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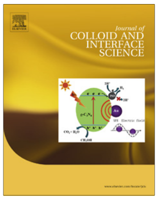

Nanoelectrical investigation and electrochemical performance of nickel-oxide/carbon sphere hybrids through interface manipulation

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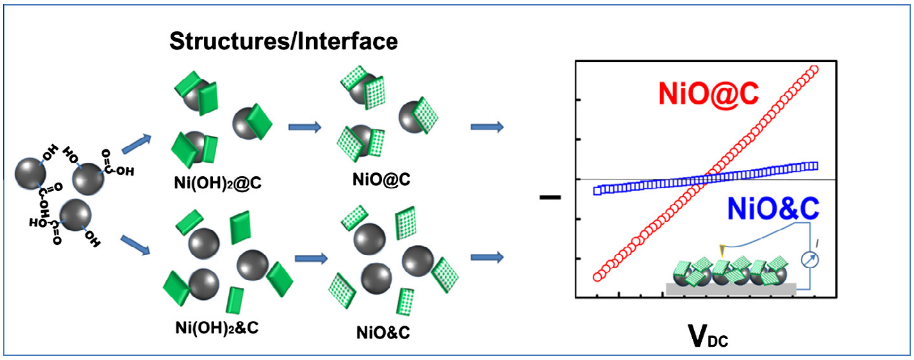
HIGHLIGHTS

- Low cost $Ni(OH)_2$@C and NiO@C hybrids have been synthesized through *in situ* seeded deposition on carbon spheres.
- The surface absorption of the Ni^{2+} cations strongly effects on the deposition in absence of sodium acetate.
- The enhanced nanoelectrical conductivity on NiO@C hybrids was higher than that on NiO&C composites.
- The cycling stability and rate capability of LiBs on hybrids higher than simple composites.
- The charge transfer resistance on hybrids is lower than that on composites.

GRAPHICAL ABSTRACT



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ABSTRACT

Advanced hetero-nanostructured materials for electrochemical devices, such as Li-ion batteries (LiBs), dramatically depend on each functional component and their interfaces to transport and storage charges, where the bottleneck is the sluggish one in series. In this work, we prepare $Ni(OH)_2$@C hybrids through a continuous feeding in reflux and followed by a hydrothermal treatment. The as-prepared $Ni(OH)_2$@C can be further converted into NiO@C hybrids after thermal annealing. As a control, $Ni(OH)_2$&C and NiO&C nanocomposites have also been prepared. Peakforce Tuna measurement shows the conductivity of the NiO@C hybrids is higher than that of NiO&C composites in nanoscale. To further investigate the quality of the interface, 100 charge/discharge cycles of the hybrids are performed in LiBs. The capacity retention of hybrid materials has significantly improved than the simple carbon composites. The enhancement of the electrochemical performance is attributed to the better electric conductivity and smaller charge transfer impedance and strong covalent interface between nickel species and carbon spheres obtained through the controlled seeded deposition.

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1. Introduction

With the increasing tremendous consumption of fossil fuels during the last several decades, more research attentions have been attracted to develop the novel electrochemical materials for energy conversion and storage devices [1,2], *e.g.* the water splitting cells [3], fuel cells [4], Li-O_2 batteries [5] and lithium ion batteries (LiBs) [6]. Due to the multiple requirements of practical electrodes, many hetero-nanostructured materials with different functional components show superior performance than single component [7,8]. Therefore, high conductive graphene [9–12], carbon nanotubes (CNTs) [13], $TiSi_2$ nanonets [14] and nickel foams [15] are widely applied as excellent electron conductive substrates for the active materials loading on. For instance, Zhu and his co-workers [16] prepared Fe_2O_3 nanoparticles/reduced graphene oxides (Fe_2O_3/RGO) and CoO/RGO sheets hybrids through a solvothermal process in ethanol solution as electrode materials for LiBs. In Dai's group, Co_3O_4/graphene and $MnCo_2O_4$/graphene hybrid were constructed by a direct nucleation and growth method [17,18], which exhibited enhanced oxygen reduction activity and oxygen evolution reaction due to the strong interaction between the transition metal oxides and graphene. Later, Li et al. reported a sol–gel method to creat TiO_2/graphene hybrid materials with strongly synergistic coupling effects for high-performance LiBs [19]. Recently, Zhang et al. prepared ultrathin $Co_{0.85}Se$/graphene nanosheets as high active oxygen reduction catalyst through an *in situ* hydrothermal synthesis [20]. The inorganic nanoparticles were strongly anchored on the oxidized graphene sheets. This concept was further extended to oxidized carbon nanotubes forming hybrids: ultrathin β-$Ni(OH)_2$/CNTs nanoplates as water oxidation catalyst [21], $NiCo_2O_4$/CNTs as high performance oxygen reduction catalyst for metal/air battery [22] and MnO_2/CNT coaxial nanotubes as electrodes for LiBs [23]. Both the graphene and carbon nanotubes are unique graphite-like carbon allotropes with high electrical conductivity and surface area, high mechanical strength and flexibility. The inorganic species usually deposited at the position of hydroxyl, carboxylic or epoxy groups, forming covalent bonds. Thus, the strong interaction between the active materials and graphene (or carbon nanotube) accounts for the high electrochemical performance. However, the applications of graphene or CNTs materials still require high-cost complicated synthetic processes [1] than the common conductive carbon does. Moreover, the high quality interface between the amorphous carbon and metal oxides are seldom reported.

To employ the practical energy storage and conversion device in large scale, strong coupled hybrids of electrochemical active inorganic oxides and low cost carbon materials would be a rational solution [24]. One of the great challenges is the electrode construction of the active materials and carbon materials with excellent interface. Previously, Lu and his coworkers deposited Al_2O_3 and Pd on carbon spheres through atomic layered deposition (ALD), showing a remarkable low over-potential for Li–O_2 battery in tetraethylene glycol dimethyl ether electrolyte [25]. Similar conclusion was obtained by Xie et al. on 3D porous carbon [26]. As the preparation of carbon spheres has been studied for long time [27,28], due to its high conductivity, low-cost, environmental-friendly, non-toxic and suitability for addressing the energy shortage [29,30] and environmental crisis [31], it is of great interest to prepare metal oxides/carbon spheres hybrid composites with strong coupling effects. The challenge is how to achieve high electric conductivity on carbon spheres as graphene and CNTs materials.

Herein, we demonstrate the strong coupling and synergetic effect between the transition metal oxides and the carbon spheres. The nickel hydroxide or oxide are chosen as an example, because they are earth abundant, widely used as active materials ($578\ mA\,h\,g^{-1}$ for $Ni(OH)_2$ and $718\ mA\,h\,g^{-1}$ for NiO) for LiBs [32–35], supercapacitor [36] and water splitting electrocatalyst [21]. An *in situ* deposition of $Ni(OH)_2$ on carbon spheres was carried out through continuous injection of $NiCl_2$ precursor solution, resulting in the surface absorption/nucleation and formation of $Ni(OH)_2$@C hybrids. For the control experiment, the $Ni(OH)_2$&C composite was produced by a similar reflux method in presence of sodium acetate (NaAc) that reduced the surface absorption of Ni^{2+}. NiO@C hybrids and NiO&C composites could also be obtained after thermal annealing, respectively. To investigate the electric conductivity, a powerful Peakforce tunneling atomic force microscopy (PF-Tuna AFM) technology is used [37,38]. The electrochemical performance was revealed through the lithium ion battery test and impedance study.

2. Experimental

2.1. Hybrids and composites preparation

All the chemical reagents were commercial available analytical grade (Sinopharm Chem. Reagent, China) and used without further purification, except for the battery materials. The $Ni(OH)_2$@carbon hybrid was prepared through a modified reflux-hydrothermal process of Dai's group [9]: briefly, 8 mg of carbon spheres (SuperP, Timcal graphite) was ultrasonically dispersed in 40 mL dimethyl formamide (DMF) for 20 min, then a 1.6 mL of $NiCl_2$ solution (0.02–0.2 M) was continuously injected into the DMF solution at 80 °C for 6 h. After hydrolysis in DMF for another 6 h, the composites were isolated from the solution through centrifugation at 10,000 rpm for 3 min. The black precipitation was washed with deionized (DI) water for 3 times and dispersed into 20 mL DI water, before transferring into a Teflon-lined autoclave. Then the autoclave was maintained at 180 °C for 12 h. After cooling to room temperature, the black hybrid was collected, and named as $Ni(OH)_2$@C. For $Ni(OH)_2$&C composite sample, the synthetic process was same as $Ni(OH)_2$@C hybrid, except the injected solution contained 0.02 M NaAc and 0.2 M $NiCl_2$.

The NiO@C hybrid and NiO&C composites were obtained through thermal annealing of $Ni(OH)_2$@C and $Ni(OH)_2$&C, respectively, in a furnace at 400 °C with Ar flow of 20 standard cubic centimeter per minute (sccm) for 1 h.

2.2. Characterization

The X-ray diffraction (XRD) was carried out on an X-ray diffractometer (Bruker D8 Advance), where the Cu Kα radiation ($\lambda = 1.5418$ Å) operating at accelerate voltage of 40 kV and current of 40 mA was used. FT-IR spectra were obtained on Infrared spectrometer (Nicolet 6700), with sample dispersed in pressed KBr pellet. Raman spectra were collected on a Confocal Raman microscope (Renishaw in Via Reflex) excited with a green laser of 532 nm in the range of 100–2000 cm^{-1}. TEM was recorded on transmission electron microscopes (JEOL JSM-2100F and Tecanai FEI F20) with an accelerating voltage of 200 kV, coupled with energy-dispersive X-ray spectroscopy (EDS).

2.3. Nanoelectrical conductivity measurement

The nanoscopic conductivity of the NiO@C hybrids and NiO&C composites were measured directly using a peakforce tunneling atomic force microcopy (Peakforce Tuna, on Bruker Dimension Icon) under ambient condition, where the samples were dispersed on a conductive F-doped SnO_2 (FTO) substrate. A Pt/Ir coated Sb-doped Si probe (Bruker SCM-PIT) with tip radius of 25 nm was