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Facile preparation of free-standing rGO paper-based Ni-Mn LDH/graphene superlattice composites as pseudocapacitive electrode

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A novel film electrode was assembled via the simple filtration process, with rGO paper as the substrate and Ni-Mn LDH/graphene superlattice composites as the functional layer. The electrode presents typical pseudocapacitive behaviours with excellent rate property and cycle stability.

To meet the demand of developing energy storage devices with high energy density and long cycle life, many metal oxides/hydroxides have been investigated intensely, including RuO$_2$, MnO$_2$, Co$_3$O$_4$, Co(OH)$_2$ et al and their binary types. Specially, Ni-Mn layered double hydroxides (Ni-Mn LDH) have been regarded as a promising candidate with environmental benignity and high capacity originating from the multivalence of Mn atoms and synergistic effects of two elements. However, as so-called extrinsic pseudocapacitive material, it would present battery-type behaviour in bulk particle size, suffering drawbacks of low rate capability and poor cycle life, because of the low conductivity and limitations from diffusion process. Accordingly, many efforts have been proposed: Hybridizing conductive carbon materials, including carbon nanotubes and graphene, with transition metal oxides/hydroxides nanostructures has been proposed to enhance the overall electrochemical performance. Especially, as graphene has an extremely high specific surface area (ca. 2600 m$^2$ g$^{-1}$ in theory) and is highly conductive (ca. 103–104 S cm$^{-1}$), it can introduce large electrochemical double layer capacitance as well as acts as an efficient current-collecting component, beneficial for transition-metal oxides/hydroxides to deliver high pseudocapacitance; In-situ growth of LDH arrays on Ni foam without binder, in favor of enhancing the electronic conductivity and interface area between electrodes and electrolytes, could also improve the performances of electrodes. Nevertheless, the effects above are still unsatisfactory because battery-type behaviours still dominate, limiting the rate property and cycle stability. Preparation of Ni-Co LDH/graphene composites with superlattice structure has been reported to overcome the problem, which exhibit typical pseudocapacitive behaviours and good rate property owing to the nano-sized effects. But the electrode fabrication process is quite complicated and hard to scale up, in which ITO glass and spin-coater are employed to obtain ultrathin functional layer.

To address the problem, we design a novel composite film with two-layer structure, which is fabricated via a simple filtration process. The electrode consists of rGO paper as the substrate and Ni-Mn LDH/graphene superlattice composites as the functional layer. Such special structure combines the advantages of high conductivity and ultralight weight of free-standing rGO paper and high rate properties of Ni-Mn LDH/graphene composites. Especially, none use of binder will improve the conductivity of electrode further. The fabrication process is illustrated in Fig. 1(a), in which rGO nanosheet solution was first filtrated through the membrane filter to form a substrate, followed by Ni-Mn LDH/graphene composites dispersed in the solution. As is shown in Fig. 1(b), the pure rGO paper prepared exhibits a glossy surface, while the composite film electrode with a functional layer possesses

Fig. 1 Fabrication of the film electrode through filtration (a); SEM image of film electrode from top-view and the macro-photograph of composite film and pure rGO paper peeled off from membrane (b).
a pale and rough surface with small open holes, due to the flocculation morphology of the composites with large specific surface area of 346 m$^2$ g$^{-1}$ (IV-typed N$_2$ adsorption/desorption isotherm, Fig. S1 (ESI†)). Such open structure will facilitate the sufficient immersion of electrolytes and induce more reaction sites.

The composition of Ni-Mn LDH and graphene nanosheets via molecular-scale heteroassembly can make full use of the maximum sheet of LDH to expose more atoms and the high conductivity of graphene. The special design can be realized through the formamide-assisted mechanical stirring method, utilizing the special feature of LDH which can be exploited into single-layer nanosheets easily. The cationic LDH nanosheets and anionic graphene could rightfully sandwich each other to form true superlattice lamellar nanocomposites. As a result, nano-sized and synergistic effects have been harvested in achieving typical pseudocapacitive behaviours with high capacity and high power rate.

Fig. 2(a) and (b) depict AFM (atomic force microscopy) images of exploited Ni-Mn LDH and graphene nanosheets, respectively. Results prove that LDH and graphene sheets have been exploited into nanosheets with thickness of about 1-2 nm after treatments in formamide, which can also be reflected by the Tyndall effects (Fig. S2, ESI†) that a green beam is transmitted through the colloidal solution. XRD results in Fig. 2(c) confirm the flocculated precipitates, with wool-like appearance (Fig. 1(b), Fig. 2(e)) contain LDH and rGO phases, while Raman spectra in Fig. 2(d) also verifies the formation of LDH/graphene hybrid composites, exhibiting well-documented D and G bands of graphene (1327 and 1586 cm$^{-1}$, respectively), and the signal peak of M-OH (M=Ni, Mn) stretching mode band (518 cm$^{-1}$). The superlattice structure of the composites can be identified by SAED (selected area electron diffractions) in Fig. 2(f), displaying that the diffraction rings of Ni-Mn LDH nanosheets and graphene nanosheets were assignable, endorsing that two component nanosheets were assembled on a molecular-scale. Furthermore, it can also be evidenced by elemental mapping results of the composites (Fig. S3, ESI†), illustrating the successful heterostacking of LDH and graphene nanosheets with homogeneous element distribution.

CV tests in Fig. 3(a) reveal that pseudocapacitive behaviours dominate for the composite film. The widened peak shape and decreased peak position separation between redox reactions compared to electrodes fabricated by traditional method indicate that the capacitance are mainly attributed to the redox pseudocapacitive behaviours of Ni-Mn LDH, of which redox equations are listed below:\(^{1,10}\)

\[
\text{LDH-Ni(OH)}_2 + \text{OH} \leftrightarrow \text{LDH-NiOOH} + \text{H}_2 \text{O} + e^- \quad (1)
\]

\[
\text{LDH-Mn(OH)}_2 + \text{OH} \leftrightarrow \text{LDH-MnOOH} + \text{H}_2 \text{O} + e^- \quad (2)
\]

\[
\text{LDH-MnOOH} + \text{OH} \leftrightarrow \text{LDH-MnO}_2 + \text{H}_2 \text{O} + e^- \quad (3)
\]

CV curve of the pure rGO paper at the same scan rate is also tested for comparison (Fig. S4(a), ESI†), implying that most of capacitance is attributed to the functional layer. Galvanostatic curves of the film electrode at different current densities are presented in Fig. 3(b). It can be seen that the plateau region has become indistinct, after reassemble with graphene on a molecular-scale, which is one typical symbol of pseudocapacitive behaviours.\(^2\) The calculated specific capacitance (Fig. S4(b), ESI†) prove that the composite film still presents 162.6 mF cm$^{-2}$ at 16 mA cm$^{-2}$ (equals about 421 F g$^{-1}$ at the current density of 36 A g$^{-1}$ based on the mass of loading materials), nearly about 75 % of 217.8 mF cm$^{-2}$ at 2 mA cm$^{-2}$, confirming its excellent rate performance. In order to reveal the effects of graphene composited and rGO paper, pure Ni-Mn LDH electrode with similar loadings was prepared via a traditional method for comparison. Results (Fig. S5(a) and (b), ESI†) show that compared to the composite film, pure Ni-Mn LDH electrode exhibits rather poor rate property and cycle stability, due to its low conductivity and structural destruction,
originating from volume change caused by the insertion of ions during energy storage process.\(^1\), \(^2\)

EIS tests of the film electrode under different open circuit potential are performed for detailed electrochemical information. Results in Fig. 3(c) indicate that the slope values of the line in low-frequency region for the film electrode under different open circuit potential are similar, quite different from typical battery electrode, impedance of which is potential-dependent.\(^3\) Furthermore, compared to pure LDH electrode, \(R_s\) (serial resistance) of the composite film is decreased from about 1.6 to 1.2 ohm (Fig. S5(b), ESI†), demonstrating that the composited graphene will improve the conductivity of electrode further, then enhancing the electrochemical performance. Therefore, Ni-Mn LDH in the composite contributes to the capacity mainly, due to its redox energy storage mechanism, while graphene and rGO paper would improve the rate property of LDH materials greatly, via providing sufficient electrons at high rates. Besides, due to the molecular-scale composition, the number of surface reaction sites could be increased greatly, inducing dominated pseudocapacitive behaviours with high rate property.

Long-time cycle stability test of the composite film is shown in Fig. 3(d). It can be seen that the film electrode exhibits excellent cycle stability with only about 5% loss after 10000 times cycles at the current density of 4 mA cm\(^{-2}\). Even under the current density increased by 4 times, it still maintains capacity retention of about 80%. Such a good cycle stability can also be attributed to the composited graphene, which helps strengthen the structure stability of LDHs. Besides, via exploitation, more atoms of Ni-Mn LDH main layers will arise on the surface of the sheet and react with OH\(^-\) ions directly, which may weaken the inner structure collapse of LDH caused by the insertion of OH\(^-\) between layers.\(^4\) Excellent cycle stability also reflects the stable combination between two layers, implying good practical utilization of the fabrication process. Compared to Co-Ni/ graphene composite film assembled onto ITO glass,\(^5\) the rate property of the composite film is comparable, meanwhile possessing better cycle stability, which further confirms the feasibility of our method. Detailed comparison information is presented in the Table S1 (ESI†), which also summarizes capacitances, cycle stability and assemble methods of rGO paper-based electrodes and LDH/graphene electrodes assembled via the traditional method. Results indicate that although the specific capacitance of our composite film is not the highest, it can be still competitive, especially considering that the facile assemble method and stable cycle stability is superior to some systems, which have been modified with more complicated and costly technology.

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Conclusions

A novel rGO paper-based Ni-Mn LDH/graphene composite film electrode prepared by a simple filtration process is reported. This two-layer film electrode, consisting of rGO paper as the substrate and LDH/graphene superlattice composites as the functional layer, combines the high conductivity, ultralight gravity of rGO paper and high rate property of LDH/graphene composites, exhibiting high rate specific capacitance and stable cycle life. Such facile fabrication process will make this free-standing film electrode with high performance become promising in the application of flexible and wearable energy storage device.

Notes and references

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