound-assisted hydrothermal process.

The atomic valence states of the HU-Co$_3$O$_4$/N-GO hybrid were studied by XPS characterization. As shown in Fig. 2(b), the principal peaks of C, N, O, and Co appear on the full survey spectrum of the HU-Co$_3$O$_4$/N-GO hybrid. Fig. 2(c)-(f) show the high-resolution C 1s, N 1s, O 1s and Co 2p fitted spectra, respectively. There are two peaks in the C 1s fitted spectra, as shown in Fig. 2(c). The peak at 284.7 eV is conformed to the C–C/C–C network and the other at 288.2 eV corresponds to C–O in graphene oxide. Fig. 2(d) shows the N 1s fitted spectra. The peak at 399.1 eV and 400.9 eV are assigned to pyrrolic nitrogen and graphitic nitrogen in graphene oxide. Fig. 2(e) shows the O 1s fitted spectra. The peak at 530.9 eV and 531.8 eV, respectively, corresponds to carbon–oxygen bonds for graphene oxide with peaks at 530.9 eV and 531.8 eV, respectively. The peaks at 778.6 and 795.9 eV correspond to the Co 2p$_{3/2}$ and Co 2p$_{1/2}$ spin-orbit peaks of Co$_3$O$_4$, as shown in Fig. 2(f). The Co 2p$_{1/2}$ peak can be further divided into Co$^{3+}$ and Co$^{2+}$ peaks.

There is a peak around the main peak of Co 2p$_{1/2}$, representing the Co$_3$O$_4$ phase. The XPS result is consistent with that in previous literature [35].

3.3. The morphology and structure of the hybrids

Fig. 3(a) shows the SEM images of as-prepared HU-Co$_3$O$_4$/N-GO hybrids and the corresponding EDS mapping analysis. The EDS mapping shows a uniform distribution of C, N, O and Co throughout the observed particle. The EDS point shooting analysis (spectrum 1 and 2) further confirms that the Co content of the particle reaches 31.2 ~ 34.7 at. %.

The EDS mapping analysis results are determined by the ICP measurement in Table 1. A large number density of fine cubic Co$_3$O$_4$ particles grow on the N-GO sheet without ultrasonication, as shown in Fig. 3(b). A large number density of fine cubic Co$_3$O$_4$ particles grow on the N-GO sheet in HU-Co$_3$O$_4$/N-GO sample (Fig. 3(c)). It clearly reveals that ultrasonication greatly promotes the production of Co$_3$O$_4$ during hydrothermal synthesis, which is quite consistent with the calculated result based on the ICP measurement in Table 1.

Fig. 4 shows the TEM images of initial GO, H-N-GO, HU-N-GO, H-Co$_3$O$_4$ and HU-Co$_3$O$_4$/N-GO, in order to further clarify the ultrasonic mechanism for the growth of Co$_3$O$_4$ on the N-GO sheets. The initial graphene oxide is crumpled sheet with curled edges, as shown in Fig. 4(a). The H-N-GO presents as thick and large sheets (Fig. 4(b)), while the N-GO transforms into the dispersed and thin sheets with ultrasonication during hydrothermal process, as shown in Fig. 4(c). It can be found that a short period ultrasonication prior to hydrothermal reaction fails to achieve high dispersion of the N-GO sheet. A persistent assistance of ultrasonication can sufficiently ensure a dispersion of fine N-GO sheets.
during the long-term hydrothermal synthesis. Furthermore, the cubic \( \text{Co}_3\text{O}_4 \) particle clusters (~700 nm) can be observed in the H-\( \text{Co}_3\text{O}_4 \) sample, as shown in Fig. 4(d). It suggests a severe agglomeration of \( \text{Co}_3\text{O}_4 \) particle (~220 nm) during the normal hydrothermal synthesis without the addition of N-GO and ultrasonication. The agglomeration of cubic \( \text{Co}_3\text{O}_4 \) particles is greatly retarded after the persistent assistance of ultrasonication in hydrothermal reaction, as shown in Fig. 4(e). Furthermore, fine \( \text{Co}_3\text{O}_4 \) nanoparticles (~30 nm) are clearly identified in HU-\( \text{Co}_3\text{O}_4 \) sample, as shown in Fig. 4(f).

It can be clearly concluded that the agglomeration of N-GO sheets and cubic \( \text{Co}_3\text{O}_4 \) particles is easily to appear during the long-term hydrothermal synthesis, even though a dispersion of N-GO sheets and precursors has been achieved prior to hydrothermal process. Ultrasonication-assisted hydrothermal synthesis can be effective to disperse the N-GO sheets and refine the cubic \( \text{Co}_3\text{O}_4 \) particles, as shown in Fig. 4. The N-GO sheets are effective sites for the nucleation and growth of \( \text{Co}_3\text{O}_4 \) particles. Thus, a persistent dispersion of N-GO sheets assisted by ultrasonication is in favor of the dispersion of \( \text{Co}_3\text{O}_4 \). As a result, the number density of \( \text{Co}_3\text{O}_4 \) growing on N-GO sheets greatly increases, as shown in Fig. 3c.

### 3.4. Electrocatalytic performance for ORR

Fig. 5 shows the electrochemical behaviors including CV, LSV and EIS of the as-prepared hybrids in alkaline solution. Both HU-\( \text{Co}_3\text{O}_4 \)/N-GO and H-\( \text{Co}_3\text{O}_4 \)/N-GO show oxygen reduction peaks, as shown in Fig. 5(a). The HU-\( \text{Co}_3\text{O}_4 \)/N-GO has a 45 mV higher ORR peak than the H-\( \text{Co}_3\text{O}_4 \)/N-GO, which manifests a high electrocatalytic activity toward ORR. Furthermore, the HU-\( \text{Co}_3\text{O}_4 \)/N-GO hybrid exhibits a half-wave potential (0.76 V vs. RHE), 50 mV higher than the H-\( \text{Co}_3\text{O}_4 \)/N-GO.
(0.71 V vs. RHE), according to the LSV curves in Fig. 5(b). The calculated ORR Tafel slope for HU-Co$_3$O$_4$/N-GO is 135 mV dec$^{-1}$, a bit lower than that of H-Co$_3$O$_4$/N-GO (160 mV dec$^{-1}$), as shown in Fig. 5(c). It fully demonstrates that HU-Co$_3$O$_4$/N-GO shows better ORR activity than H-Co$_3$O$_4$/N-GO. Fig. 5(d) shows the Nyquist plots of the HU-Co$_3$O$_4$/N-GO and H-Co$_3$O$_4$/N-GO at 1.023 V. The Nyquist plots consist of two capacitive circles and straight line, which can be fitted by the equivalent circuit model in Fig. 5(d). $R_e$ is resistance of electrolyte, $R_{||\text{CPE}_{\text{int}}}$ represents the interphase contact resistance and related capacitance in the electrode. $R_{\text{ct}}$||$\text{CPE}_{\text{dl}}$ is the charge-transfer resistance and related

Fig. 4. TEM images of the prepared catalysts. (a) Initial GO; (b) N-GO; (c) HU-N-GO; (d) H-Co$_3$O$_4$; (e) and (f) HU-Co$_3$O$_4$. 
capacitance, and $W_1$ is ionic diffusion impedance. According to the fitted results in Table 2, HU-Co$_3$O$_4$/N-GO has lower $R_e$, $R_{int}$ and $R_{ct}$ values than the H-Co$_3$O$_4$/N-GO, suggesting the fast electron transportation and high ORR activity. Thus, HU-Co$_3$O$_4$/N-GO hybrid exhibits a better electrocatalytic activity than H-Co$_3$O$_4$/N-GO. This means that ultrasonication can effectively alleviate the agglomeration degree of graphene oxide and make the Co$_3$O$_4$ uniformly growing on graphene oxide. Therefore, it is in favor of increasing the number density of active catalytic sites accessible to oxygen, hence greatly promoting ORR activities [36].

### 3.5. Al-air battery tests

Fig. 6 shows the discharge curves of the assembled Al-air batteries with the prepared hybrids as ORR electrocatalysts in 4 M KOH solutions at a scan rate of 5 mV s$^{-1}$; (c) Tafel plots derived from LSV curves; (d) Nyquist plot of HU-Co$_3$O$_4$/N-GO and H-Co$_3$O$_4$/N-GO air electrodes in 1 M KOH solutions between 0.1 Hz and 100 kHz at 1.023 V and the equivalent circuit.

![Fig. 5](image_url)

**Table 2**

| Hybrid            | $R_e$ (Ω cm$^2$) | $R_{int}$ (Ω cm$^2$) | $R_{ct}$ (Ω cm$^2$) |
|-------------------|------------------|----------------------|---------------------|
| HU-Co$_3$O$_4$/N-GO | 0.61             | 2.22                 | 0.80                |
| H-Co$_3$O$_4$/N-GO | 0.63             | 2.40                 | 3.10                |

Fig. 5. (a) CV curves of HU-Co$_3$O$_4$/N-GO and H-Co$_3$O$_4$/N-GO in an oxygen-saturated 0.1 M KOH solutions; (b) LSV curves of HU-Co$_3$O$_4$/N-GO and H-Co$_3$O$_4$/N-GO in an oxygen-saturated 0.1 M KOH solutions at a scan rate of 5 mV s$^{-1}$; (c) Tafel plots derived from LSV curves; (d) Nyquist plot of HU-Co$_3$O$_4$/N-GO and H-Co$_3$O$_4$/N-GO air electrodes in 1 M KOH solutions between 0.1 Hz and 100 kHz at 1.023 V and the equivalent circuit.

performance of the Co$_3$O$_4$/N-GO hybrid. This is well consistent with the measured electrochemical behaviors in Fig. 5. Furthermore, Al-air battery with HU-N-GO catalyst has an average working voltage of ~0.79 V (at 60 mA cm$^{-2}$), 20 mV higher than that with H-N-GO. This clearly implies that the catalytic activity of N-GO is slightly enhanced with the persistent assistance of ultrasonication, as shown in Fig. 6. However, such enhancement is much smaller than that (~60 mV) on the Co$_3$O$_4$/N-GO hybrid induced by ultrasonication. This implies that Co$_3$O$_4$ particles play dominating role in the catalytic activity of as-prepared hybrid, and the improved catalytic activity induced by ultrasonication is primarily attributed to the modification of Co$_3$O$_4$. Such improvement can be of relative great significance for a better discharge performance with a lower material cost for Al-air battery. Firstly, the preparation of the hybrid N-GO/Co$_3$O$_4$ ORR catalyst, even though with ultrasonication, is still quite cost-effective in battery operation compared to use of the precious metal-based catalysts. Secondly, more effective utilization of Co$_3$O$_4$ recourse with ultrasonication preparation also means a trade-off reduction in materials cost (using less Co$_3$O$_4$ for Al battery construction, compared to the convention hydrothermal preparation method that usually consumes more expensive Co-containing raw materials.

Fig. 7 schematically illustrates the mechanism for persistently ultrasound-assisted hydrothermal synthesis of Co$_3$O$_4$/N-GO hybrids. Ultrasonication improves both the yield and number density of Co$_3$O$_4$ particles. To the authors’ best knowledge, disperse and fine particles with high number density are more important than the yield, regarding the ORR activity, since a high yield of Co$_3$O$_4$ may contribute to a rapid growth of coarse Co$_3$O$_4$ particles with low number density, which is detrimental to electrocatalytic activity (low number density of catalytic sites). Ultrasonication prior to hydrothermal synthesis can perform sufficient dispersion of both graphene oxides and precursors for Co$_3$O$_4$ via the outstanding ultrasonic cavitation and streaming effects.
However, the dispersed graphene oxides gradually agglomerate to large and thick sheets (Fig. 4(b)) during a 10 h hydrothermal process at 150 °C. Since the agglomerated GO serve as effective substrates for the nucleation of Co$_3$O$_4$ particles, it would further result in the agglomeration of the latterly precipitated Co$_3$O$_4$ particles, as shown in Fig. 4(d). A persistent assistance of ultrasonication in hydrothermal synthesis can effectively maintain a sufficient dispersion of the precursors and GO, as shown in Fig. 4c. Thus, the latterly precipitated Co$_3$O$_4$ particles effectively and uniformly nucleate and grow on the dispersed GO under the persistent assistance of ultrasonication. Furthermore, the significant ultrasonic cavitation can enhance the nucleation events of Co$_3$O$_4$ particles by activating the surface of solid particles [39,40] (possibly graphene oxides in this work). In addition, the enhanced mass transfer would also be beneficial for uniform distribution of precursors [41–43], refining Co$_3$O$_4$ particles via the eliminating the solute segregation upon the solid-liquid interface. This explains that the persistently ultrasound-assisted hydrothermal synthesis process creates large number density of fine cubic Co$_3$O$_4$ growing on the dispersed GO sheet, as shown in Fig. 3c. In a word, the persistently ultrasound-assisted hydrothermal synthesis can efficiently prepare well

Fig. 6. Discharge curves of the assembled Al-air batteries with the prepared hybrids as the ORR electrocatalysts in 4 M KOH using at current densities ranging from 20 to 60 mA·cm$^{-2}$.

Fig. 7. Schematic illustration of the persistent ultrasound-assisted hydrothermal synthesis of Co$_3$O$_4$/N-GO hybrid.
dispersed and fine CoOx/N-GO hybrids, which exhibit better electrocatalytic (ORR) activity as cathode materials for Al-air battery.

4. Conclusions
In this work, a persistently ultrasound-assisted hydrothermal method has been developed to prepare cobalt oxide incorporated nitrogen-doped graphene hybrids. The electrochemical behaviors and catalytic activity of the prepared hybrids have been systematically investigated for cathode materials of Al-air battery. The results show that ultrasonication can promote the yield ratio of CoOx from 63.1% to 70.6%. It can effectively disperse and refine the cubic CoOx growing nitrogen-doped graphene oxides, as well as increase the number density of CoOx particles. The half-wave potential of the CoOx/N-GO hybrid with ultrasonication is 50 mV higher than that without ultrasonication. The assembled Al-air battery using the ultrasonicated CoOx/N-GO hybrid exhibits an average working voltage of 1.02 V in 4 M KOH electrolyte, approximately 60 mV higher than that using the hybrid without ultrasonication at 60 mA·cm⁻². This should be asserted that the persistently ultrasonication in hydrothermal synthesis can maintain a favorable dispersion of graphene oxides, allowing the effective and uniform nucleation and growth of CoOx particles.

CRediT authorship contribution statement
Z. Wang: Writing - original draft, Methodology. Hongpeng Zhou: Investigation. Jilai Xue: Conceptualization, Supervision. Xuan Liu: Writing - review & editing. Shizhe Liu: Validation. Xiangle Li: Visualization. Dingyong He: Resources.

Declaration of Competing Interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data
Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultrasch.2020.105457.

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