MOFs nanosheets derived porous metal oxide-coated three-dimensional substrates for lithium-ion battery applications

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\begin{abstract}
Porosity nanosheet-structured materials have received great attention because of their promising applications in energy field. Construction of porous metal oxides nanosheets on three-dimensional (3D) electro-conductive substrates is an effective way to further enhance electrochemical performance of energy storage devices. Herein, porous transition metal oxides (i.e. ZnO, Co\textsubscript{3}O\textsubscript{4}) nanosheets derived from MOFs coated 3D substrates (i.e. 3D nickel foam, carbon fiber) are successfully synthesized by a facile liquid-phase deposition method with subsequent calcination. The growth mechanism of MOFs with nanosheet morphology coated 3D substrates is investigated. As a proof of concept application, the Co\textsubscript{3}O\textsubscript{4}/3DNF hybrid, possessing the advantages of porous nanosheet-structured and 3D electro-conductive substrates, is used as a binder-free anode material for lithium-ion battery, which exhibits high-rate capability and long-term cyclic stability. High discharge capacities of 1135, 1268, 1130, 923, 751, and 543 mA h g\textsuperscript{-1} are obtained at the current densities of 0.2, 0.5, 1, 2, 5, 10, and 20 A g\textsuperscript{-1}, respectively. Even measured at 25 A g\textsuperscript{-1}, it still retains a desired discharge capacity of 364 mA h g\textsuperscript{-1}. Besides, the long-term cyclic stability up to 2000 cycles can be obtained at 5 A g\textsuperscript{-1} and 20 A g\textsuperscript{-1}.
\end{abstract}

\section{Introduction}

Metal-organic frameworks (MOFs), a class of organic-inorganic hybrid materials, have received great interest over the past decades [1–3]. Due to their ultrahigh porosity, high internal surface area, exceptional thermal and chemical stability, MOFs hold great promise as porous materials for a variety of applications such as separation, gas storage, and catalysis [4–7]. In addition, MOFs are proved to be ideal self-sacrificial templates to fabricate porous transition metal oxides, such as ZnO [8], Fe\textsubscript{2}O\textsubscript{3} [9], and Co\textsubscript{3}O\textsubscript{4} [10–12], and they demonstrate a good utilization efficiency in energy field. However, although great efforts have been made, the low electrical conductivity of MOFs or MOF-derived materials greatly limits their application. In this respect, to explore a viable approach to overcome this defect is necessary.

An effective way to improve electrical conductivity of MOFs or MOF-derived materials is to combine them with other materials such as graphene-based nanosheets, metal nanoparticles, MoS\textsubscript{2} nanosheet, and so on [13–16]. In the meantime, MOFs/three-dimensional (3D) graphene networks was reported by Zhang’s group and their derived hybrids demonstrate excellent performances in photo-catalysis and lithium-ion battery applications [8]. It is believed that MOFs or MOF-derived materials combined with 3D electro-conductive substrates like 3D graphene networks, nickel foams, and carbon fibers can gain the maximum efficiencies because 3D substrates possess not only large internal surface area for anchoring nanomaterials, but also high-efficiency electrical conductivity for electron transfer [17–21]. Therefore, rational design and synthesis of MOFs or MOF derived materials coating 3D substrates may represent a promising direction for efficient energy storage. However, there is very few work involved in this field. Specially, to the best of our knowledge, there has been no report concerning the preparation of MOF nanosheets-derived porous metal oxide-coated 3D substrates with great promise for various applications.

Porous nanosheet-structured materials have been widely investigated and proven to be critical role for many applications in energy field due to their large specific surface area and abundant active sites for chemical reactions and their porous structures that ease strain of materials [22–27]. Herein, we have successfully fabricated Zn/Co-MOF nanosheets coated on 3D nickel foam (3DNF) or carbon fiber (CF) and their grown mechanism was studied. In particular, Zn/Co-MOF nanosheets can directly derived
into highly porous metal oxides (i.e. ZnO, Co$_3$O$_4$) nanosheets by calcining in air. As a proof-of-concept application of the hybrids, Co-MOF derived porous Co$_3$O$_4$ nanosheets on 3D nickel foam, referred to as Co$_3$O$_4$/3DNF, is used as a binder-free anode electrode for lithium-ion batteries (LIBs). The hybrids show excellent electrochemical performances with superior long-term cycling performance up to 2000 cycles and high rate capability at 25 A g$^{-1}$. To the best of our knowledge, lithium storage performances of Co$_3$O$_4$/3DNF in this work are the best among the Co$_3$O$_4$-based anode materials, demonstrating a potential prospect of practical application.

2. Experimental section

Chemicals: Cobalt nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O), zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O), and 2-methylimidazole (Hmim) are of analytical grade and used as received without any purification process. The Ni foam substrate (2 × 2 cm$^2$) was cleaned and etched with 6 M HCl for 30 min to remove the surface NiO layer, and then rinsed with deionized water and absolute ethanol for 3 times respectively. Carbon fiber (2 × 2 cm$^2$) was cleaned for 30 min of successive sonication cleaning using acetone, ethanol, and deionized water, respectively.

Synthesis of porous ZnO nanosheets grown on Ni foam/Carbon fiber: In a typical procedure, 0.595 g of Zn(NO$_3$)$_2$·6H$_2$O and 1.3 g of 2-methylimidazole (Hmim) were dissolved in 40 mL deionized water, respectively, and following 30 min magnetic stirring at room temperature. Then the Zn(NO$_3$)$_2$·6H$_2$O solution was poured into the Hmim solution quickly and a piece of cleaned Ni foam/Carbon fiber (2 × 2 cm$^2$) was placed in above mixing solution immediately. Being kept still for a period of time, Ni foam/Carbon fiber was washed with deionized water and dried in an oven at 60 °C. Finally, the as-grown Ni foam/Carbon fiber was placed in a muffle furnace and then heated to 300 °C with a ramping rate of 1 °C min$^{-1}$ for 1 h to get porous ZnO nanosheets grown on Ni foam or Carbon fiber.

Synthesis of porous Co$_3$O$_4$ nanosheets grown on Ni foam/Carbon fiber: The synthetic procedures are similar to that of porous ZnO nanosheets grown on Ni foam/Carbon fiber, except that we used 0.582 g of Co(NO$_3$)$_2$·6H$_2$O to replace Zn(NO$_3$)$_2$·6H$_2$O.

Synthesis of porous Co$_3$O$_4$ powder: The synthetic procedure is similar to that of porous Co$_3$O$_4$ nanosheets grown on Ni foam/Carbon fiber, but without adding Ni foam or Carbon fiber. The reaction time was kept still for 1 h. And then the Co-MOF powder was washed and centrifuged with deionized water three times and dried in an oven at 60 °C. Finally, the as-obtained powder was placed in a muffle furnace and then heated to 300 °C with a ramp of 1 °C min$^{-1}$ for 1 h to get porous Co$_3$O$_4$ nanosheets.

Electrochemical measurements of Co$_3$O$_4$/3DNF and Co$_3$O$_4$ powder: The electrochemical properties were carried out via stainless-steel coin cells (CR 2016). A solution of 1 M LiPF$_6$ in ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 v/v) was used as the electrolyte, and lithium foil was used as both the counter and the reference electrode. The Co$_3$O$_4$/3DNF hybrid was used directly as the working electrode, without adding any conductive materials and binders. For the Co$_3$O$_4$ powder, working electrode was obtained with 80% as-synthesized Co$_3$O$_4$ powder, 10% acetylene black, and 10% polyvinylidene fluoride (PVDF) binder. Cyclic voltammetry (CV) of Co$_3$O$_4$/3DNF-based coin cell was measured.

![Fig. 1.](image-url) (a) XRD patterns and (b) FT-IR spectrums of Zn-MOF/3DNF and Co-MOF/3DNF. Various magnification SEM images of (c and d) Zn-MOF/3DNF, (e and f) Co-MOF/3DNF grown for 1 h.
tested using an electrochemical workstation (CHI660C, China) at a scan rate of 0.1 mV s\(^{-1}\) in the voltage range of 0.01–3 V (vs. Li/Li\(^+\)). The galvanostatic charge/discharge experiments were studied in a potential range of 0.01–3 V (vs. Li/Li\(^+\)) using a multichannel battery testing system (Land CT 2001 A) at room temperature. The electrochemical impedance spectrometry (EIS) was performed on a ZAHNER-IM6ex electrochemical workstation (ZAHNER Co., Germany) in the frequency range of 100 kHz to 10 m Hz on a cell.

Characterization: The crystallographic phases of the samples were performed by X-ray diffraction (XRD, Rigaku D/max 2500) and FT-IR spectrometer (Nicolet 6700). The morphologies and sizes were characterized by scanning electron microscopy (SEM, Quanta FEG 250). Transmission electron microscope (TEM) images, high-resolution transmission electron microscope (HRTEM) image, and selected area electron diffraction (SAED) image were recorded by using JEOL JEM-2100F transmission electron microscope.

3. Results and discussion

The synthetic procedure for MOFs derived ZnO or Co\(_3\)O\(_4\) nanosheets coated three-dimensional substrates includes two main steps. Recently, Chen et al. reported a new 2D zeolitic imidazolate framework with unique cushion-shaped cavities and leaf-like crystal morphology at room temperature [28]. The synthesis method of MOFs in this work is similar to the approach developed by Chen et al. [28]. Firstly, Zn- or Co-MOF were directly grown on 3D substrates via a facile liquid-phase deposition method at room temperature. Fig. 1a shows the X-ray diffraction (XRD) patterns of Zn- or Co-MOF/3DNF synthesized for 1 h. It can be obviously seen that the XRD pattern of Co-MOF matches well with the pattern of Zn-MOF, indicating Co-MOF has an isostructure with Zn-MOF. Both the XRD patterns are consistent well with the XRD patterns of Zn/Co-MOF powder (shown in Fig. S1 in Electronic Supporting Information (ESI\(^\ddagger\))) and also match well with the previous work [28], confirming the successfully preparation of Zn- and Co-MOF on Ni foam, which is further proved by FT-IR spectrums (Fig. 1b). The corresponding FT-IR spectrums of Zn- and Co-MOF exhibit the similar shape, showing nine main vibration modes between 400 and 1600 cm\(^{-1}\), which correspond well to the previous study [29].

Taking the FT-IR spectrum of Zn-MOF for example, the peak at 424 cm\(^{-1}\) corresponds to Zn-N stretching, while the peak around 1148 and 1304 cm\(^{-1}\) belongs to the C-H vibrations, 1566 cm\(^{-1}\) to C=O vibration, respectively. This class of MOFs is structurally two-dimensional, which shows 2D layer network along the ab plane and these layers are stacked along the c direction [28]. The morphology of Zn-MOF/3DNF (Fig. 1c and d) and Co-MOF/3DNF (Fig. 1e and f) is investigated by the field emission scanning electron microscopy (FE-SEM). The SEM images indicate that 3DNF is covered with uniform nanosheets for both samples. The surface of the nanosheets is smooth. The thickness of each nanosheet for Zn-MOF is 50–100 nm, while for Co-MOF is 100–150 nm. The ZnO/3DNF and Co3O4/3DNF can be prepared by calcinating Zn- and Co-MOF/3DNF at 300 °C in air (step 2). Identification about the phase purity and crystal structure of the final products are provided by XRD. As is shown in Fig. 2a and d, except for three typical peaks of nickel, other diffraction peaks can be well indexed to ZnO phase [JCPDS Card No. 43–1003] and Co3O4 phase [JCPDS Card No. 43–1003], respectively, indicating the complete conversion of Zn- and Co-MOF. The representative SEM images of ZnO/3DNF and Co3O4/3DNF are shown in Fig. 2b–c and Fig. 2e–f, respectively. As showed in Fig. 2b, the ZnO nanosheets are connected with each
other to form a nanoarray network. Leaf-like nanosheets morphology can be clearly observed for Co$_3$O$_4$/3DNF (Fig. 2e). Moreover, the nanosheets exhibit ultrahigh porosities as depicted in high-magnification SEM images (Fig. 2c and f). Similar porous structures can also be found in other type of MOFs derived materials [7–9,11,12].

Besides ZnO/3DNF and Co$_3$O$_4$/3DNF, other hybrids, such as ZnO coated carbon fiber (ZnO/CF), Co$_3$O$_4$ coated carbon fiber (Co$_3$O$_4$/CF) can also be successfully fabricated and their phases and morphologies are characterized by XRD and SEM (see Fig. S2 and S3 in ESI†). Generally, our method could be extended to fabricate other hybrids by the appropriate choice of a specific MOF. Therefore, understanding the mechanism of MOFs with nanosheet morphology grown on the surface of 3D substrates is necessary and important. Based on this consideration, we chose Co-MOF/3DNF as research object and exposed its growth process.

We propose the nucleation growth mechanism for the synthesis of Co-MOF/3DNF. The growth process of Co-MOF/3DNF are characterized by XRD and SEM. Firstly, cobalt ions and 2-methylimidazole molecules are adsorbed on the surface of 3DNF to form...
a thin film at a short time of 2 min, as shown in Fig. 3b. Then the sample is forming nucleus with large amounts of small particles coated on 3DNF (Fig. 3c), which was the early stage of crystallization of Co-MOF. With long reaction time, nucleus grows up (Fig. 3d and e) and acts as buds for crystal growth to form uniform leaf-like nanosheets, as discussed earlier. However, if the growth time is too long, some leaf-like nanosheets aggregate together (Fig. 3f). Fig. S4 in ESI† showed the corresponding XRD pattern of Co-MOF grown at different time. It can be clearly seen that Co-MOF grown for 5 min exhibited some week diffraction peaks, confirming the initial crystallization of Co-MOF. The diffraction peaks become much more obvious when prolonging the reaction time, indicating that the increasing crystallinity with the reaction time. Porous Co₃O₄ nanosheets coated 3DNF is obtained after annealing Co-MOF/3DNF at 300 °C in air and its detailed formation process is illustrated in Scheme 1. It is worth noting that porous Co₃O₄ nanosheets are composed of many infinitesimal nanosheets. The connected nanosheets can improve electronic conductivity of electrode material. The highly porous structure of Co₃O₄ nanosheets would enlarge the contact area between electrode and electrolyte and facilitate Li⁺ ion diffusion.

The transmission electron microscopy (TEM) image in Fig. 4a further confirms that annealed products demonstrate the porous leaf-like nanosheet structure. High-resolution transmission electron microscopy (HRTEM) showed in Fig. 4b reveals that the nanosheets are composed of many interconnected nanoparticles, and each nanoparticle has a diameter of 5–10 nm. Importantly, numerous nanopores around 1–3 nm in diameter between nanoparticles are observed. The nanoparticles are randomly oriented, and the representative interplanar spacings of ~4.67 Å and 2.43 Å are match well with the (111) and (311) planes of Co₃O₄ phase [JCPDS Card No. 43–1003], respectively. Electron diffraction rings depicted in Fig. 4c have been indexed, further indicating the polycrystalline structure of the as-prepared leaf-like Co₃O₄.
The electrochemical performances of porous Co$_3$O$_4$/3DNF hybrids as anode electrodes for lithium ion storage are evaluated in the following section.

Electrochemical behavior of Co$_3$O$_4$/3DNF as anode for LIB is evaluated by cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) testing. The CV profiles are recorded for the initial three cycles in the voltage window of 0.01–3.0 V (vs Li/Li$^+$) at a scan rate of 0.1 mV s$^{-1}$. As shown in Fig. 5a, the first cathodic scan exhibits an irreversible reduction peak at around 0.95 V, which is mainly attributed to the reduction of cobalt-based species to metallic cobalt and the formation of the solid electrolyte interphase (SEI) film [30]. It should be noted that there is one slight reduction peak located at 0.7 V following the reduction peak at 0.95 V, which is in accordance with the previous report [31–34]. Two anodic peaks, observed at around 1.25 V and 2.05 V, are associated with the multistep oxidation reactions of Co$^0$ to CoO. According to the previous reports, the peak at 1.25 V may be ascribed to an intermediate state CoO$_x$ (0 < x < 1) between Co and CoO [12]. In the subsequent cycles, the oxidation peaks are almost unchanged, but the reduction peak shifts to 1.15 V, suggesting the existence of the polarization effect after first cycle. The nearly overlapped CV curves after first cycle demonstrate excellent reversibility and stability of Co$_3$O$_4$/3DNF anodes. Fig. 5b displays the discharge/charge profiles of the initial five cycles at a constant current density of 0.5 A g$^{-1}$. The initial discharge curve depicts a distinct discharge plateau at around 1.0 V, following by a slight plateau at
around 0.7 V, which is consistent well with the first CV curve. The discharge voltage plateaus of subsequent cycles are higher, corresponding well to the previous reports on the typical lithium-ion intercalation behavior for CoO2x anodes [12,30,34–37]. The large overlap of the following four charge/discharge curves suggests the good structural reversibility of CoO2x/3DNF after initial cycle. Fig. 5c gives an intuitive instruction of cycling performance of CoO2x/3DNF electrode at 0.5 A g−1. In the initial 60 cycles, the discharge capacity demonstrates the rising trend, which may be ascribed to the formation of a gel-like surface film during the initial activation process and the improvement of Li+ accessibility [11]. In the subsequent cycles, the capacity of the electrode becomes quite stable. High discharge capacity of 1217 mA h g−1 can be maintained at 150th cycle. Even after 300 cycles, the electrode can also deliver a stable capacity of 1204 mA h g−1, indicating exceptional cyclic stability of the CoO2x/3DNF hybrid. Furthermore, the coulombic efficiency is around 99%, illustrating the excellent reversible Li+ insertion/extraction of electrode.

In order to illustrate the advantage of the hybrid, cycling performance of CoO2x powder derived from Co-MOF (crystal phase and morphology of CoO2x powder are shown in Fig. S5 in ESI†) at 0.5 A g−1 is tested. The discharge capacity of CoO2x powder is 872 mA h g−1 at second cycle and then drops rapidly to 138 mA h g−1 at 20th cycle, showing serious capacity fading upon cycling. This result indicates that the cycling performance can be remarkably enhanced by using 3D Ni foam substrate to grow CoO2x nanosheets, which is confirmed by the electrochemical impedance spectroscopy (EIS) data shown in Fig. S6 and Table S1 in ESI†. It can be seen that the charge transfer resistance (Rct) of CoO2x/3DNF is 53.93 Ω and much smaller than that of CoO2x powder (373.3 Ω), suggesting that 3DNF can effectively enhance the kinetics of electronic transportation in electrodes resulting in an excellent electrochemical performances for LIBs.

Fig. 6a shows the rate performance of CoO2x/3DNF evaluated at various current densities from 0.2 to 25 A g−1. It is found that the discharge capacity increased in the first 20 cycles (0.2 and 0.5 A g−1) from 1135 mA h g−1 at 2nd cycle and then reversible capacities of 1226, 1130, 923, 751, and 543 mA h g−1 can be maintained with increasing the current densities to 1, 2, 5, 10, and 20 A g−1, respectively. After the high-rate measurement, the electrode is able to recover a high specific capacity of 1192 mA h g−1 at 1 A g−1. Furthermore, when the current densities are reset to high rates again after 100 cycles, it still retain desired discharge capacities at various current densities and a high capacity of 364 mA h g−1 is observed even at 25 A g−1, highlighting the remarkable rate capability of CoO2x/3DNF hybrid. When reset to 1 A g−1, it shows no capacity fading after 400 cycles. Notably, the result reveals outstanding rate capability when compared to the previous reported high rate values of CoO2x-based anode materials, such as CoO2x@carbon nanotube arrays (408 mA h g−1 at 5 A g−1) [35], snowflake-shaped CoO2x (977 mA h g−1 at 3 A g−1) [38], multiwalled carbon nanotubes/CoO2x nanocomposites (514 mA h g−1 at 1 A g−1) [11], and CoO2x-carbon nanosheet hybrid (390 mA h g−1 at 10 A g−1) [39]. More comparisons are listed in the Table S2 in ESI†. As is known to all, rate capability is one of the most critical requirements for LIBs. Hence, CoO2x/3DNF obtained in our work will have a potential prospect of practical application.

Besides the high rate performance, long-term cyclic stability, particularly under heavy current charge/discharge, is another critical requirement for practical applications. As depicted in Fig. 6b, the CoO2x/3DNF hybrid shows superior cyclic stability over 2000 cycles at the current density of 5 and 20 A g−1. When evaluated at 5 A g−1, the hybrid exhibits a high discharge capacity of 896 mA h g−1 at the second cycle, keeping about 80% of that at the first cycle. It can maintain a reversible capacity of 976 mA h g−1 after 500 cycles, showing no capacity fading based on the second cycle. Even after 2000 cycles, the reversible capacity of the CoO2x/3DNF hybrid can still reach about 600 mA h g−1, corresponding to a capacity fading rate of 0.016% per cycle. Further measured at a higher rate of 20 A g−1, CoO2x/3DNF hybrid also demonstrates excellent cycling performance. In spite of the rapid decrease of capacity from 630 mA h g−1 at the second cycle, it can fortunately maintain a reversible capacity of 366 mA h g−1 at the 50th cycle. And then, CoO2x/3DNF hybrid keeps a relatively stable capacity up to 2000 cycles with a remarkable discharge capacity of 300 mA h g−1. The capacity fading rates are 0.026% and 0.009% per cycle based on the capacity of 2nd cycle and 50th cycle, respectively. In order to illustrate the capacity fading at 20 A g−1 before 50 cycles, the SEM images of electrode materials after 1, 10, and 50 cycles are displayed. The drastic capacity fading may result from lithiation-induced mechanical degradation and the formation of unstable solid electrolyte interphase (SEI) [40–42]. As depicted in Fig. 6c, a thick layer of SEI film was formed and covered on CoO2x nanosheets after first cycle. However, the SEI film became thinner upon cycling (see SEM image after 10 cycles in Fig. 6d). Sun et al. have demonstrated the evolution of the SEI film during cycling, concluding that the thick SEI film was formed in capacity fading process, but evolved into stable thin SEI film in capacity stabilization [43]. Fig. 6e shows that the surface of CoO2x nanosheets after 50 cycles is clean and smooth, indicating the SEI films tend to be stable, which lead to good cyclic stability in the following cycles.

According to the analysis above, CoO2x/3DNF hybrid exhibits both ultrahigh rate capacities and outstanding cyclic stability. To the best of our knowledge, the electrochemical results obtained in this work are the best among the CoO2x-based anode materials. Among all the binder-rich electrodes, mesoporous CoO2x hollow spheres prepared by Sun et al. exhibit the best performance with a long-term cyclic stability of 7000 cycles at 5 A g−1 [43]. However, the electrodes suffer from low specific capacity and need to experience a complex reactivation process. Wang et al. reported triple-shelled CoO2x hollow microsphere which exhibited a ultrahigh specific capacity of 1615.8 mA h g−1, but the cycling was only up to 30 cycles [44]. For most of the binder-free CoO2x-based electrodes, they are subjected to either poor cycling performance (e.g. CoO2x nanobelts array [45], CoO2x/3D graphene [46]), or inferior rate capability (e.g. CoO2x nanowire arrays [20], CoO2x nanoparticles films [47]). None of them can reach a long-term life of 2000 cycles and high rate of 25 A g−1 [12,48–50]. The superior electrochemical performance of CoO2x/3DNF hybrid could probably be attributed to the optimized structure and mechanical properties. i) 2D porous leaf-like CoO2x nanosheets not only possess large surface areas with the maximum exposure of active sites for electrochemical reactions, but also shorten Li ion diffusion length and effectively buffer the volume expansion during cycling [51]; ii) 3D nickel foam with outstanding electrical conductivity facilitates electron transportation and improves the poor electrical conductivity of the MOF-derived leaf-like CoO2x nanosheets, which decreases the inner resistance of LIBs [8]; iii) The synergistic effect of 2D porous CoO2x nanosheets and 3D nickel foam lead to excellent cycling stability and ultrahigh rate capability.

4. Conclusions

In summary, we have demonstrated that an advanced hybrid material based on MOF nanosheets derived porous transition metal oxide-coated 3D substrates can successfully be prepared. As a proof of concept application, the CoO2x/3DNF hybrid is applied as anode material for rechargeable lithium-ion batteries. Combined with the advantages of porous nanosheet-structured and 3D
electro-conductive substrates, the hybrids exhibit excellent electrochemical performances, including long-term stability up to 2000 cycles at 5 A g\(^{-1}\) and 20 A g\(^{-1}\), and ultrahigh rate capability at 25 A g\(^{-1}\). We believe that these hybrids could be extended to other field of applications, such as sodium-ion battery, supercapacitor, catalysis, photocatalysis, gas storage, etc.

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Appendix A. Supplementary material

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References


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