Iron based Dual-metal Oxides on Graphene for Lithium-ion Batteries

Anode: Effects of Composition and Morphology

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Abstract

Dual-transition-metal oxide (DTMO) nanostructures are emerging materials for lithium-ion battery (LIB) anodes with improved structural stability, electronic conductivity and electrochemical performance compared to their single-metal counterpart. Herein, composites of graphene with DTMOs (MFeO, M=Co, Mn, Zn) were controllably prepared by harnessing the synthesis atmospheres and the nanoscale diffusion couple. Their composition and morphology were characterized by TEM, EDS mappings, XRD and XPS. The NH₃ treatment resulted in the formation of hollow DTMO nanoparticles on nitrogen-doped graphene, while H₂ and Ar gave graphene-supported hollow and solid DTMO particles, respectively. Electrochemical tests were applied to compare the performance of these composites as LIB anodes.

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The superior anode performance DTMO electrodes was demonstrated to the corresponding iron oxide composite. CoFe₂O/RGO composites exhibit excellent rate capability and high-rate cycling stability for lithium storage, due to its stable solid structure. However, the hollowing of DTMO particles cannot elevate the capacity and stability, due to the interfacial resistance and structural changes upon cycling.

Keywords: dual-transition-metal oxide; graphene; lithium-ion battery anode; hollow nanostructure

Introduction

Lithium-ion batteries (LIBs) have become one of the most important energy storage devices in a wide range of applications, including portable electronics, electric vehicles, storage of renewable energy, etc., due to its high energy densities, high working voltage and environmental benignness.[1, 2] However, to meet the increasing demand of high density energy storage, there are still challenges to continuously improve the reversible capacity, cycling performance and rate capability of LIBs.[3] Commercialized graphite is currently used as the anode material in LIBs, but it suffers from a low theoretical capacity of 372 mAh g^{-1} . Transition metal oxides (TMOs) have been regarded as a promising alternative to graphite for their high lithium storage. Through the conversion reaction mechanism,[4, 5] TMO anode materials, including MnO_2 , Fe_2O_3 , Co_3O_4 , NiO , CuO , etc., could deliver reversible capacity higher than 600 mAh g^{-1} . [6-12] However, the battery performance might be limited by the low electrical conductivity,[13] large volume changes upon cycling[14] and the formation of solid-electrolyte interface (SEI) layer by electrolyte decomposition on the surface of anode materials.[10, 15]

As one of the approaches proposed to address these issues, combining two metallic cations in a single crystal structure has been developed to improve the structural stability, electronic conductivity and electrochemical performance of its single metal counterpart.[16, 17] The internal stress of crystallites could be relieved with the anisotropic volume change of the two elements and thus the capacity stability can be improved.[18] The electronic conductivity of dual-transition-metal oxides (DTMOs)

may be enhanced because of the relatively lower activation energy for electron transport between the heterogeneous cations with multiple valence states.[19, 20] As a result, the electrochemical properties can be tuned by metal substitution, as the redox potential of the electrode composed of dual-metal oxide is quite different from the single components and their mixture.[21] Recently, Fe-based DTMOs (MFe_2O_4 , $M=Mn, Co, Ni, Cu, Zn$, etc.), working through an eight electrons conversion reaction during the lithiation process, have been investigated as anode materials in LIBs, showing high reversible capacity.[22-26] However, DTMOs still deliver a poor cycling performance caused by the volume expansion and contraction so far. Dispersing TMOs on graphene as a matrix with high surface area and good chemical stability can improve the conductivity of the electrode and alleviating the volume change of the supported particles.[27, 28] In addition, heteroatom doping of graphene could further increase its electronic conductivity and hence the lithium storage performance of the resulting composite is improved.[29]

Besides, controlling the morphology and structure significantly influences the performance of TMOs. Sizing-down TMO particles to nanoscale has been widely proved beneficial to shorten the Li^+ insertion/extraction pathway and thus to increase the reversible capacity and rate capability.[30] However, the larger amount of SEI layer may be formed on the smaller particles because of the relatively high contact area with the electrolyte, resulting in the rapid capacity fading.[15] Furthermore, a rational design of materials structure is desired for the nanosized particles. A variety of designs have been proposed to be effective for improving the electrochemical

property, including generating hierarchical meso-/micro-pores,[26] hollow spheres[31] and core/shell structures[28]. These novel geometries display less surface SEI layer compared with plain solid particles.[32-35] Among them, hollow structures would be attractive to give a higher Li^+ permeability to reduce the diffusion length and also a large cavity to cushion the volume variation during the cycling.[36] However, so far, the synthesis and lithium storage study on DTMOs with hollow nanostructures have been rarely reported, due to the difficulties in obtaining the materials with well-defined composition and morphology.

Herein, we present a systematic study on the influential factors and constructing strategies of the Fe-based DTMOs supported on graphenes as LIBs anodes. Three substitutional metals were investigated to optimize the composition of Fe-based DTMOs (MFeO , $\text{M}=\text{Co}$, Mn , Zn). Two fundamental issues are addressed, i.e. the effects of hollowing the nanoparticles and N-doping the graphene as supports on the performance of TMOs as LIB anodes. Through the comparative investigations on the DTMO samples with different structures and compositions, the optimized Fe-based DTMO anode materials could be reached.

Experimental

Preparation of graphene oxide

Graphene oxide (GO) was synthesized with a modified Hummers method. 5 g graphite and 3.75 g NaNO_3 were added into 150 mL concentrated H_2SO_4 and the mixture was stirred for 30 min. Then 20 g KMnO_4 was slowly added to the ice-cooled

mixture with continuously stirring. After 4 days, the above muddy mixture was diluted with 400 mL DI water in an ice bath. Then the reaction was ended with the addition of 30 mL H₂O₂ solution (30%). The suspension was stirred for 30 min, followed by standing and washing with H₂O/HCl solution (9/1, v/v, 8 L). The mixture was dialyzed for at least one week to remove excess ions. Finally, the resulting suspension was dispersed with DI water and sonicated to form graphene oxide (GO).

Preparation of MFe_x(OH)(y)/GO composites

20 mL aqueous solution of Co(OAc)₂·4H₂O and Fe(SO₄)₂·7H₂O (molar ratio of Co²⁺ : Fe²⁺ 1:x) was added dropwise into 300 mL GO/DI suspension (1 mg/mL) under vigorous stirring. The mixture was dispersed by sonication for 2 h and then stirred overnight, followed by the addition of 0.6 mL NH₃·H₂O. Afterwards, the suspension was refluxed at 90 °C for 4 h. It was then centrifuged, rinsed with DI water and lyophilized to obtain CoFe_x(OH)(y)/GO, where y represents the weight percentage of metal oxide in the final product. Synthesis of MnFe_x(OH)(y)/GO and ZnFe_x(OH)(y)/GO was similar to that of CoFe_x(OH)(y)/GO, except for modifying the precursor to Mn(OAc)₂·4H₂O or Zn(OAc)₂·2H₂O. All these three samples are denoted as MFe_x(OH)(y)/GO.

Preparation of MFe_xO(y)-graphene composites

To prepare MFe_xO(y)/NG, MFe_x(OH)(y)/GO samples were thermally treated at 500 °C for 2 h under 50% NH₃/Ar, followed by the passivation in 1% O₂/Ar at room temperature (R.T.) for 1 h before being exposed to air. After that, the samples were

further heated at 300 °C for 2 h in 1% O₂/Ar to obtain MFe_xO(y)/NG-h, where h stands for hollow MFe_xO NPs. 50% H₂/Ar or Ar atmosphere were applied instead of NH₃/Ar to give MFe_xO(y)/G-H₂ and MFe_xO(y)/G-Ar, respectively. The samples were subsequently pyrolyzed with the same oxidation process as above, yielding hollow MFe_xO(y)/G-h and solid MFe_xO(y)/G-s, respectively.

FeO(y)/NG-h, FeO(y)/G-h and FeO(y)/G-s were prepared through the same procedures as synthesizing MFe_x(OH)(y)/GO composites only with Fe(SO₄)₂·7H₂O as salt precursor.

Electrochemical Test

Electrochemical tests were carried out in coin cells (CR2025) which assembled in Ar-filled glovebox. 80 wt% active materials (graphene-metal oxide composites), 10 wt% carbon black (Super P) and 10 wt% polyvinylidene fluoride (PVDF) were mixed well in N-methyl-2-pyrrolidinone (NMP). The obtained slurry was pasted onto Cu foil to form the working electrode, which was dried in vacuum at 100 °C and compressed under the pressure at 20 MPa. The coating density of the active materials was about 1.0 mg cm⁻². Lithium metal was used as the counter and reference electrode, while Celgard 2325 membrane was used as the separator. The electrolyte was obtained by dissolving 1 mol L⁻¹ LiPF₆ in the mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v). The charge/discharge tests were performed using a BTS battery test system at a voltage window of 0.01-3.0 V (vs. Li/Li⁺). CV (0.01-3.0 V, 0.2 mV s⁻¹) was performed on a ZAHNER electrochemical workstation. EIS

measurements were recorded on the same electrochemical workstation with amplitude of 5 mV in the frequency range of 10 mHz-100 kHz.

Characterizations

Transmission electron microscopy (TEM) images were obtained using a JEM-2100F (JEOL) microscope operating at 200 kV, while STEM images and EDS mapping of the samples obtained with the accessories attached to the instrument. X-ray diffraction (XRD) patterns were collected with a D8-advance X-ray diffractometer (Bruker) with Cu Ka radiation (40 kV, 40 mA) at a scan rate of $1^{\circ}\cdot\text{min}^{-1}$. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis ultra DLD equipped with an Al Ka X-ray source. All XPS spectra were calibrated by setting the graphitic C1s signal to 284.6 eV and were fitted after a Shirley type background subtraction.

Results and discussion

Synthesis and characterizations of DTMO samples

Fig. 1 Diagrammatic representation of DTMO NPs grown on NG or RGO. Gray: complex metal hydroxide; blue: M-Fe alloy NPs; yellow: MFeO complex metal oxide NPs; purple: M metal; pink: M oxide (MO_x) NPs.

Fig. 1 presents the synthesis strategy of DTMO NPs on NG or RGO. M^{2+} and Fe^{2+} were firstly hydrolyzed with the assistance of ammonia and deposited on GO in the form of hydroxide. Then three kinds of atmosphere, i.e., ammonia, hydrogen and argon, were applied to transform the hydroxide to NPs with different composition and morphology. The reductive NH_3 atmosphere reduced the M-Fe hydroxide to metal or M-Fe alloy.[37, 38] At the meantime, N atoms were doped into GO to form NG. After the passivation with 1% O_2 at R.T., oxide shells were formed on the surface of the M-Fe alloy to protect the inner core from further oxidation as exposed to air. Similarly, dual-metal hydroxides were decomposed and reduced to metallic NPs with H_2

treatment, followed by the formation of the alloy/metal@oxide core@shell structure. The hydroxides can be directly decomposed into metal oxide NPs under Ar. To transfer the alloy NPs to oxides, the three intermediate products were heated in 1% O₂ at 300 °C. For the NH₃ and H₂ treated core@shell samples, the outward diffusion of metal atoms (Fe and M) are more rapid than the inward diffusion of oxygen,[39-41] which lead to the formation of the hollow structure with the quick consumption of the core. However, the oxides prepared by Ar treatment simply resulted in solid structure because of the lack of the formation of diffusion couple.

Fig. 2 TEM images and size distributions of (a-c) $\text{CoFe}_2\text{O}(60)/\text{NG-h}$, $\text{MnFe}_2\text{O}(60)/\text{NG-h}$, $\text{ZnFe}_2\text{O}(60)/\text{NG-h}$, (d-f) $\text{CoFe}_2\text{O}(60)/\text{G-h}$, $\text{MnFe}_2\text{O}(60)/\text{G-h}$, $\text{ZnFe}_2\text{O}(60)/\text{G-h}$ and (g-i) $\text{CoFe}_2\text{O}(60)/\text{G-s}$, $\text{MnFe}_2\text{O}(60)/\text{G-s}$, $\text{ZnFe}_2\text{O}(60)/\text{G-s}$.

Fig. 2 shows the TEM images of the MFe_2O (molar ratio 1:2) NPs supported on graphene prepared by NH_3 , H_2 and Ar, respectively. $\text{CoFe}_2\text{O}(60)/\text{NG-h}$ and $\text{MnFe}_2\text{O}(60)/\text{NG-h}$ show the similar hollow morphology, while the former have the more homogeneous particle size distribution and smaller average diameter. Meso-sized voids can be observed in the particles of $\text{ZnFe}_2\text{O}(60)/\text{NG-h}$ (Fig. 2c), which could be explained by the outward diffusion rate difference between Zn and Fe atoms caused by the large atomic weight difference. H_2 treatment can also create hollow structures (Fig. 2d-f). Compared with their counterparts with NH_3 , $\text{CoFe}_2\text{O}(60)/\text{G-h}$ and $\text{ZnFe}_2\text{O}(60)/\text{G-h}$ show smaller particle average sizes and narrower distributions. However, the morphology of $\text{MnFe}_2\text{O}(60)/\text{G-h}$ particles are mostly irregular, probably caused by the phase segregation of Mn and Fe in a highly reducing atmosphere. This situation could be relieved by changing the stoichiometry to MnFeO , as shown in Fig. S1c. As expected, all the Ar-treated samples display solid structure with smaller average diameters (Fig. 2 g-i), compared with the hollow particles.

Fig. 3 (a, b) High resolution TEM images, (c) STEM image, (d) EDS spectrum, and (e) element mappings of Fe, Co, O, C of $\text{CoFe}_2\text{O}_4(60)/\text{NG-h}$.

The formation of DTMO hollow/solid particles was further confirmed by HRTEM and EDS. Figs. 3a, b show the HRTEM image of one particle in $\text{CoFe}_2\text{O}_4(60)/\text{NG-h}$, which clearly exhibits hollow structure with the shell thickness of about 4.7 nm. The fringe spacings of 0.248 and 0.292 nm agree with the (311) and (220) planes of CoFe_2O_4 . The formation of CoFe_2O_4 can be reflected by STEM and EDS mapping (Fig. 3c-e). Fe, Co and O elements are homogeneously distributed on the periphery of the NP, suggesting that the shell of NP is composed of DTMO without phase segregation. The C element mapping confirms the existence of graphene. In the cases of Ar atmosphere, the formation of solid NPs is revealed by HRTEM, as shown in Fig. 4. Clear lattice fringes of CoFe_2O_4 , MnFe_2O_4 and ZnFe_2O_4 phases could be observed. Furthermore, the corresponding element mappings also confirm the homogeneous

distributions of Co-Fe, Mn-Fe, Zn-Fe within the solid particles. Taking into account the small size of the NP (ca. 20 nm), above results demonstrate the effectiveness of our strategy to fabricating DTMO NPs with controllable morphology.

Fig. 4 High resolution TEM images, STEM images and element mappings of (a-c) $\text{CoFe}_2\text{O}(60)/\text{G-s}$, (d-f) $\text{MnFe}_2\text{O}(60)/\text{G-s}$, and (g-i) $\text{ZnFe}_2\text{O}(60)/\text{G-s}$.

Fig. 5 XRD patterns of (a) $\text{CoFe}_2\text{O}(60)/\text{NG-h}$, $\text{MnFe}_2\text{O}(60)/\text{NG-h}$ and $\text{ZnFe}_2\text{O}(60)/\text{NG-h}$; (b) $\text{CoFe}_2\text{O}(60)/\text{G-s}$, $\text{MnFe}_2\text{O}(60)/\text{G-s}$ and $\text{ZnFe}_2\text{O}(60)/\text{G-s}$.

The compositions of the samples were further examined by XRD. As shown in Fig. 5, the diffraction peaks at about 25.5° correspond to the (002) characteristic peak of NG. Its smaller angle than that of graphite ($\sim 26.5^\circ$) represents the effective inhibition of the restacking of graphene by supporting metal oxide NPs. Without the secondary metal, the reflections of $\text{FeO}/\text{NG-h}$ are in agreement with Fe_2O_3 (JCPDS 39-1346, Fig. S2). Among the three types of DTMOs, the (hollow or solid) CoFe_2O samples are composed of almost phase pure CoFe_2O_4 (JCPDS 03-0864), despite a small amount of Co_3O_4 (JCPDS 42-1467) phase detected in $\text{CoFe}_2\text{O}(60)/\text{NG-h}$. Strong peaks from Fe_2O_3 (JCPDS 39-1346) can be found in both $\text{MnFe}_2\text{O}(60)/\text{NG-h}$ and $\text{MnFe}_2\text{O}(60)/\text{G-s}$, rather than MnFe_2O_4 (JCPDS 10-0319), indicating the serious phase separation, which is consistent with TEM observation. The diffraction peaks of $\text{ZnFe}_2\text{O}(60)/\text{G-s}$ can be indexed to ZnFe_2O_4 (JCPDS 22-1012), indicating the formation of phase pure DTMO NPs. However, considerable ZnO (JCPDS 36-1451) can be detected in the hollow sample $\text{ZnFe}_2\text{O}(60)/\text{NG-h}$, indicating the phase segregation probably due to the different diffusion rates of Zn and Fe as afore-discussed.

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Fig. 6 (a) XPS survey, high-resolution (b) Fe 2p, and (c) Co 2p spectra of CoFe₂O(60)/NG-h and CoFe₂O(60)/G-s. Inset of (a) shows a high resolution N 1s spectrum of CoFe₂O(60)/NG-h.

Fig. 6 shows the XPS spectra of the hollow/solid DTMO samples, represented by CoFe₂O samples. The XPS survey spectra of CoFe₂O(60)/NG-h and CoFe₂O(60)/G-s suggest that the composites are composed of C, O, Fe, Co elements. As shown in the inset of Fig. 6a, NH₃ treatment at 500 °C resulted in N doping in the forms of pyridinic N (N1, 398.3 eV) and pyrrolic N (N2, 399.7 eV). In the high-resolution Fe 2p spectra (Fig. 6b), the separation of 13.3 eV between Fe2p_{3/2} and Fe2p_{1/2} is the characteristic of Fe³⁺. The existence of Fe²⁺ can be excluded because the signal of Fe²⁺ is centered at ~708.6 eV.[42, 43] Co 2p spectra feature two peaks of Co2p_{3/2} and Co2p_{1/2} spin orbit (Fig. 6c). The deconvolution of Co2p_{3/2} suggests the coexistence of

Co^{3+} (~ 780.4 eV) and Co^{2+} (~ 782.3 eV) states in the composites. The obvious satellite around 786.2 eV can be assigned to Co^{2+} .^[44] It is concluded that Co^{2+} , Fe^{3+} and relatively small amounts of Co^{3+} existed on the surface of $\text{CoFe}_2\text{O}_4(60)/\text{NG-h}$ and $\text{CoFe}_2\text{O}_4(60)/\text{G-s}$, being consistent with the oxidation state in CoFe_2O_4 .^[45]

Effect of DTMO composition on LIB anode performance

Fig. 7 (a) Cycling performance at a current density of 200 mA g⁻¹ and (b) Nyquist plots of FeO(45)/NG-h, CoFeO(45)/NG-h, MnFeO(45)/NG-h and ZnFeO(45)/NG-h. For (a), empty and filled symbols represent charge and discharge capacity, respectively. [See Fig. S3 for corresponding CV curves and voltage profiles.](#)

The improvement of anode performance by the formation of DTMO composites was demonstrated by comparing the capacities of FeO(45)/NG-h and MnFeO(45)/NG-h samples. As shown in Fig. 7a, the discharge capacities of CoFeO(45)/NG-h and FeO(45)/NG-h in the first cycle were close at 1184.1 and 1185.7 mAh g⁻¹, respectively. However, fast capacity decay of FeO(45)/NG-h was observed, giving a lower initial Coulombic efficiency (44.7%) than that of CoFeO(45)/NG-h (63.6%). After 40 cycles, the reversible capacities of CoFeO(45)/NG-h, ZnFeO(45)/NG-h and

MnFeO(45)/NG-h leveled off at 621.5, 547 and 400 mAh g⁻¹, respectively, which are all superior to that of single metal oxide FeO(45)/NG-h. This result clearly proves that the formation of DTMO is beneficial for the electrochemical property. The highest capacity of CoFeO sample might stem from the high fraction of DTMO, as revealed by XRD analysis, and the homogeneous particle size, as displayed in Figs. S2 and S1. EIS measurements were conducted to investigate the conductivity of the materials. As shown in Fig. 7b, the Nyquist plots for the samples are composed of two separated or overlapped semicircles in the high-to-medium frequencies region. The diameters of the semicircles of CoFeO(45)/NG-h and ZnFeO(45)/NG-h are much smaller than that of MnFeO(45)/NG-h, implying the smaller charge-transfer resistance between electrode and electrolyte of the formers. The depressed semicircle in high frequency for FeO(45)/NG-h represents the Li⁺ migration through the SEI layer,[46] which is the main cause for the initial irreversible capacity loss.[15] It is clear that DTMO composites showed superior performance to FeO/NG-h composites, among which Co-Fe oxides material exhibits the best specific capacity and cycling stability.

Effect of DTMO structure on LIB anode performance

Fig. 8 Cycling performance of CoFe₂O₄(60)/NG-h, CoFe₂O₄(60)/G-h and CoFe₂O₄(60)/G-s at a density of (a) 200 mA g⁻¹ and (b) 1000 mA g⁻¹. (c) Rate capability at different current densities and (d) Nyquist plots of CoFe₂O₄(60)/NG-h, CoFe₂O₄(60)/G-h and CoFe₂O₄(60)/G-s. For (c-e), empty and filled symbols represent charge and discharge capacity, respectively.

A comparison of the cycling performance at a current density of 200 mA g⁻¹ for CoFe₂O₄(60)/NG-h, CoFe₂O₄(60)/G-h and CoFe₂O₄(60)/G-s is shown in Fig. 8a (see Figs. S4 and S5 for CV curves and voltage profiles). CoFe₂O₄(60)/G-s electrode gave an initial discharge capacity of 1294.6 mAh g⁻¹ and retained at 837.7 mA h g⁻¹ after 50 cycles, while the hollow structures, CoFe₂O₄(60)/G-h and CoFe₂O₄(60)/NG-h, exhibited lower reversible capacities. The low initial capacity of CoFe₂O₄(60)/G-h was probably due to the slight external short circuit of the electrode after the battery

assembling, which may recover after several cycles. CoFe₂O(60)/G-s still displays the best cycling performance at a higher density of 1000 mA g⁻¹ (Fig. 8b). The discharge capacity decreased slightly during the first 30 cycles. From the 30th to 200th cycles, the capacity increased gradually to 1000.3 mA g⁻¹, probably due to the reactivation process on the electrodes.[17, 47] In contrast, it can be noted that limited reactivation capacities were achieved at 200 mA g⁻¹ (Fig. 8a), which can be explained by the larger capacity fading during the initial cycles and thus more obvious capacity recoveries were observed at higher current density.[31] The enhancement of the capacity beyond the theoretical value (914 mAh g⁻¹ of CoFe₂O₄) suggests the synergistic effect between the well-fabricated DTMO and graphene. By contrast, the discharge capacity of CoFe₂O(60)/NG-h and CoFe₂O(60)/G-h dropped to 549 and 302 mAh g⁻¹ after the same cycle numbers, respectively. This further demonstrates the more excellent cycling stability of CoFe₂O(60)/G-s than those of CoFe₂O(60)/NG-h and CoFe₂O(60)/G-h, since the reactivation process of the latter cannot compensate their capacity fading. In addition, CoFe₂O(60)/G-s provided a better rate capability at various current densities ranging from 200 to 2000 mA g⁻¹ compared with the two hollow structure electrodes (Fig. 8c). The specific capacity of CoFe₂O(60)/G-s decreased steadily as the current density increased but still remained a relatively high value. When the current density returned back to 200 mA g⁻¹ after 50 cycles, a highly reversible capacity of 800 mAh g⁻¹ can be restored.

Previous literatures suggested that the hollow sphere geometry could be better than the solid one in the terms of volumetric and gravimetric capacities.[36, 48] Our results

clearly indicate that the solid DTMO particles perform better than their hollow counterparts, which is quite different from the previous literatures. EIS measurements were carried out to understand this behavior. Fig. 8d shows the Nyquist plots of the above three samples after 5 cycles. It can be seen that the charge-transfer resistance for $\text{CoFe}_2\text{O}(60)/\text{G-s}$ is smaller than that of $\text{CoFe}_2\text{O}(60)/\text{G-h}$. Correspondingly, $\text{CoFe}_2\text{O}(60)/\text{G-s}$ performed the better rate capability than $\text{CoFe}_2\text{O}(60)/\text{G-h}$. This result indicates that the solid NPs are beneficial to the charge transfer kinetics. It should be noted that, compared with literatures on hollow LIB anode materials synthesized by various template methods,[47, 49] our synthesis strategy delivers much smaller hollow NPs in the size range from 4.5 to 26.5 nm, composed of smaller crystallites in the shells, as revealed in Figs 3a, b. The large resistance across the crystallite interfaces may reduce the charge transfer kinetics and result in poor rate capability of $\text{CoFe}_2\text{O}(60)/\text{G-s}$. The dominant role of the limited charge transfer across crystallite interfaces could be proved by improving the overall electrical conductivity by doping graphenes with nitrogen. As shown in Fig. 8d, the $\text{CoFe}_2\text{O}(60)/\text{NG-h}$ sample prepared by NH_3 treatment shows the lowest resistance, originated from the enhanced electron mobility by N-doping. However, it exhibited the poorest rate capability, which suggests that the faradic performance of DTMO polycrystallites cannot be compensated by the improved conductivity of carbon. Moreover, the worse rate capability of $\text{CoFe}_2\text{O}(60)/\text{NG-h}$ than $\text{CoFe}_2\text{O}(60)/\text{G-h}$ may be attributed to the thinner shell walls of $\text{CoFe}_2\text{O}(60)/\text{NG-h}$, which may have smaller crystallites and more interfaces, as revealed in Fig. 2.

Moreover, the morphology of the hollow and nonhollow samples after 200 cycles at a current density of 1000 mA g^{-1} were examined by TEM (Fig. 9). It reveals that the hollow structure of the composite cannot be retained and cracked into small pieces during cycling process. However, $\text{CoFe}_2\text{O}_4(60)/\text{G-s}$ showed a superior structural stability as the particles are still in the origin size distribution range (Fig. 9b). The result suggests the solid particles in $\text{CoFe}_2\text{O}_4(60)/\text{G-s}$ tolerates larger strain, while the hollow particles suffer from serious volume change and cracking. The fractures formed during cycling will provide new sites for SEI layer growth, which should contribute to the irreversible capacity fading of the hollow structures electrodes.[15] The similar phenomenon has been observed for the nanosized single metal oxide hollow particles. The structural collapse owing to the volumetric stress and/or the pulverization of the hollow NPs was also regarded as the main cause of the decay in capacity.[50]

Fig. 9 TEM images of (a) CoFe₂O(60)/G-h and (b) CoFe₂O(60)/G-s upon cycling at a density of 1000 mA g⁻¹ for 200 cycles.

Conclusions

In summary, DTMO NPs with hollow and solid structures supported on graphene were successfully synthesized through controlling the atmosphere where precursors decomposed. Nanosized phase pure CoFe₂O with hollow structure was prepared through Kirkendall effect. The NH₃ and H₂ treated samples exhibited hollow structure, while the Ar treatment resulted in the fabrication of solid NPs. HRTEM, EDS mapping and XRD analysis revealed the uniform distribution of two metallic elements in the NPs and the formation of phase pure DTMO composites. Electrochemical tests demonstrated that the DTMO composites showed superior performance to the iron oxide/graphene composite, revealing the vital role of dual-metal components in regulating the electrochemical performance. The CoFe₂O(60)/G-s sample exhibited an excellent capacity up to 1000 mAh g⁻¹ and cycling stability. Interestingly, our results show that, as LIB anodes, the nanosized hollow DTMOs exhibited inferior performance to the solid one, because of the large interfacial resistance and structural changes upon cycling for the nanosized hollow particles.

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