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Hierarchical flower-like NiCo₂O₄@TiO₂ hetero-nanosheets as anodes for lithium ion batteries

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Flower-like NiCo₂O₄ consisting of nanosheets are synthesized by hydrothermal technique and subsequently surface-modified with a TiO₂ ultrathin layer by a hydrolysis process at low temperature. It is found that NiCo₂O₄@TiO₂ exhibits superior electrochemical performances over NiCo₂O₄ in terms of rate capability and cyclability. After 60 cycles at 100 mA g⁻¹, NiCo₂O₄@TiO₂ showed 78% capacity retention compared with 57% for bare NiCo₂O₄. Analysis from the electrochemical measurements indicates that the improved electrochemical performances of NiCo₂O₄@TiO₂ might be attributed to a higher lithium diffusion rate, smaller charge-transfer resistance and more structural stability. Kelvin probe force microscopy measurements reveal that NiCo₂O₄@TiO₂ has a lower work function than those of the pristine one, which help to facilitate electron transfer in composites. In addition, the electric field between NiCo₂O₄ and TiO₂ resulting from the difference in work functions is also expected to enhance the electrochemical performances.

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1. Introduction

Owing to their advantages on lifespan and energy density, rechargeable lithium-ion batteries have attracted increasing interest due to their wide application in energy storage systems (ESSs) and electric vehicles (EV/HEV/PHEV).¹⁻⁵ The increasing demands for high-energy or high-power batteries are driving the research interest in electrode materials with a large specific energy.⁶⁻⁸ Unfortunately, graphite or carbon-based materials with low theoretical specific capacity (*ca.* 372 mA h g⁻¹) are not highly desirable for the high energy-density batteries.^{9,10} In contrast, binary metal oxides, such as ZnFe₂O₄, NiFe₂O₄, ZnMn₂O₄ and NiCo₂O₄, seem to be a more promising alternative because of their high theoretical capacity and high redox activity.¹¹⁻¹⁴ Among the numerous investigated binary metal oxides, spinel nickel cobaltite (NiCo₂O₄) has been regarded as a promising electrode composite due to the high specific capacity (890 mA h g⁻¹), environmental friendliness and low cost.^{15,16} However, NiCo₂O₄ also suffers from sluggish reaction kinetics and drastic volume change during lithium insertion/extraction processes, resulting in the structure deterioration (pulverization or aggregation) and consequent severe decay in capacity.^{17,18} To address above significant drawbacks, lots of

effective strategies have been implemented and surface-modification has been proved to be an effective way to improve electrochemical performances, which not only suppresses the formation of excessive amounts of SEI but also stabilizes structure of the active materials.¹⁹ Kou *et al.*¹⁹ reported that Al₂O₃-coated NiCo₂O₄ exhibits improved cyclability with a reversible capacity of 395 mA h g⁻¹ after 50 cycles. Titanium oxide (TiO₂) has been investigated extensively as an anode material, whose volume expansion is less than 4% during the lithium insertion processes.^{20,21} The low volume expansion would be desirable for adhesion of the coating to the matrix materials, resulting in the enhanced structural stability and a excellent cycle life. On the other hand, TiO₂-coating layer acting as an interfacial barrier can also significantly enhance cyclic performances by suppressing the exothermic reaction between the active material and the electrolyte.

In view of all the above, we employ hydrolysis technique to coat TiO₂ on flower-like NiCo₂O₄ consisting of nanosheets at low temperature, and the effect of TiO₂-coating on the kinetics of Li⁺ insertion/extraction is systematically investigated. It is found that the high capacity of NiCo₂O₄ and the excellent stability of TiO₂ as well as the hierarchical structure make the designed composite demonstrate improved rate capability and cycling stability.

2. Experimental

2.1 Preparation and characterization of anode materials

Flower-like NiCo₂O₄ consisting of nanosheets are prepared by hydrothermal technique. All chemicals are purchased from

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Aladin and used without further purification. In a typical synthesis, 6 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 12 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ are thoroughly dissolved in 30 ml of deionized water and 30 ml of absolute ethanol, followed by stirring until a light pink solution is formed. Then, 0.1 g of polyvinyl pyrrolidone (PVP) is added to the above aqueous solution under continuous stirring. After vigorous stirring for another 60 min, the resulted mixture is transferred into a 100 ml Teflon-lined autoclave, sealed and maintained at 180 °C for 36 h. After being cooled to room temperature, the precipitates are collected through centrifugation, washed several times with de-ionized water and ethanol, dried at 100 °C overnight under vacuum. The obtained precursors (Ni–Co–O) are calcinated at 450 °C for 5 h in air to get flower-like NiCo_2O_4 powders. $\text{NiCo}_2\text{O}_4@ \text{TiO}_2$ composites are synthesized by a hydrolysis process at low temperature using tetrabutyl titanate ($\text{Ti}(\text{OC}_4\text{H}_9)_4$) and Ni–Co–O powders as precursors. 0.23 g of the as-prepared Ni–Co–O precursors are dispersed in 20 ml of absolute ethanol and 1 ml of deionized water under vigorous stirring at 4 °C. Then, 10 ml 10^{-3} M $\text{Ti}(\text{OC}_4\text{H}_9)_4$ ethanol solution is added dropwise into above solution. After stirring at 4 °C for another 24 h, the resulting precipitates are isolated by centrifugation, dried at 60 °C for 12 h and subsequently sintered at 450 °C for 5 h to obtain flower-like NiCo_2O_4 surface-modified with TiO_2 . The schematic illustration of the synthesis process for the NiCo_2O_4 and $\text{NiCo}_2\text{O}_4@ \text{TiO}_2$ characterized anode materials is shown in Fig. 1.

The crystalline structure of the as-synthesized powders is characterized by X-ray diffraction (XRD, Rigaku MiniFlex II) using CuK_α radiation ($\lambda = 0.15405$ nm). Thermo-gravimetric analysis (TGA) analysis are carried out using

thermogravimetric analysis (TGA, Netzsch STA449F3) from 30 to 600 °C at a heating rate of 5 °C min^{-1} under an air atmosphere. Scanning electron microscope (SEM) images are obtained on a Hitachi SU8010 field-emission scanning electron microscope equipped with an energy-dispersive spectroscopy (EDS). The TiO_2 content in the composite is determined by inductively coupled plasma OES spectrometer (ICP). Raman scattering is carried out on a Horiba/Jobin Yvon Raman instrument using a 532 nm emission line. Nitrogen sorption isotherms are measured at 77 K using a Micromeritics Tristar 3020 analyzer. Specific surface areas of the as-prepared powders are calculated according to the Brunauer–Emmett–Teller (BET) method. The pore size distribution is determined according to the theory of Barrett, Joyner and Halenda (BJH).

The surface potentials of NiCo_2O_4 and $\text{NiCo}_2\text{O}_4@ \text{TiO}_2$ are measured by Kelvin probe atomic force microscopy (KPFM) (Bruker dimension ICON, Germany).

2.2 Cell fabrication and characterization

The electrochemical performances of the as-fabricated samples are evaluated with CR2025-type coin cell and assembled in an argon-filled glove box (O_2 , $\text{H}_2\text{O} < 1$ ppm). The working electrodes are prepared by coating anode slurries which are made up of 70 wt% active material (NiCo_2O_4 or $\text{NiCo}_2\text{O}_4@ \text{TiO}_2$) with 10 wt% polyvinylidene fluoride (PVDF) and 20 wt% super-P in *N*-methyl-2-pyrrolidone. The anode slurry is cast onto a copper current collector and dried in vacuum at 110 °C for 12 h to remove the residual solvent. A lithium foil is used as the reference and counter electrodes, Cellgard 2300 microporous polyethylene membrane as separator. The electrolyte consists of 1 M

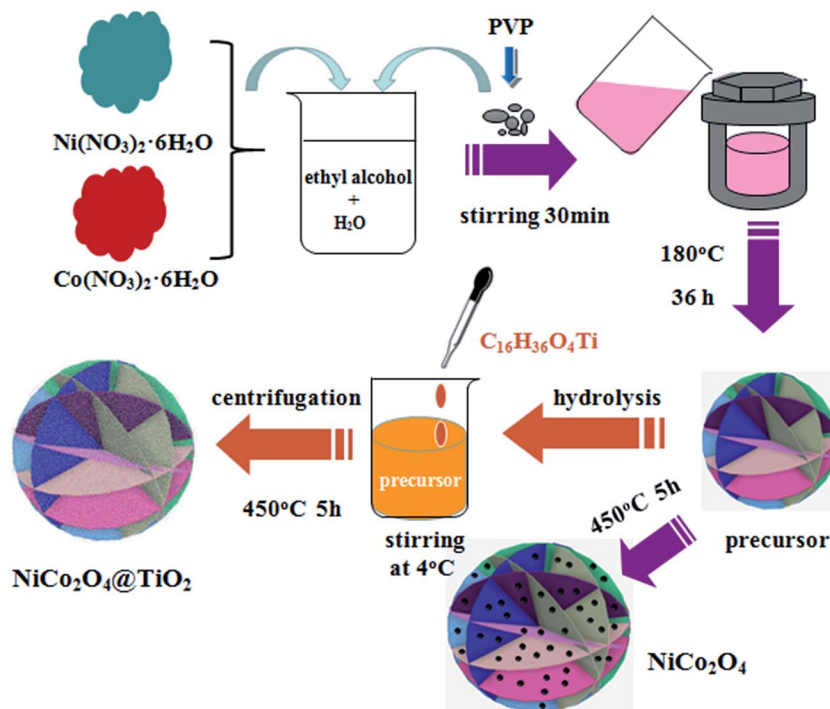


Fig. 1 Schematic illustration of the preparation process for NiCo_2O_4 and $\text{NiCo}_2\text{O}_4@ \text{TiO}_2$ powders.



LiPF_6 in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1 : 1 in volume). The cells are galvanostatically charged and discharged on a multichannel battery testing system (Land CT2001A, Wuhan, China) in the voltage range of 0.01–2.5 V. The cyclic voltammetry (CV) measurements are carried out using an Arbin instruments BT-2000 battery testing station, and the electrochemical impedance spectra of the electrodes are determined by an electrochemical workstation

(Zahner-Zennium) in the frequency range of 100 kHz to 10 mHz with an amplitude of 5 mV.

3. Results and discussion

3.1 Material characterization

Fig. 2 shows the thermogravimetric (TGA) curve of the as-synthesized Ni–Co–O precursor, measured from 30 to 800 °C at a heating rate of 3 °C min⁻¹ in air atmosphere. The initial 1.1% weight loss at the low temperature (30–250 °C) would result from the loss of the evaporation of moisture and the decomposition of crystal water in the precursor. The following 20.4% weight loss with a big step occurs between 250 and 450 °C, which might be attributed to the conversion of anhydrous precursors to spinel cubic crystals. Therefore, we reasonably chose 450 °C as calcination temperature in our experiment.

The morphology and microstructure of the as-prepared NiCo_2O_4 and $\text{NiCo}_2\text{O}_4@/\text{TiO}_2$ powders are characterized by scanning electron microscopy as shown in Fig. 1. It is clear that NiCo_2O_4 powders are all rose flower-like morphology (Fig. 3(a)), which is composed of thin transparent nanosheets with a thickness of ~20 nm. Fig. 3(b) reveals that the nanosheets of NiCo_2O_4 contains many micro-pores, which is mainly attributed to the organics loss accompanying removal of PVP and gases during the calcination process.^{22,23} Such hierarchical structure would be

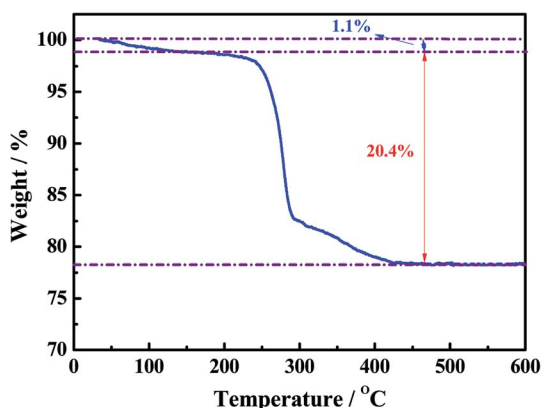


Fig. 2 TGA curves of the Ni–Co precursor in air atmosphere.

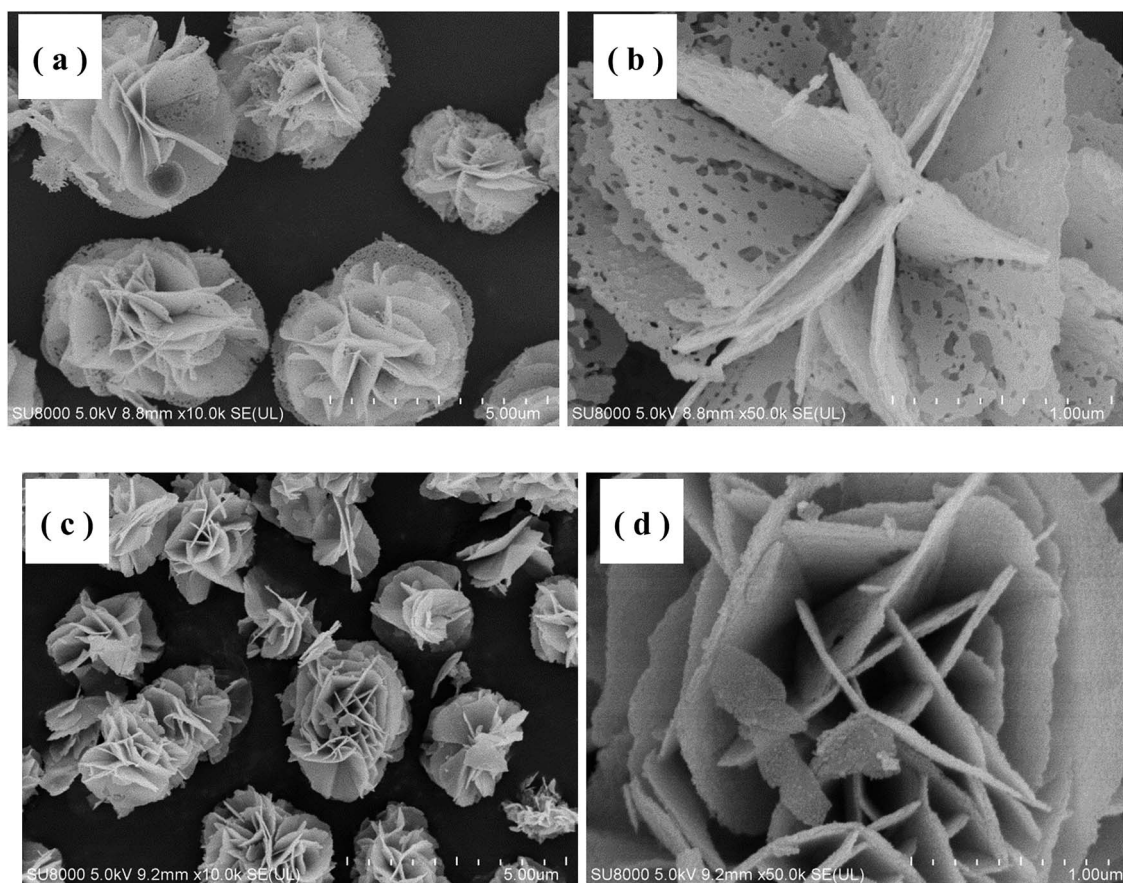


Fig. 3 SEM images of the as-prepared NiCo_2O_4 and $\text{NiCo}_2\text{O}_4@/\text{TiO}_2$ powders.



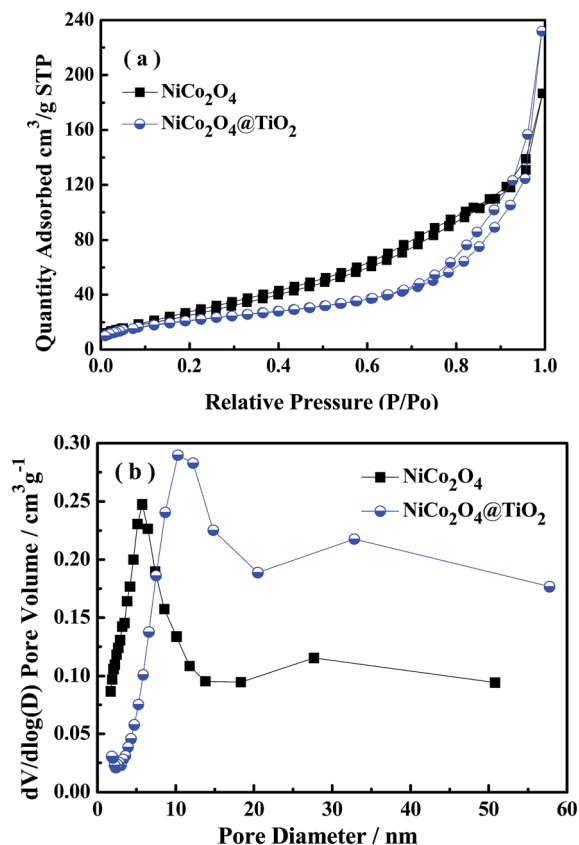


Fig. 4 (a) Nitrogen sorption isotherms and (b) pore diameter distribution of NiCo₂O₄ and NiCo₂O₄@TiO₂ powders.

highly desirable for rapid Li-ion diffusion and electron transfer. Porosity structure of the NiCo₂O₄ nanosheet may be benefit for lithium-ion transportation from the electrolyte into the active sites with less resistance, and buffer efficiently large volume expansion during the Li-ion insertion/extraction processes.²⁴ With TiO₂-coating, NiCo₂O₄@TiO₂ powders also maintain the nanosheet-built flower-like nanostructure as same to the bare one, shown in Fig. 3(c). In contrast, the nanosheets of NiCo₂O₄@TiO₂ have a smooth and integrated surface morphology and the micro-pores on the “petals” disappears, indicating TiO₂ layer is uniformly coated on the nanosheet surface.

Fig. 4(a) presents nitrogen adsorption–desorption isotherms of NiCo₂O₄ and NiCo₂O₄@TiO₂ powders, indicating a typical hysteresis mesoporous system.^{12,25} According to Brunauer–Emmett–Teller (BET) equation, the specific surface areas of NiCo₂O₄ and NiCo₂O₄@TiO₂ are calculated to be 98.78 and 78.09 m² g⁻¹, respectively. Fig. 4(b) shows the corresponding pore-size distribution based on Barrett–Joyner–Halenda (BJH) method, indicating that NiCo₂O₄@TiO₂ have larger average pore size (10.3 nm) than (5.6 nm) of NiCo₂O₄. An increase in average pore size and reduction in surface area could be reasonably explained by the disappearance of micro-pores (5.6 nm) because of TiO₂-coating. The obtained results are consistent with the analysis from SEM images. The distribution of corresponding elements of NiCo₂O₄@TiO₂ is investigated by EDS. Element mapping images for Ni, Co and Ti in NiCo₂O₄@TiO₂ powders (Fig. 5) reveal that the corresponding elements uniformly distribute on the surface of the NiCo₂O₄@TiO₂ particles.

Fig. 6(a) shows the XRD patterns of NiCo₂O₄ and NiCo₂O₄@TiO₂ powders. All of the diffraction peaks are characteristic

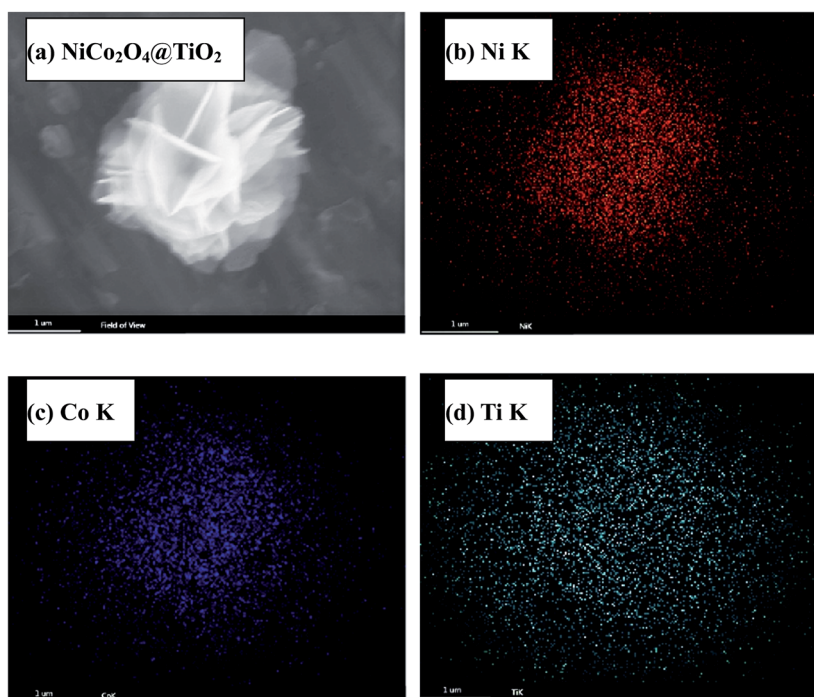


Fig. 5 Element mapping images of NiCo₂O₄@TiO₂ powders.



of a spinel NiCo_2O_4 structure with space group $Fd3m$ (JCPDS card no. 73-1702).^{22,26} It is found that no visible differences in XRD patterns between two composites, which is attributed to the low content of TiO_2 phase. Fig. 6(b) presents Raman spectra of the as-prepared $\text{NiCo}_2\text{O}_4@/\text{TiO}_2$ samples. Five obvious peaks at 212, 313, 366, 536 and 671 cm^{-1} are found in the Raman spectrum of $\text{NiCo}_2\text{O}_4@/\text{TiO}_2$ composites, which can be assigned to the vibrational modes of spinel NiCo_2O_4 .^{27,28} The peak at around 149 cm^{-1} is related to the E_g vibration modes of the TiO_2 anatase structure.²⁹ The TiO_2 content in $\text{NiCo}_2\text{O}_4@/\text{TiO}_2$ composite is further determined to be *ca.* 3.53 wt% by inductively coupled plasma OES spectrometer (ICP).

The elemental composition and the oxidation state of the $\text{NiCo}_2\text{O}_4@/\text{TiO}_2$ powder is further characterized by X-ray photoelectron spectroscopy (XPS) measurements and the corresponding results are present in Fig. 7(a–e). The survey spectrum (Fig. 7(a)) reveals the presence of Ni, Co, Ti and O as well as C elements without any other impurities. By using a Gaussian fitting method, the Ni 2p core-level spectrum (Fig. 7(b)) has two spin-orbit doublets and two shake-up satellites, which are in good agreement with the characteristic of Ni^{2+} and Ni^{3+} .³⁰ Similarly, two spin-orbit doublets and shake-up satellites can

also be observed in the Co 2p spectrum, corresponding to the characteristic of Co^{2+} and Co^{3+} .³⁰ The peaks located at 458.7 and 464.4 eV are attributed to the Ti 2p_{3/2} and Ti 2p_{1/2} spin-orbit doublets, indicating the predominant state of the Ti element in composite is Ti^{4+} .³¹ The O 1s spectra can be divided into two main oxygen peaks at 529.6 and 531 eV. The peak located at 529.6 eV is typical characteristic of metal–oxygen bonds.³² The XPS results are in good agreement with the analysis from XRD and ED measurements.

Fig. 8(a) shows the rate capabilities of NiCo_2O_4 and $\text{NiCo}_2\text{O}_4@/\text{TiO}_2$ electrodes at various current density, measured from 100 to 2000 mA g^{-1} in rising order and subsequently followed by returning 1000, 500 and 200 mA g^{-1} . In comparison, $\text{NiCo}_2\text{O}_4@/\text{TiO}_2$ composite exhibits better rate performance than that of the bare one, especially at a higher rate. When the current density increases to 100, 200, 500, 1000 and 2000 mA g^{-1} , the $\text{NiCo}_2\text{O}_4@/\text{TiO}_2$ electrode shows reversible discharge capacities of 988, 930, 840, 750 and 624 mA h g^{-1} , respectively. Even at a high current density of 2000 mA g^{-1} , the discharge capacity still retains 63.2%. When the current density returns back to 1000, 500 and 200 mA g^{-1} , the $\text{NiCo}_2\text{O}_4@/\text{TiO}_2$ electrode still recovers 735, 837 and 1004 mA h g^{-1} , indicating excellent structure stability of the nano-composite. In contrast, the NiCo_2O_4 electrode delivers a lower discharge capacity at current density. The discharge capacities of the NiCo_2O_4 electrode are measured to be 983, 878, 778, 683 and 562 mA h g^{-1} at the same respective current density. It has been reported that small anatase TiO_2 particles would be turning from an insulator into an electronic conductor during the Li^+ insertion process.^{33,34} Therefore, TiO_2 -coating on NiCo_2O_4 nanosheets is beneficial for both structural stability as well as the rate capability.

Fig. 8(b) presents the cycling performance of NiCo_2O_4 and $\text{NiCo}_2\text{O}_4@/\text{TiO}_2$ electrodes at a current density of 100 mA g^{-1} . In comparison with NiCo_2O_4 , the capacity loss is significantly suppressed after coating with TiO_2 . The initial discharge capacity at 100 mA g^{-1} of NiCo_2O_4 is 1424 mA h g^{-1} and found to decrease to 815 mA h g^{-1} after 60 cycles (*i.e.*, only 57% of its initial discharge capacity). The discharge capacity of the $\text{NiCo}_2\text{O}_4@/\text{TiO}_2$ is found to decay gradually with continuous cycling, retaining 78% of its maximum discharge capacity after 60 cycles. In addition, the coulombic efficiency of NiCo_2O_4 is relatively low and unstable, which might result from the SEI formation repeatedly on NiCo_2O_4 nanosheet during the charge/discharge processes.¹⁹ Similar results are reported in Lotfabad's work.³³ Here, we have made a comparison of the electrochemical performances between our $\text{NiCo}_2\text{O}_4@/\text{TiO}_2$ and other NiCo_2O_4 with different morphologies previously reported, as summarized in Table 1. It is found that $\text{NiCo}_2\text{O}_4@/\text{TiO}_2$ nano-composites exhibit superior cycling stability, indicating its potential application in high-energy lithium-ion batteries.

Fig. 9(a and b) shows cyclic voltammetry profiles of NiCo_2O_4 and $\text{NiCo}_2\text{O}_4@/\text{TiO}_2$ electrode for the first six cycles at a scan rate of 0.1 mV s^{-1} and from 0.01 to 2.5 V. Two peaks are observed at around 0.6 and 0.9 V in the initial cathodic sweep for both samples, which are assigned to the formation of the solid electrolyte interface layer and the reaction of Co^{3+} and Ni^{2+} to Co^0 and Ni^0 , respectively.⁴¹ Two oxidation peaks at around 1.4

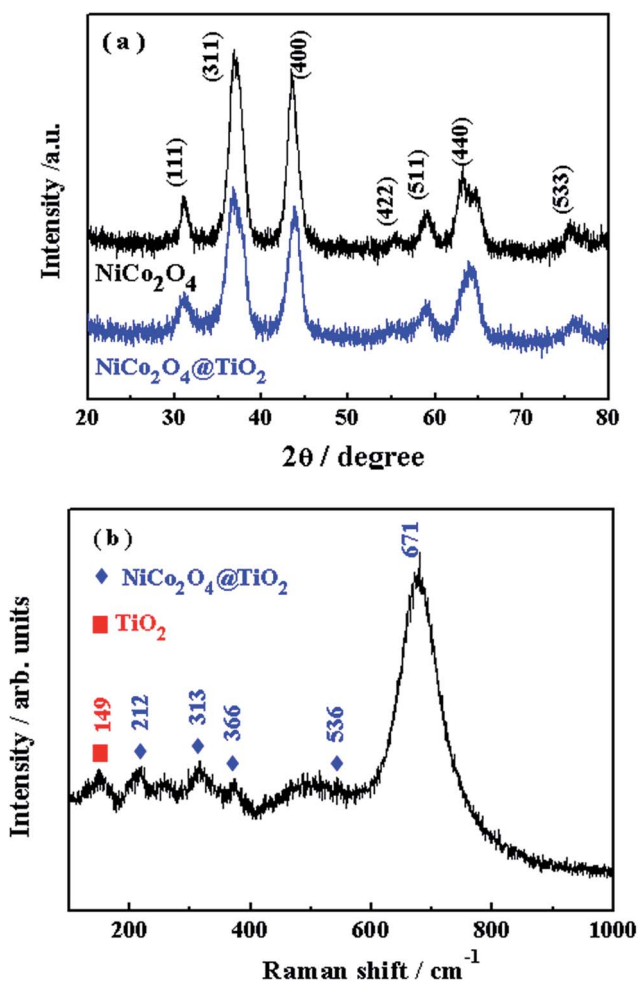


Fig. 6 (a) XRD patterns of NiCo_2O_4 and $\text{NiCo}_2\text{O}_4@/\text{TiO}_2$ powders; (b) Raman spectra of the as-prepared $\text{NiCo}_2\text{O}_4@/\text{TiO}_2$ powders.



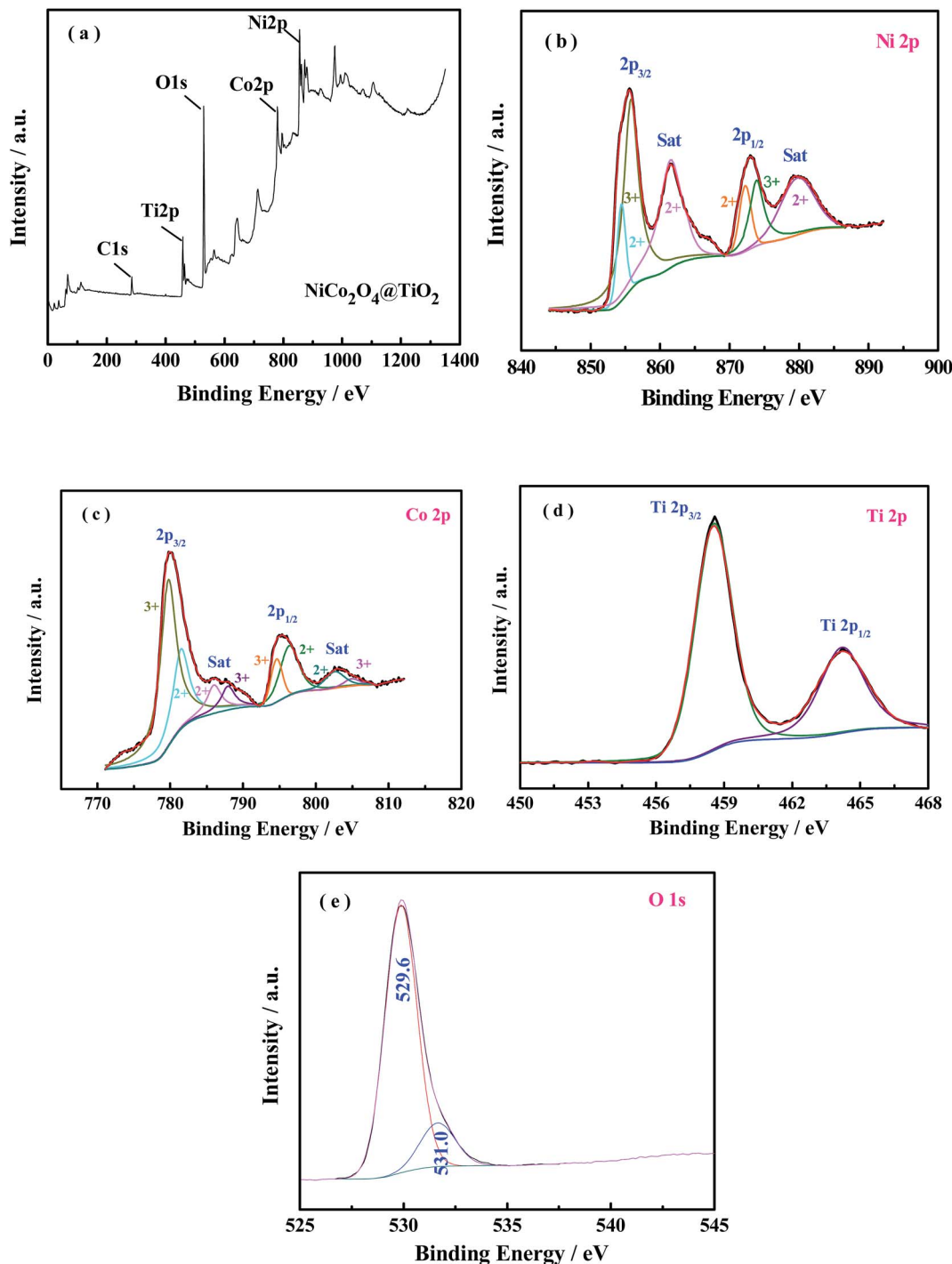
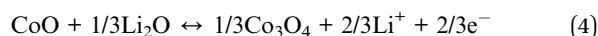
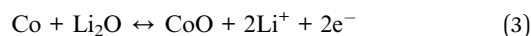
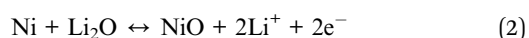


Fig. 7 XPS spectra of (a) survey spectrum, (b) Ni 2p, (c) Co 2p, (d) Ti 2p and (e) O 1s for the NiCo₂O₄@TiO₂ product.

and 2.2 V are also observed in the initial anodic sweep, which are attributed to the oxidation of Co⁰ and Ni⁰ to Co³⁺ and Ni²⁺, respectively.⁴² According to the previous reports,⁴³ the redox reactions can be expressed as follows:



In comparison with NiCo₂O₄, the CV curves from 2nd to 6th cycles for NiCo₂O₄@TiO₂ exhibit a better overlapping degree, indicating a better reversibility of the electrochemical reactions.



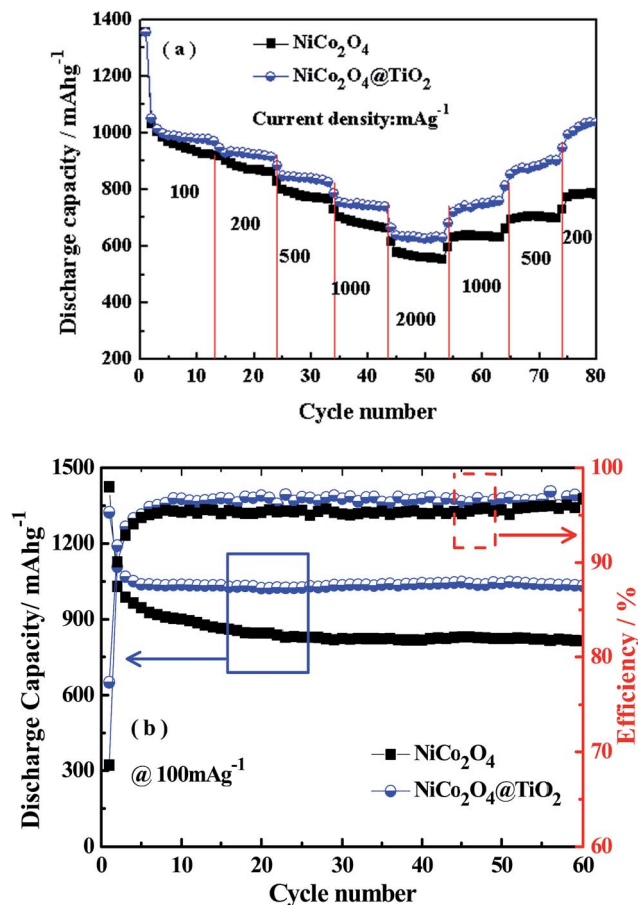


Fig. 8 (a) Rate capability and (b) cyclic performances of NiCo_2O_4 and $\text{NiCo}_2\text{O}_4@/\text{TiO}_2$ electrodes.

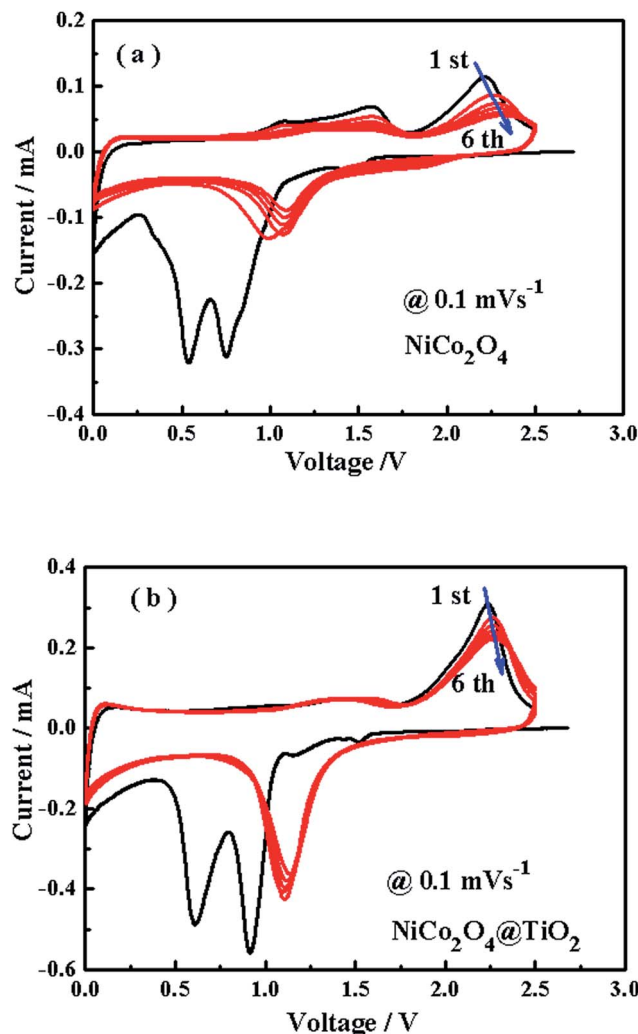


Fig. 9 Cyclic voltammety profiles of NiCo_2O_4 and $\text{NiCo}_2\text{O}_4@/\text{TiO}_2$ electrodes.

Table 1 Comparison of the electrochemical performances of the $\text{NiCo}_2\text{O}_4@/\text{TiO}_2$ electrode in this work with other similar materials reported previously

Materials	Current density (mA g^{-1})	Capacity (mA h g^{-1})	Ref.
Plum-like NiCo_2O_4	0.1	801 after 50 cycles	22
$\text{NiCo}_2\text{O}_4/3\text{DGN}$	0.5	790 after 50 cycles	35
$\text{NiCo}_2\text{O}_4/\text{Ni}$	0.1	413 after 50 cycles	36
$\text{NiCo}_2\text{O}_4@/\text{SnO}_2@/\text{C-HSS}$	0.1	720 after 100 cycles	37
$\text{NiCo}_2\text{O}_4@/\text{G}$	0.3	806 after 55 cycles	38
NiCo_2O_4 nanosheets	0.1	767 after 50 cycles	17
$\text{NiCo}_2\text{O}_4@/\text{RGO}$	0.1	816 after 70 cycles	39
$\text{NiCo}_2\text{O}_4@/\text{NiCo}_2\text{O}_4$ NCAs	0.12	830 after 100 cycles	40
$\text{NiCo}_2\text{O}_4@/\text{TiO}_2$	0.1	1033 after 60 cycles	This work

To further investigate the potential mechanism behind the improved performances with surface-modified of TiO_2 layer, the cells after cycling are disassembled, washed, dried in vacuum and characterized by SEM. Fig. 10 presents the morphologies of NiCo_2O_4 and $\text{NiCo}_2\text{O}_4@/\text{TiO}_2$ powders characterized by SEM after 10 and 30 cycles, respectively. It is obvious that NiCo_2O_4 powders has serious structure-deterioration (pulverization or

aggregation) and losses its flower-like structure with increasing cycles due to the repeated volume change between metals and metal oxides. The aggregation of the active materials tends to reduce the effective contact areas between active materials and the electrolyte. In contrast, $\text{NiCo}_2\text{O}_4@/\text{TiO}_2$ powders can remain in the flower-like structure well, which further confirms that TiO_2 -layer would stabilize structure of the active materials and consequently offer more active sites during the lithium-ion insertion/extraction process. Combined with the analysis of the SEM images after cycling, it is expected that stable hierarchical nanostructures are desirable for the improved electrochemical performances.

Electrochemical impedance spectra are carried out to get insight into the improved rate and cyclic performances of $\text{NiCo}_2\text{O}_4@/\text{TiO}_2$. Fig. 11(a) presents the typical EIS of NiCo_2O_4 and $\text{NiCo}_2\text{O}_4@/\text{TiO}_2$ electrode in the fully discharged state. Both EIS profiles consist of two depressed semicircles in the medium-to-high frequency range and a straight line in the low-frequency region. According to the equivalent circuit in the inset of Fig. 11(a), the charge-transfer resistance (R_{ct}) are



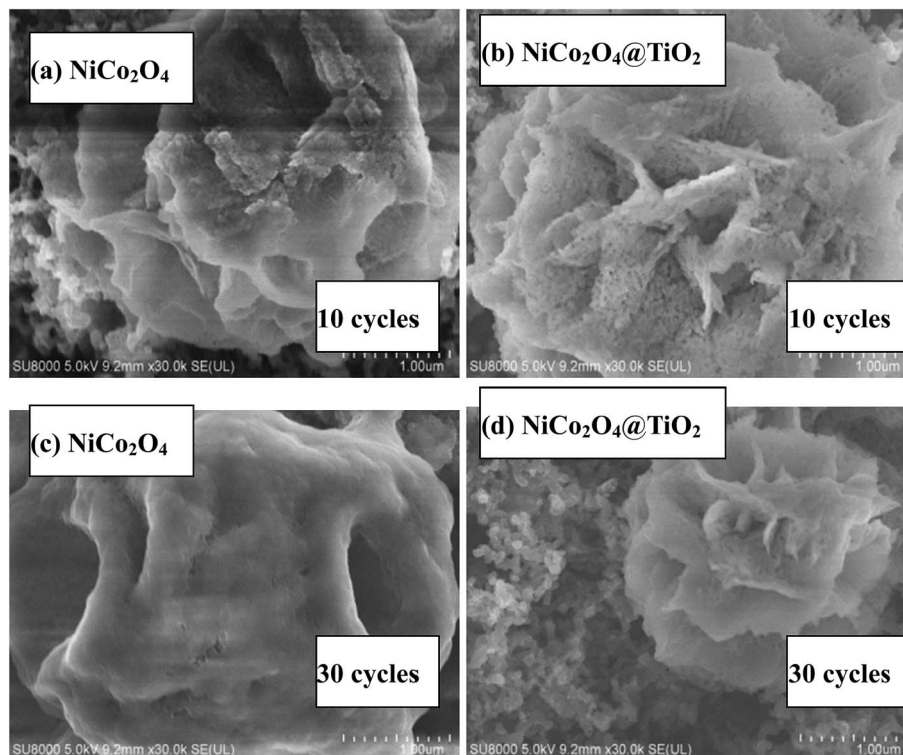


Fig. 10 SEM images of the NiCo_2O_4 and $\text{NiCo}_2\text{O}_4@\text{TiO}_2$ powders after 10 and 30 cycles, respectively.

calculated as 36.6Ω for NiCo_2O_4 and 20.4Ω for $\text{NiCo}_2\text{O}_4@\text{TiO}_2$, respectively. The decrease in R_{ct} for $\text{NiCo}_2\text{O}_4@\text{TiO}_2$ would derive from the more stable structure by TiO_2 -coating with continuous cycling.⁴⁴ The TiO_2 -coating layer is expected to efficiently prevent the pulverization of NiCo_2O_4 during the Li^+ intercalation/extraction process and mediate the increase in charge transfer resistance of the composites, which facilitates Li^+ transfer at the interface between the active material and electrolyte. As a result, the electrochemical performances are improved.

The diffusion coefficients (D_{Li}) of the Li^+ kinetic of the cells can be also calculated according to the EIS profiles in the low frequency.

$$\sigma = \frac{RT}{n^2 F^2 A \sqrt{2}} \left(\frac{1}{C_{\text{Li}} D_{\text{Li}}^{1/2}} \right) \quad (5)$$

$$Z_{\text{re}} = R + \sigma \omega^{-1/2} \quad (6)$$

R , T and F are the mass gas constant, absolute temperature and Faraday's constant; A , n and C_{Li} are the surface area of the electrode, the number of electrons per molecule during oxidation and the molar volume of active material; σ , Z_{re} and ω are the Warburg factor, the real part of the impedance and the frequency. Based on the slope coefficient of Z_{re} to $\omega^{-1/2}$ (see Fig. 11(b)), the corresponding lithium diffusion coefficients D_{Li} of NiCo_2O_4 and $\text{NiCo}_2\text{O}_4@\text{TiO}_2$ powders are calculated as $2.57 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ and $8.18 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ respectively, suggesting the rapid diffusion of lithium-ions of $\text{NiCo}_2\text{O}_4@\text{TiO}_2$ electrode.

To evaluate the effect of TiO_2 -coating on the Li^+ ion diffusion during the charge/discharge process, the impedance spectra under different discharge states for NiCo_2O_4 and $\text{NiCo}_2\text{O}_4@\text{TiO}_2$ electrodes are continuously measured, shown in Fig. 12(a and b). According to eqn (5) and (6), the corresponding Li^+ ion diffusion coefficients of NiCo_2O_4 and $\text{NiCo}_2\text{O}_4@\text{TiO}_2$ electrodes are calculated. Fig. 12(c) presents lithium-ion diffusion behaviors during the lithium-ion insertion process. Both electrodes demonstrate similar lithium-ion diffusion behavior. On the whole, $\text{NiCo}_2\text{O}_4@\text{TiO}_2$ electrode exhibits larger Li^+ diffusion coefficients than those of the bare one, indicating that TiO_2 -coating does readily facilitate the Li^+ diffusion in composites. It is worth noting that $\text{NiCo}_2\text{O}_4@\text{TiO}_2$ electrode has much larger diffusion coefficients of lithium-ions in the voltage range from 1.0 to 0.01 V, which might be attributed to the lithium ion insertion in TiO_2 . It is expected that lithium-inserted Li_xTiO_2 anatase would turn from an insulator into an electronic conductor during the Li^+ insertion process, resulting in enhanced electron-transfer in composites.³³ As a result, TiO_2 coating on NiCo_2O_4 is potentially beneficial for the improved rate capability as well as the structural integrity of the composite.

Kelvin probe atomic force microscopy is used to study the influence of TiO_2 -coating on the Li^+ ion kinetic behavior in composites. Fig. 13(a and b) shows the surface potential maps over a scan area of $200 \text{ nm} \times 200 \text{ nm}$ of NiCo_2O_4 and $\text{NiCo}_2\text{O}_4@\text{TiO}_2$ powders before cycling. Fig. 13(c) presents the surface potential image of Au foil acting as reference sample. According to our prior work,⁴⁵ the work functions of NiCo_2O_4 and $\text{NiCo}_2\text{O}_4@\text{TiO}_2$ powders are calculated based on the surface potential



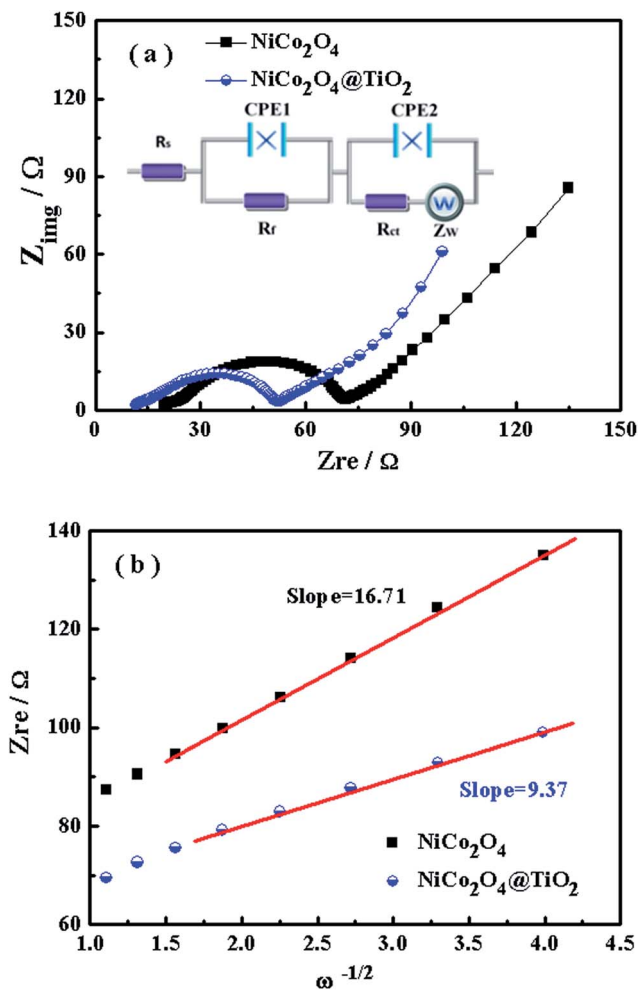


Fig. 11 (a) Typical EIS of NiCo_2O_4 and $\text{NiCo}_2\text{O}_4@\text{TiO}_2$ electrode in the fully discharged state and the equivalent circuit for EIS fitting; (b) real parts of the complex impedance Z_{re} vs. $\omega^{-1/2}$ for NiCo_2O_4 and $\text{NiCo}_2\text{O}_4@\text{TiO}_2$ electrodes.

profiles and the corresponding results are shown in Fig. 13(d). Here, the work functions of the SFM-tip (ϕ_{tip}) is calibrated by Au foil, whose work function (ϕ_{Au}) is 5.31 eV. It is found that $\text{NiCo}_2\text{O}_4@\text{TiO}_2$ has a smaller work function (~ 5.41 eV) than that (~ 5.51 eV) of the NiCo_2O_4 . The measured work function of NiCo_2O_4 is close to the reported value (5.53 eV).^{46,47} The larger work function suggests the more energy required for electrons to escape from the composites. As a result, the electrochemical performances of the composites are enhanced with surface-modified with TiO_2 -coating. These obtained results are consistent with the analysis of EIS measurements.

The reduced work function of $\text{NiCo}_2\text{O}_4@\text{TiO}_2$ could be explained phenomenologically based on the energy-band model. As shown in Fig. 14(a), electrons transfer occurs from TiO_2 to NiCo_2O_4 until the Fermi levels are aligned due to the smaller work function (~ 4.5 eV) of anatase TiO_2 .⁴⁸ As a result, the TiO_2 is positively charged and the NiCo_2O_4 is negatively charged near its surface due to electrostatic induction because of electrostatic induction. Meanwhile, a corresponding electric field (E) is built up between them, shown in Fig. 14(b). Such

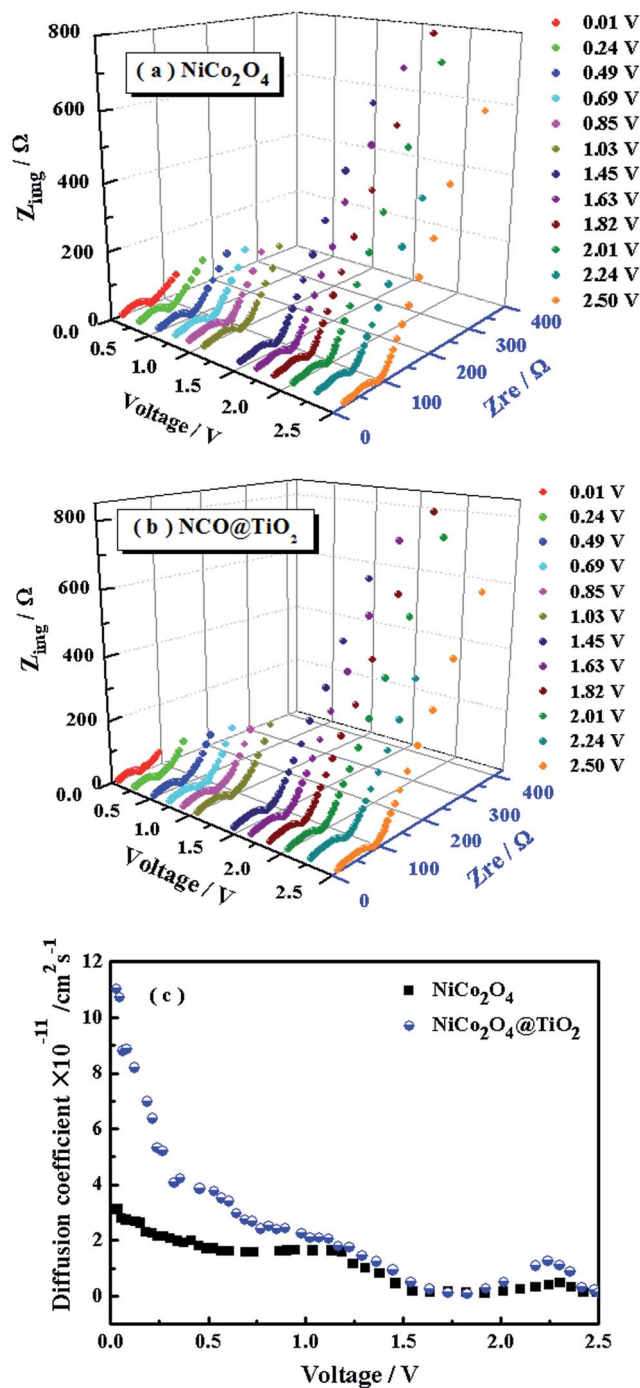


Fig. 12 (a, b) The impedance spectra and (c) corresponding Li-ion diffusion coefficients of NiCo_2O_4 and $\text{NiCo}_2\text{O}_4@\text{TiO}_2$ electrodes under different discharge states.

electric field could facilitate Li-ion diffusion from positively-charged TiO_2 to negatively-charged NiCo_2O_4 , and electron transfer from NiCo_2O_4 to TiO_2 across heterojunction interfaces. With the help of the electric field, more electrons in NiCo_2O_4 matrix would transfer through TiO_2 rather than $\text{NiCo}_2\text{O}_4/\text{NiCo}_2\text{O}_4$ interface during the lithium insertion process. Moreover, TiO_2 coated on NiCo_2O_4 could effectively suppress the pulverization of NiCo_2O_4 matrix due to the volume change in



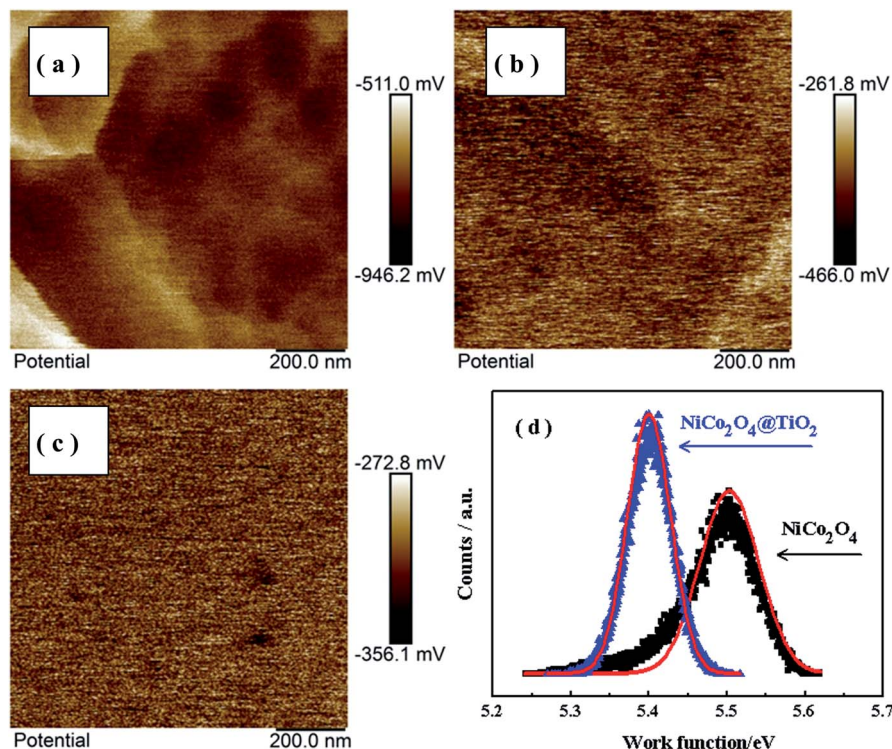


Fig. 13 (a, b) Surface potential maps over a scan area of 200 nm \times 200 nm of NiCo₂O₄ and NiCo₂O₄@TiO₂ powders before cycling; (c) surface potential image of Au foil acting as reference sample; (d) work functions of NiCo₂O₄ and NiCo₂O₄@TiO₂ electrodes.

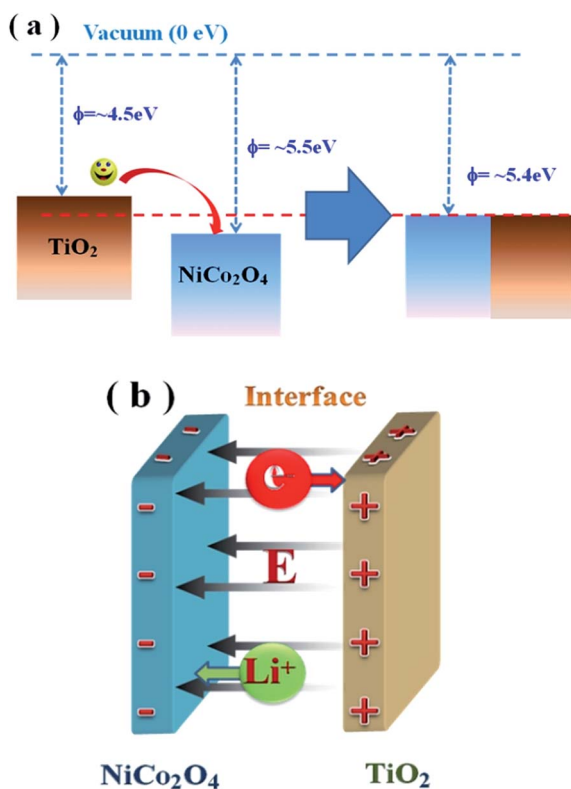


Fig. 14 (a) The energy-level model for explaining the improved electron transfer in NiCo₂O₄@TiO₂ electrodes; (b) a built electric field (E) between NiCo₂O₄ and TiO₂.

the charge/discharge process. As a result, the electrochemical performances are enhanced.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 M. Armand and J.-M. Tarascon, Building better batteries, *Nature*, 2008, **451**, 652–657.
- 2 J. B. Goodenough, Electrochemical energy storage in a sustainable modern society, *Energy Environ. Sci.*, 2014, **7**, 14–18.
- 3 R. A. Huggins, Review—a new class of high rate, long cycle life, aqueous electrolyte battery electrodes, *J. Electrochem. Soc.*, 2017, **164**, A5031–A5036.
- 4 J. Lu, Z. H. Chen, Z. F. Ma, F. Pan, A. L. Curtiss and K. Amine, The role of nanotechnology in the development of battery materials for electric vehicles, *Nat. Nanotechnol.*, 2016, **11**, 1031–1038.



- 5 G. E. Blomgren, The development and future of lithium ion batteries, *J. Electrochem. Soc.*, 2017, **164**, A5019–A5025.
- 6 Z. Y. Wang, L. Zhou and X. W. Lou, Metal oxide hollow nanostructures for lithium-ion batteries, *Adv. Mater.*, 2012, **24**, 1903–1911.
- 7 M. V. Reddy, G. V. S. Rao and B. V. R. Chowdari, Metal oxides and oxysalts as anode materials for Li ion batteries, *Chem. Rev.*, 2013, **113**, 5364–5457.
- 8 M. Freire, N. V. Kosova, C. Jordy, D. Chateigner, O. I. Lebedev, A. Maignan and V. Pralong, A new active Li-Mn-O compound for high energy density Li-ion batteries, *Nat. Mater.*, 2016, **15**, 173–177.
- 9 H. Buqa, D. Goers, M. Holzapfel, M. E. Spahr and P. Novák, High rate capability of graphite negative electrodes for lithium-ion batteries, *J. Electrochem. Soc.*, 2005, **152**, A474–A481.
- 10 J. F. Li, S. L. Xiong, Y. R. Liu, Z. C. Ju and Y. T. Qian, High electrochemical performance of monodisperse NiCo₂O₄ mesoporous microspheres as an anode material for Li-ion batteries, *ACS Appl. Mater. Interfaces*, 2013, **5**, 981–988.
- 11 B. B. Jiang, C. P. Han, B. Li, Y. J. He and Z. Q. Lin, In-situ crafting of ZnFe₂O₄ nanoparticles impregnated within continuous carbon network as advanced anode materials, *ACS Nano*, 2016, **10**, 2728–2735.
- 12 R. C. Jin, H. Jiang, Y. X. Sun, Y. Q. Ma, H. H. Li and G. Chen, Fabrication of NiFe₂O₄/C hollow spheres constructed by mesoporous nanospheres for high-performance lithium-ion batteries, *Chem. Eng. J.*, 2016, **303**, 501–510.
- 13 X. Q. Chen, Y. M. Zhang, H. B. Lin, P. Xia, X. Cai, X. G. Li, X. P. Li and W. S. Li, Porous ZnMn₂O₄ nanospheres: facile synthesis through microemulsion method and excellent performance as anode of lithium ion battery, *J. Power Sources*, 2016, **312**, 137–145.
- 14 G. Zhou, C. Wu, Y. H. Wei, C. C. Li, Q. W. Lian, C. Cui, W. F. Wei and L. B. Chen, Tufted NiCo₂O₄ nanoneedles grown on carbon nanofibers with advanced electrochemical property for lithium ion batteries, *Electrochim. Acta*, 2016, **222**, 1878–1886.
- 15 C. Zhang and J. S. Yu, Morphology-tuned synthesis of NiCo₂O₄-Coated 3D graphene architectures used as binder-free electrodes for lithium-ion batteries, *Chem.–Eur. J.*, 2016, **22**, 4422–4430.
- 16 Y. Lei, J. Li, Y. Wang, L. Gu, Y. Chang, H. Yuan and D. Xiao, Rapid microwave-assisted green synthesis of 3D hierarchical flower-shaped NiCo₂O₄ microsphere for high-performance supercapacitor, *ACS Appl. Mater. Interfaces*, 2014, **6**, 1773–1780.
- 17 A. K. Mondal, D. W. Su, S. Q. Chen, K. Kretschmer, X. Q. Xie, H. J. Ahn and G. X. Wang, A microwave synthesis of mesoporous NiCo₂O₄ nanosheets as electrode materials for lithium-ion batteries and supercapacitors, *ChemPhysChem*, 2015, **16**, 169–175.
- 18 L. L. Li, S. J. Peng, Y. L. Cheah, P. F. Teh, J. Wang, G. Wee, Y. Ko, C. L. Wong and M. Srinivasan, Electrospun porous NiCo₂O₄ nanotubes as advanced electrodes for electrochemical capacitors, *Chem.–Eur. J.*, 2013, **19**, 5892–5898.
- 19 H. R. Kou, X. F. Li, H. Shan, L. L. Fan, B. Yan and D. J. Li, An optimized Al₂O₃ layer for enhancing the anode performance of NiCo₂O₄ nanosheets for sodium-ion batteries, *J. Mater. Chem. A*, 2017, **5**, 17881–17888.
- 20 Z. H. Chen, I. Belharouak, Y. K. Sun and K. Amine, Titanium-based anode materials for safe lithium-ion batteries, *Adv. Funct. Mater.*, 2013, **23**, 959–969.
- 21 J. H. Lee, M. H. Hon, Y. W. Chung and I. C. Leu, The effect of TiO₂ coating on the electrochemical performance of ZnO nanorod as the anode material for lithium-ion battery, *Appl. Phys. A*, 2011, **102**, 545–550.
- 22 T. Li, X. Li, Z. Wang, H. Guo and Y. Li, A novel NiCo₂O₄ anode morphology for lithium-ion batteries, *J. Mater. Chem. A*, 2015, **3**, 11970–11975.
- 23 J. Xu, D. W. Su, W. Z. Bao, Y. F. Zhao, X. Q. Xie and G. X. Wang, Rose flower-like NiCo₂O₄ with hierarchically porous structures for highly reversible lithium storage, *J. Alloys Compd.*, 2016, **684**, 691–698.
- 24 F. C. Zheng, D. Q. Zhu and Q. W. Chen, Facile fabrication of porous Ni_xCo_{3-x}O₄ nanosheets with enhanced electrochemical performance as anode materials for li-ion batteries, *ACS Appl. Mater. Interfaces*, 2014, **6**, 9256–9264.
- 25 Y. D. Mo, Q. Ru, X. Songa, L. Y. Guo, J. F. Chen, X. H. Hou and S. J. Hu, The sucrose-assisted NiCo₂O₄@C composites with enhanced lithium-storage properties, *Carbon*, 2016, **109**, 616–623.
- 26 A. K. Mondal, D. W. Su, S. Q. Chen, X. Q. Xie and G. X. Wang, Highly porous NiCo₂O₄ nanoflakes and nanobelts as anode materials for lithium-ion batteries with excellent rate capability, *ACS Appl. Mater. Interfaces*, 2014, **6**, 14827–14835.
- 27 H. Zheng, S. Xu, L. Li, C. Feng and S. Q. Wang, Synthesis of NiCo₂O₄ microellipsoids as anode material for lithium-ion batteries, *J. Electron. Mater.*, 2016, **45**, 4966–4972.
- 28 L. B. Ma, X. P. Shen, Z. Y. Ji, X. Q. Cai, G. X. Zhu and K. M. Chen, Porous NiCo₂O₄ nanosheets/reduced graphene oxide composite: facile synthesis and excellent capacitive performance for supercapacitors, *J. Colloid Interface Sci.*, 2015, **440**, 211–218.
- 29 Y. Zhang, W. Wu, K. Zhang, C. H. Liu, A. F. Yu, M. Z. Peng and J. Y. Zhai, Raman study of 2D anatase TiO₂ nanosheets, *Phys. Chem. Chem. Phys.*, 2016, **18**, 32178–32184.
- 30 R. X. Ge, M. Ma, X. Ren, F. L. Qu, Z. A. Liu, G. Du, A. M. Asiri, L. Chen, B. Zheng and X. Sun, A NiCo₂O₄@Ni–Co–C core-shell nanowire array as an efficient electrocatalyst for water oxidation at near-neutral pH, *Chem. Commun.*, 2017, **53**, 7812–7815.
- 31 M. C. Biesinger, L. W. Lau, A. R. Gerson and R. S. C. Smart, Resolving surface chemical states in XPS analysis of first row transition metals oxides and hydroxides: Sc, Ti, V, Cu and Zn, *Appl. Surf. Sci.*, 2010, **257**, 887–898.
- 32 Y. D. Mo, Q. Ru, X. Song, S. J. Hu, L. Y. Guo and X. Q. Chen, 3-dimensional porous NiCo₂O₄ nanocomposite as a high-rate capacity anode for lithium-ion batteries, *Electrochim. Acta*, 2015, **176**, 575–585.
- 33 E. M. Lotfabad, P. Kalisvaart, K. Cui, A. Kohandehghan, M. Kupsta, B. Olsena and D. Mitlin, ALD TiO₂ coated silicon nanowires for lithium ion battery anodes with



- enhanced cycling stability and coulombic efficiency, *Phys. Chem. Chem. Phys.*, 2013, **15**, 13646–13657.
- 34 W. J. H. Borghols, D. Lutzenkirchen-Hecht, U. Haake, E. R. H. van Eck, F. M. Mulder and M. Wagemaker, The electronic structure and ionic diffusion of nanoscale LiTiO₂ anatase, *Phys. Chem. Chem. Phys.*, 2009, **11**, 5742–5748.
- 35 S. N. Liu, J. Wu, J. Zhou, G. Z. Fang and S. Q. Liang, Mesoporous NiCo₂O₄ nanoneedles grown on three dimensional graphene networks as binder-free electrode for high-performance lithium-ion batteries and supercapacitors, *Electrochim. Acta*, 2015, **176**, 1–9.
- 36 G. H. Chen, J. Yang, J. J. Tang and X. Y. Zhou, Hierarchical NiCo₂O₄ nanowire arrays on Ni foam as an anode for lithium-ion batteries, *RSC Adv.*, 2015, **5**, 23067–23072.
- 37 G. X. Gao, H. B. Wu, S. J. Ding and X. W. Lou, Preparation of carbon-coated NiCo₂O₄@SnO₂ hetero-nanostructures and their reversible lithium storage properties, *Small*, 2015, **11**, 432–436.
- 38 Y. J. Chen, J. Zhu, B. H. Qu, B. A. Lun and Z. Xu, Graphene improving lithium-ion battery performance by construction of NiCo₂O₄/graphene hybrid nanosheet arrays, *Nano Energy*, 2014, **3**, 88–94.
- 39 Y. J. Chen, M. Zhuo, J. W. Deng, Z. Xu, Q. H. Li and T. H. Wang, Graphene improving lithium-ion battery performance by construction of NiCo₂O₄/graphene hybrid nanosheet arrays, *J. Mater. Chem. A*, 2014, **2**, 4449–4456.
- 40 J. B. Cheng, Y. Lu, K. W. Qiu, H. L. Yan, J. Y. Xu, L. Han, X. M. Liu, J. S. Luo, J. K. Kim and Y. S. Luo, Hierarchical core/shell NiCo₂O₄@NiCo₂O₄ nanocactus arrays with dual-functionalities for high performance supercapacitors and Li-ion batteries, *Sci. Rep.*, 2015, **5**, 12099.
- 41 Y. Chen, J. Zhu, B. Qu, B. Lu and Z. Xu, Graphene improving lithium-ion battery performance by construction of NiCo₂O₄/graphene hybrid nanosheet arrays, *Nano Energy*, 2014, **3**, 88–94.
- 42 C. F. Zhang and J. S. Yu, Morphology-tuned synthesis of NiCo₂O₄-coated 3D graphene architectures used as binder-free electrodes for lithium-ion batteries, *Chem.–Eur. J.*, 2016, **22**, 4422–4430.
- 43 L. L. Li, Y. Cheah, Y. W. Ko, P. Teh, G. Wee, C. L. Wong, S. J. Peng and M. Srinivasan, The facile synthesis of hierarchical porous flower-like NiCo₂O₄ with superior lithium storage properties, *J. Mater. Chem. A*, 2013, **1**, 10935–10941.
- 44 W. Shi, H. T. Zhao and B. G. Lu, Core-shell ZnCo₂O₄@TiO₂ nanowall arrays as anodes for lithium ion batteries, *Nanotechnology*, 2017, **28**, 165403.
- 45 L. C. Chen, Y. M. Yang, Z. S. Wang, J. Y. Zhang, Q. L. Su, Y. Chen, Y. B. Lin and Z. G. Huang, Enhanced electrochemical performances and thermal stability of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ by surface modification with YF₃, *J. Alloys Compd.*, 2017, **711**, 462–472.
- 46 K. K. Naik, R. T. Khare, R. V. Gelamo, M. A. More, R. Thapa, D. J. Late and C. S. Rout, Enhanced electron field emission from NiCo₂O₄ nanosheet arrays, *Mater. Res. Express*, 2015, **2**, 095011.
- 47 C. Zhang, X. P. Geng, S. L. Tang, M. S. Deng and Y. W. Du, NiCo₂O₄@rGO hybrid nanostructures on Ni foam as high-performance supercapacitor electrodes, *J. Mater. Chem. A*, 2017, **5**, 5912–5919.
- 48 L. X. Zheng, S. C. Han, H. Liu, P. P. Yu and X. S. Fang, Hierarchical MoS₂ nanosheet@TiO₂ nanotube array composites with enhanced photocatalytic and photocurrent performances, *Small*, 2016, **12**, 1527–1536.

