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Hierarchical flower-like $NiCo_2O_4@TiO_2$ hetero-nanosheets as anodes for lithium ion batteries

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Flower-like $NiCo_2O_4$ consisting of nanosheets are synthesized by hydrothermal technique and subsequently surface-modified with a TiO_2 ultrathin layer by a hydrolysis process at low temperature. It is found that $NiCo_2O_4@TiO_2$ exhibits superior electrochemical performances over $NiCo_2O_4$ in terms of rate capability and cyclability. After 60 cycles at 100 mA g^{-1}, $NiCo_2O_4@TiO_2$ showed 78% capacity retention compared with 57% for bare $NiCo_2O_4$. Analysis from the electrochemical measurements indicates that the improved electrochemical performances of $NiCo_2O_4@TiO_2$ might be attributed to a higher lithium diffusion rate, smaller charge-transfer resistance and more structural stability. Kelvin probe force microscopy measurements reveal that $NiCo_2O_4@TiO_2$ 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 $NiCo_2O_4$ and TiO_2 resulting from the difference in work functions is also expected to enhance the electrochemical performances.

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 $ZnFe_2O_4$, $NiFe_2O_4$, $ZnMn_2O_4$ and $NiCo_2O_4$, 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 ($NiCo_2O_4$) 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, $NiCo_2O_4$ 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 Al_2O_3-coated $NiCo_2O_4$ exhibits improved cyclability with a reversible capacity of 395 mA h g^{-1} after 50 cycles. Titanium oxide (TiO_2) 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, TiO_2-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 TiO_2 on flower-like $NiCo_2O_4$ consisting of nanosheets at low temperature, and the effect of TiO_2-coating on the kinetics of Li^+ insertion/extraction is systematically investigated. It is found that the high capacity of $NiCo_2O_4$ and the excellent stability of TiO_2 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 $NiCo_2O_4$ 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 $Ni(NO_3)_2 \cdot 6H_2O$ and 12 mmol of $Co(NO_3)_2 \cdot 6H_2O$ 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. $NiCo_2O_4$@TiO_2 composites are synthesized by a hydrolysis process at low temperature using tetrabutyl titanate ($Ti(OC_4H_9)_4$) 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 $Ti(OC_4H_9)_4$ 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 $NiCo_2O_4$@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 determinated according to the theory of Barrett, Joyner and Halenda (BJH).

The surface potentials of $NiCo_2O_4$ and $NiCo_2O_4$@TiO_2 are measured by Kelvin probe atomic force microscopy (KPAFM) (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, $H_2O < 1$ ppm). The working electrodes are prepared by coating anode slurries which are made up of 70 wt% active material ($NiCo_2O_4$ or $NiCo_2O_4$@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

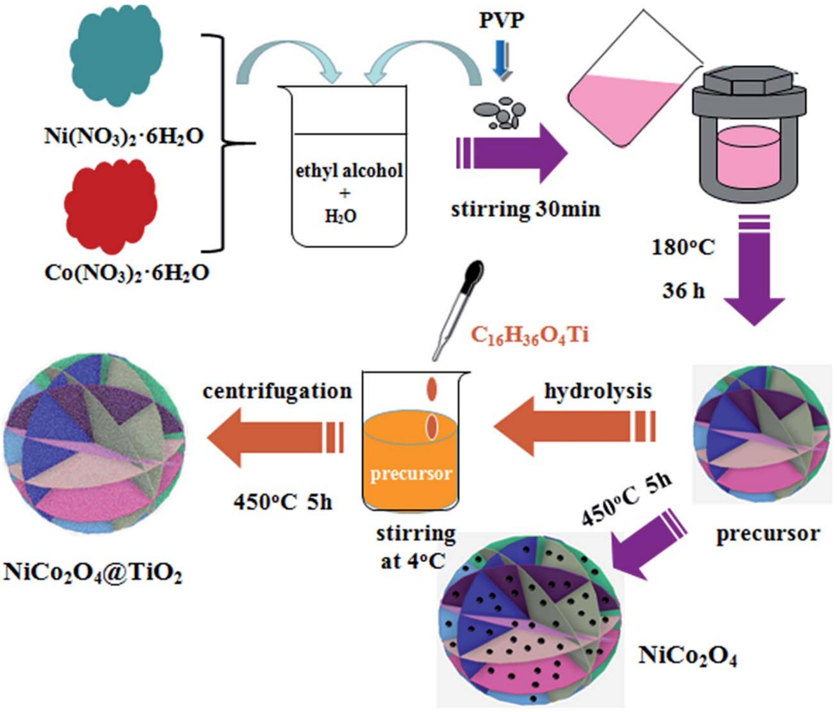

Fig. 1 Schematic illustration of the preparation process for $NiCo_2O_4$ and $NiCo_2O_4$@TiO_2 powders.

$LiPF_6$ 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.

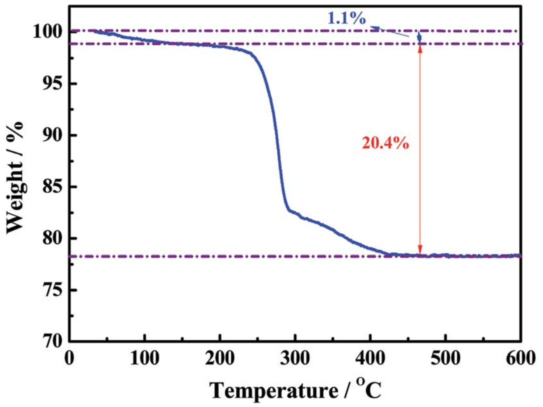

Fig. 2 TGA curves of the Ni–Co precursor in air atmosphere.

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 $NiCo_2O_4@TiO_2$ 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

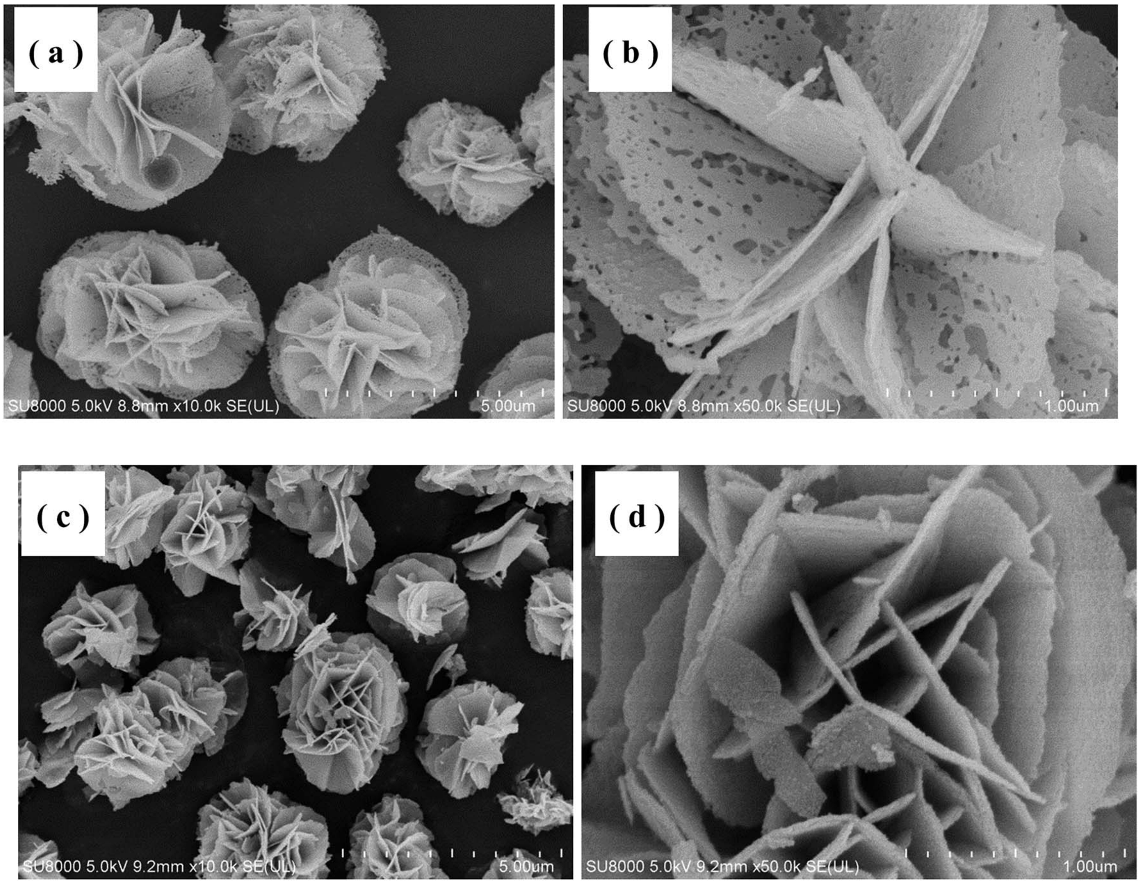

Fig. 3 SEM images of the as-prepared $NiCo_2O_4$ and $NiCo_2O_4@TiO_2$ powders.

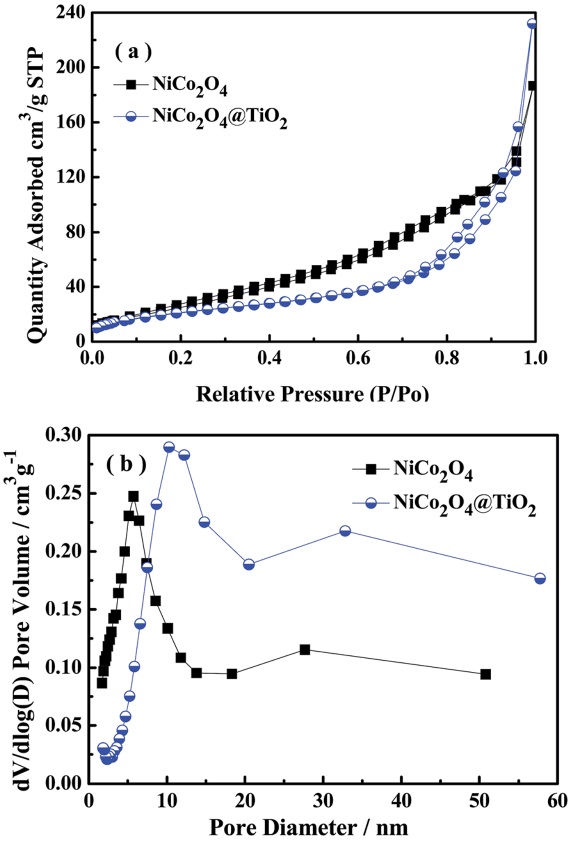

Fig. 4 (a) Nitrogen sorption isotherms and (b) pore diameter distribution of $NiCo_2O_4$ and $NiCo_2O_4@TiO_2$ powders.

highly desirable for rapid Li-ion diffusion and electron transfer. Porosity structure of the $NiCo_2O_4$ 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 TiO_2-coating, $NiCo_2O_4@TiO_2$ 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 $NiCo_2O_4@TiO_2$ have a smooth and integrated surface morphology and the micro-pores on the "petals" disappears, indicating TiO_2 layer is uniformly coated on the nanosheet surface.

Fig. 4(a) presents nitrogen adsorption–desorption isotherms of $NiCo_2O_4$ and $NiCo_2O_4@TiO_2$ powders, indicating a typical hysteresis mesoporous system.[12,25] According to Brunauer–Emmett–Teller (BET) equation, the specific surface areas of $NiCo_2O_4$ and $NiCo_2O_4@TiO_2$ are calculated to be 98.78 and 78.09 $m^2\ g^{-1}$, respectively. Fig. 4(b) shows the corresponding pore-size distribution based on Barrett–Joyner–Halenda (BJH) method, indicating that $NiCo_2O_4@TiO_2$ have larger average pore size (10.3 nm) that (5.6 nm) of $NiCo_2O_4$. 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 TiO_2-coating. The obtained results are consistent with the analysis from SEM images. The distribution of corresponding elements of $NiCo_2O_4@TiO_2$ is investigated by EDS. Element mapping images for Ni, Co and Ti in $NiCo_2O_4@TiO_2$ powders (Fig. 5) reveal that the corresponding elements uniformly distribute on the surface of the $NiCo_2O_4@TiO_2$ particles.

Fig. 6(a) shows the XRD patterns of $NiCo_2O_4$ and $NiCo_2O_4@TiO_2$ powders. All of the diffraction peaks are characteristic

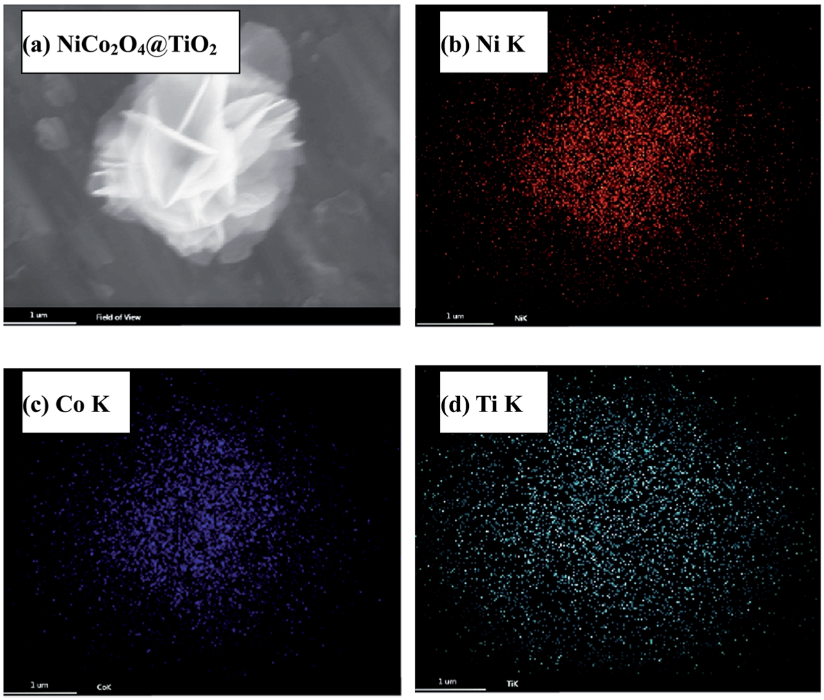

Fig. 5 Element mapping images of $NiCo_2O_4@TiO_2$ powders.

of a spinel $NiCo_2O_4$ structure with space group *Fd*3*m* (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 $NiCo_2O_4$@TiO_2 samples. Five obvious peaks at 212, 313, 366, 536 and 671 cm^{-1} are found in the Raman spectrum of $NiCo_2O_4$@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 $NiCo_2O_4$@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 $NiCo_2O_4$@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.

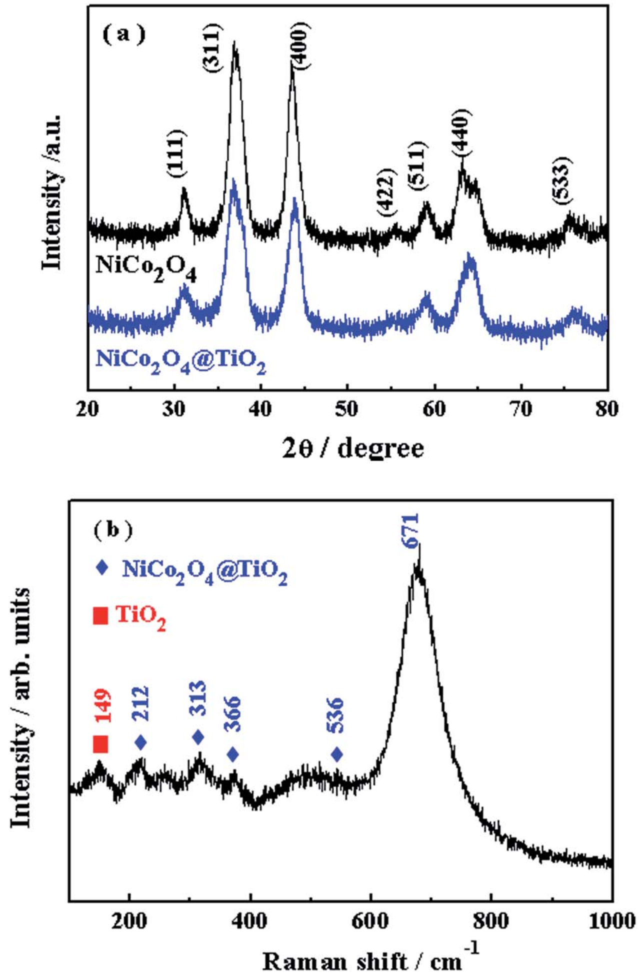

Fig. 6 (a) XRD patterns of $NiCo_2O_4$ and $NiCo_2O_4$@TiO_2 powders; (b) Raman spectra of the as-prepared $NiCo_2O_4$@TiO_2 powders.

Fig. 8(a) shows the rate capabilities of $NiCo_2O_4$ and $NiCo_2O_4$@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, $NiCo_2O_4$@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 $NiCo_2O_4$@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 $NiCo_2O_4$@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 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 possess.[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 $NiCo_2O_4$@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 $NiCo_2O_4$@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 $NiCo_2O_4$@TiO_2 and other $NiCo_2O_4$ with different morphologies previously reported, as summarized in Table 1. It is found that $NiCo_2O_4$@TiO_2 nanocomposites 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 $NiCo_2O_4$@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

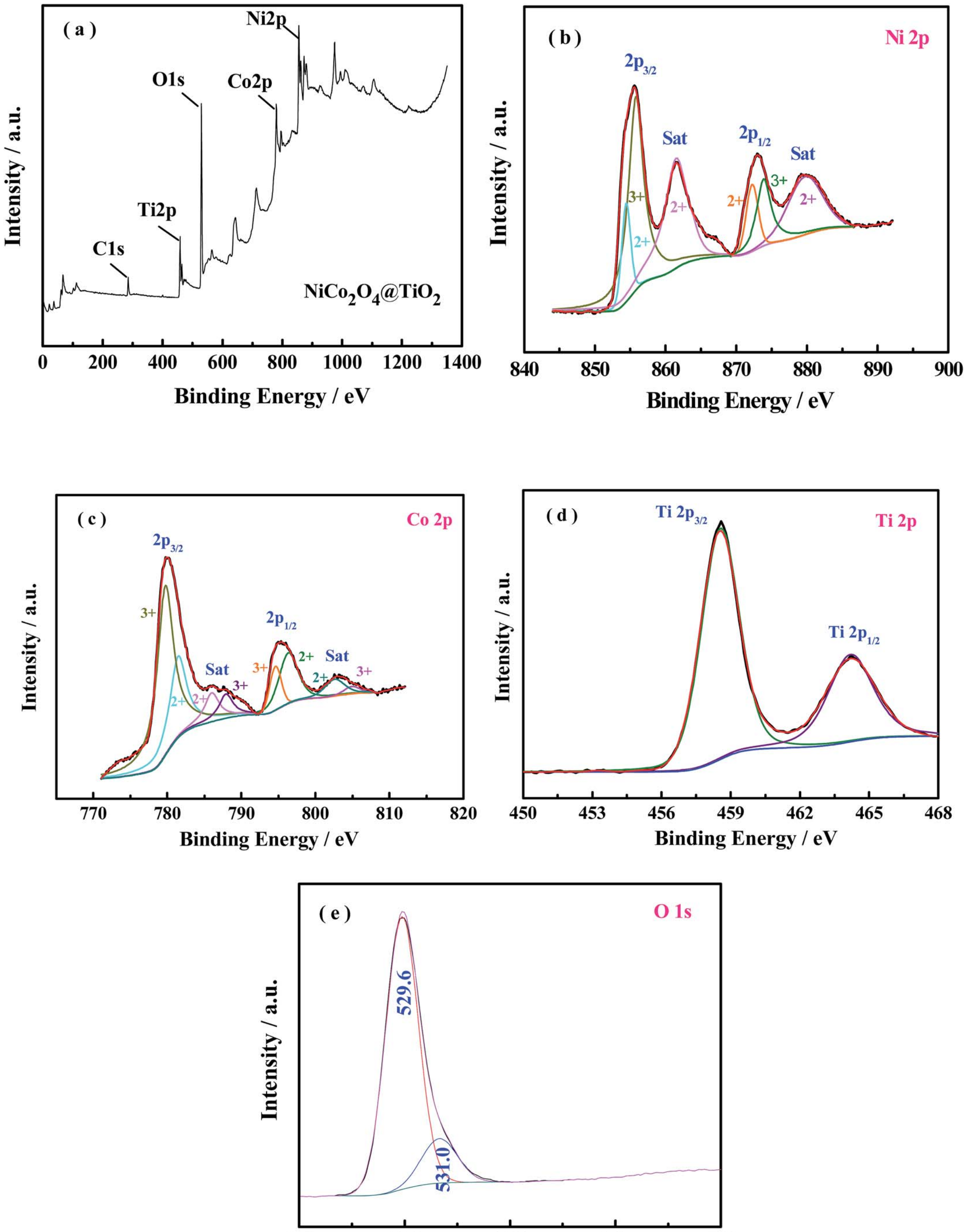

Fig. 7 XPS spectra of (a) survey spectrum, (b) Ni 2p, (c) Co 2p, (d) Ti 2p and (e) O 1s for the $NiCo_2O_4$@TiO_2 product.

and 2.2 V are also observed in the initial anodic sweep, which are attributed to the oxidation of Co^0 and Ni^0 to Co^{3+} and Ni^{2+}, respectively.[42] According to the previous reports,[43] the redox reactions can be expressed as follows:

$$NiCo_2O_4 + 8Li^+ + 8e^- \rightarrow Ni + 2Co + 4Li_2O \quad (1)$$

$$Ni + Li_2O \leftrightarrow NiO + 2Li^+ + 2e^- \quad (2)$$

$$Co + Li_2O \leftrightarrow CoO + 2Li^+ + 2e^- \quad (3)$$

$$CoO + 1/3Li_2O \leftrightarrow 1/3Co_3O_4 + 2/3Li^+ + 2/3e^- \quad (4)$$

In comparison with $NiCo_2O_4$, the CV curves from 2nd to 6th cycles for $NiCo_2O_4$@TiO_2 exhibit a better overlapping degree, indicating a better reversibility of the electrochemical reactions.

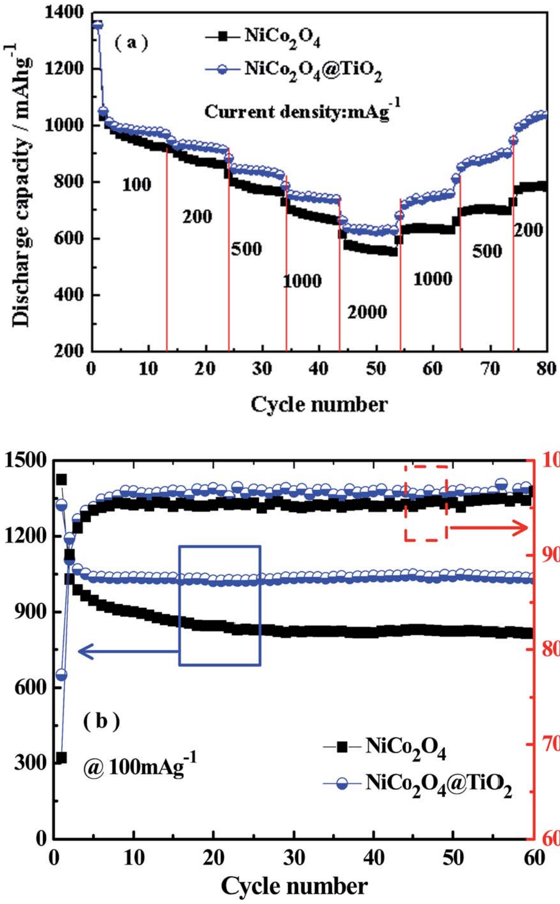

Fig. 8 (a) Rate capability and (b) cyclic performances of $NiCo_2O_4$ and $NiCo_2O_4@TiO_2$ electrodes.

Table 1 Comparison of the electrochemical performances of the $NiCo_2O_4@TiO_2$ 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
$NiCo_2O_4$/3DGN	0.5	790 after 50 cycles	35
$NiCo_2O_4$/Ni	0.1	413 after 50 cycles	36
$NiCo_2O_4@SnO_2@C$-HSs	0.1	720 after 100 cycles	37
$NiCo_2O_4$@G	0.3	806 after 55 cycles	38
$NiCo_2O_4$ nanosheets	0.1	767 after 50 cycles	17
$NiCo_2O_4$@RGO	0.1	816 after 70 cycles	39
$NiCo_2O_4@NiCo_2O_4$ NCAs	0.12	830 after 100 cycles	40
$NiCo_2O_4@TiO_2$	0.1	1033 after 60 cycles	This work

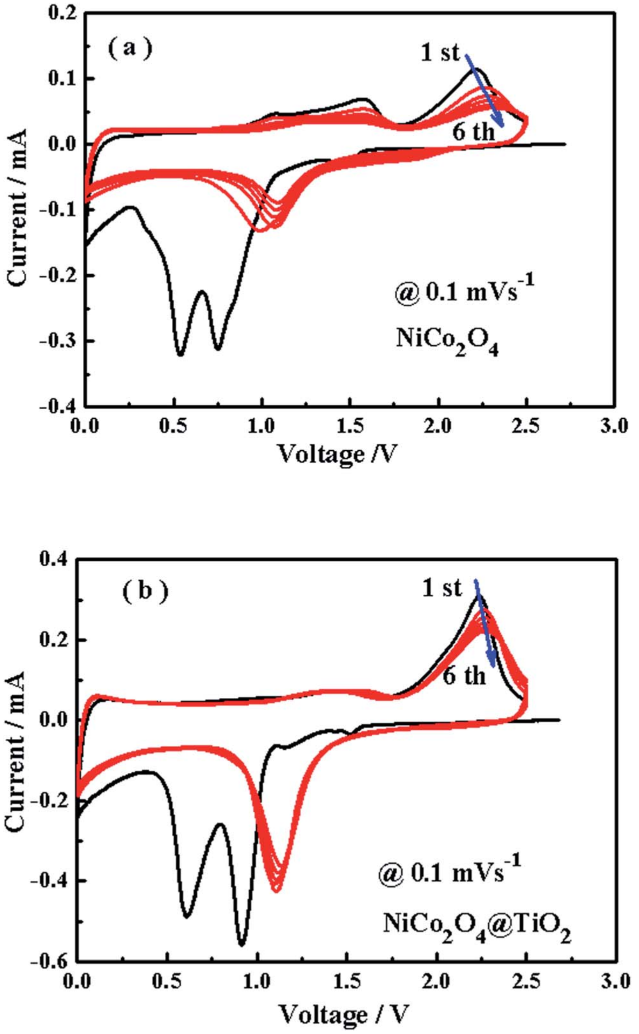

Fig. 9 Cyclic voltammetry profiles of $NiCo_2O_4$ and $NiCo_2O_4@TiO_2$ electrodes.

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 $NiCo_2O_4@TiO_2$ 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, $NiCo_2O_4@TiO_2$ 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 $NiCo_2O_4@TiO_2$. Fig. 11(a) presents the typical EIS of $NiCo_2O_4$ and $NiCo_2O_4@TiO_2$ 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

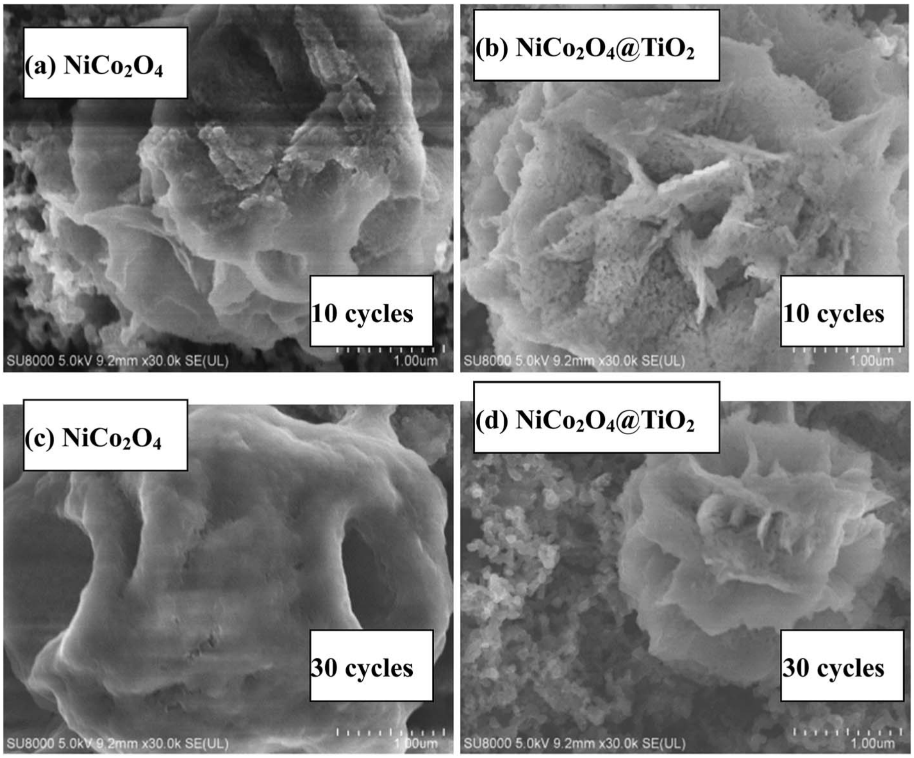

Fig. 10 SEM images of the $NiCo_2O_4$ and $NiCo_2O_4$@TiO_2 powders after 10 and 30 cycles, respectively.

calculated as 36.6 Ω for $NiCo_2O_4$ and 20.4 Ω for $NiCo_2O_4$@TiO_2, respectively. The decrease in R_{ct} for $NiCo_2O_4$@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-ions 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-ion kinetic of the cells can be also calculated according to the EIS profiles in the low frequency.

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

$$Z_{re} = R + \sigma\omega^{-1/2} \tag{6}$$

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 $NiCo_2O_4$@TiO_2 powders are calculated as 2.57×10^{-12} cm^2 s^{-1} and 8.18×10^{-12} cm^2 s^{-1} respectively, suggesting the rapid diffusion of lithium-ions of $NiCo_2O_4$@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 $NiCo_2O_4$@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 $NiCo_2O_4$@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, $NiCo_2O_4$@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 $NiCo_2O_4$@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 possess, 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 nm × 200 nm of $NiCo_2O_4$ and $NiCo_2O_4$@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 $NiCo_2O_4$@TiO_2 powders are calculated based on the surface potential

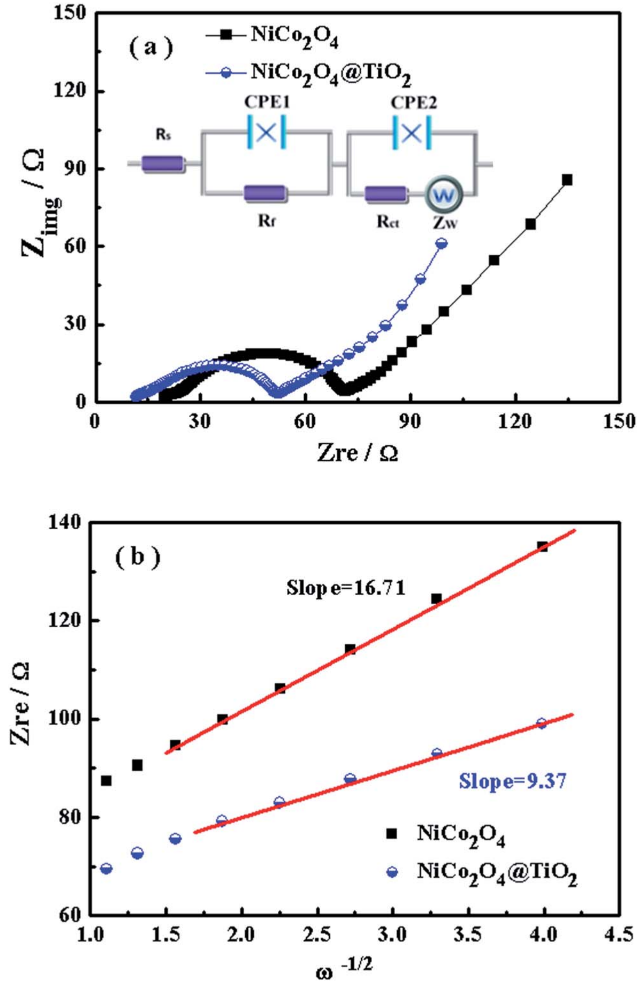

Fig. 11 (a) Typical EIS of $NiCo_2O_4$ and $NiCo_2O_4@TiO_2$ electrode in the fully discharged state and the equivalent circuit for EIS fitting; (b) real parts of the complex impedance Z_{re} *vs.* $\omega^{-1/2}$ for $NiCo_2O_4$ and $NiCo_2O_4@TiO_2$ electrodes.

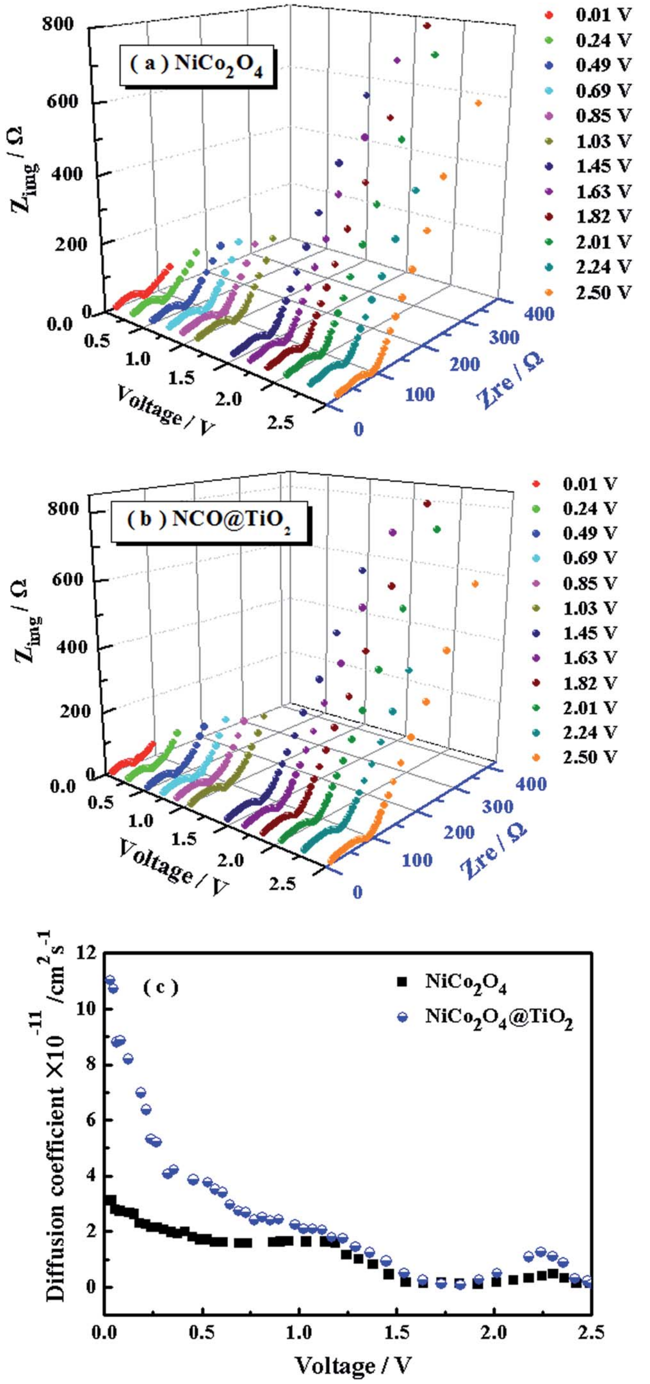

Fig. 12 (a, b) The impedance spectra and (c) corresponding Li-ion of diffusion coefficients of $NiCo_2O_4$ and $NiCo_2O_4@TiO_2$ electrodes under different discharge states.

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 $NiCo_2O_4@TiO_2$ 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 consist with the analysis of EIS measurements.

The reduced work function of $NiCo_2O_4@TiO_2$ 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 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 $NiCo_2O_4$/$NiCo_2O_4$ 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

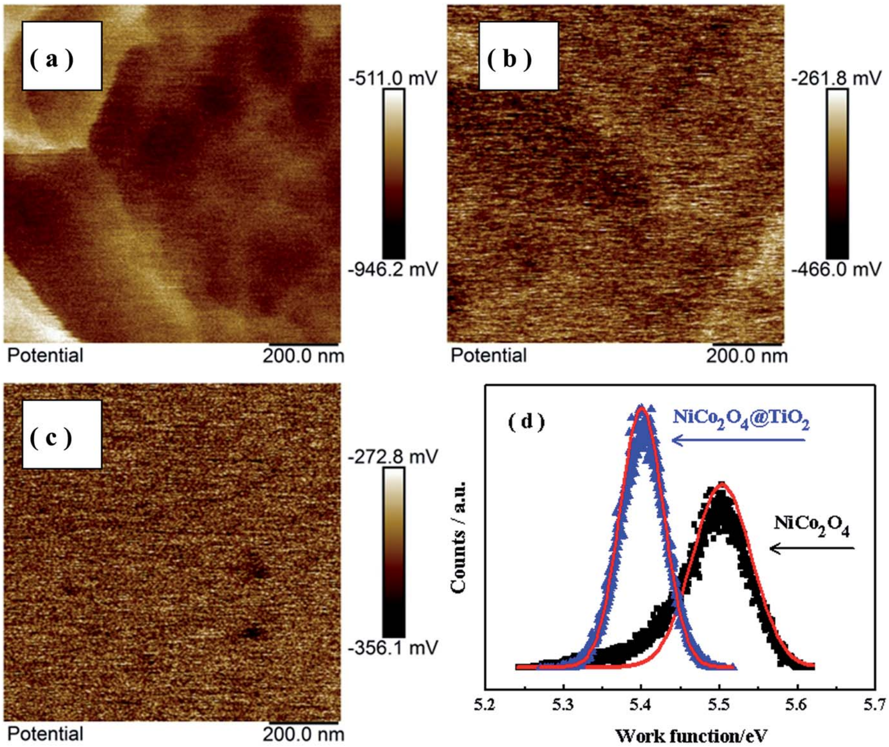

Fig. 13 (a, b) Surface potential maps over a scan area of 200 nm × 200 nm of $NiCo_2O_4$ and $NiCo_2O_4$@TiO_2 powders before cycling; (c) surface potential image of Au foil acting as reference sample; (d) work functions of $NiCo_2O_4$ and $NiCo_2O_4$@TiO_2 electrodes.

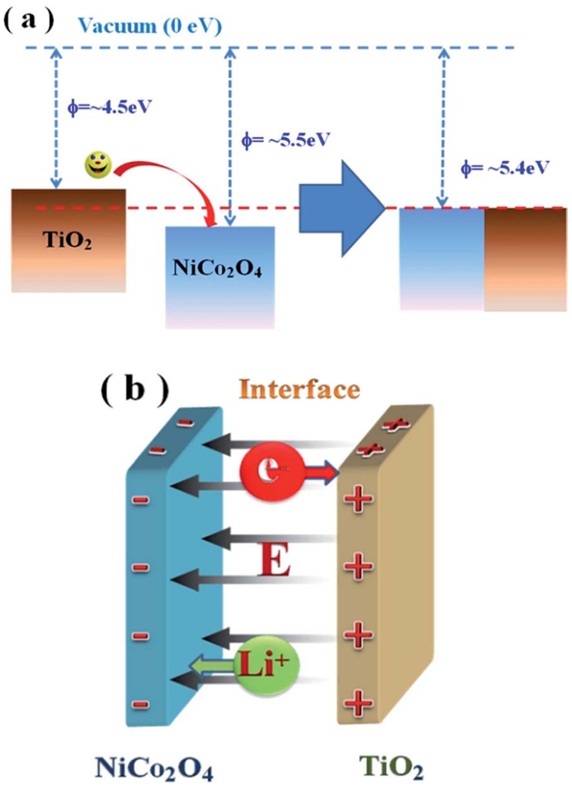

Fig. 14 (a) The energy-level model for explaining the improved electron transfer in $NiCo_2O_4$@TiO_2 electrodes; (b) a built electric field (*E*) between $NiCo_2O_4$ and TiO_2.

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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