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Layered cobalt nickel silicate hollow spheres as a highly-stable supercapacitor material ☆

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HIGHLIGHTS

- Layered cobalt nickel silicate hollow nanospheres were prepared for by a facile hydrothermal method.
- The mechanism of the layered cobalt nickel silicate hollow nanospheres growth was investigated.
- The prepared material exhibited specific capacitance and outstanding long-term cycling stability.

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ABSTRACT

Among the actively studied electrode materials, layered cobalt or nickel compounds have been recognized as a family of promising electrode materials for supercapacitor. However, the cycling performance of these materials is unsatisfactory by far. In this work, a novel and stable layered cobalt nickel silicate hollow sphere compound was prepared for supercapacitor application using a facile hydrothermal synthetic approach. The obtained material exhibited a good specific capacitance and outstanding long-term cycling stability (only 0.7% and 5% losses of its initial specific capacitance after 10,000 and 20,000 cycles, respectively) at a high current density of 20 A/g after annealing at 600 °C. This work provides new insights of designing novel cobalt or nickel compounds for supercapacitor with excellent stability, and promotes the application of layered metal silicates as advanced supercapacitor materials.

1. Introduction

The consumption of fossil fuels and the environment pollution problems have stimulated the rapid development of sustainable energy. Supercapacitor, a system for electrochemical energy storage and conversion, has attracted numerous interests because of its rapid charge and discharge rates, high power density, long cycle lifetime and high reliability in comparison with conventional batteries [1]. There are two types of supercapacitor in terms of the different charge storage mechanisms. One is double-layer capacitor, which arises from the charge separation at the interface between solid electrode and electrolyte. Another is pseudocapacitor, which entails the fast reversible faradaic redox reactions occurring at or near a solid electrode surface [2,3]. Especially, the specific capacitance of a pseudocapacitor is usually 10–100 times larger than that of a double-layer capacitor, attracting more extensive studies [4,5].

The exploration of suitable electrode materials is the key challenge for the application of pseudocapacitors. Numerous electroactive materials have been developed for pseudocapacitor application. It is highly desirable to obtain electroactive materials with rich redox capacity for generating pseudocapacitance with a consideration of the charge storage mechanism of pseudocapacitor [3,6–8]. RuO_2 has been widely studied as the electrode material of the electrochemical capacitor because of its high specific capacitance. However, the application of RuO_2 is hindered by its high costs and toxicity. To resolve this problem, various attempts have been made to replace RuO_2 with inexpensive transition-metal oxides [9]. Layered cobalt and nickel compounds such as $Co(OH)_2$, $Ni(OH)_2$, Co_3O_4 and NiO, because of the good redox reversibility and high activity, have been shown to be promising electrode materials for the pesudocapacitor [10–18]. Although the capacitance has been increased substantially, the cycle performance of the cobalt and nickel compounds is insufficient yet and thus needs further improvement.

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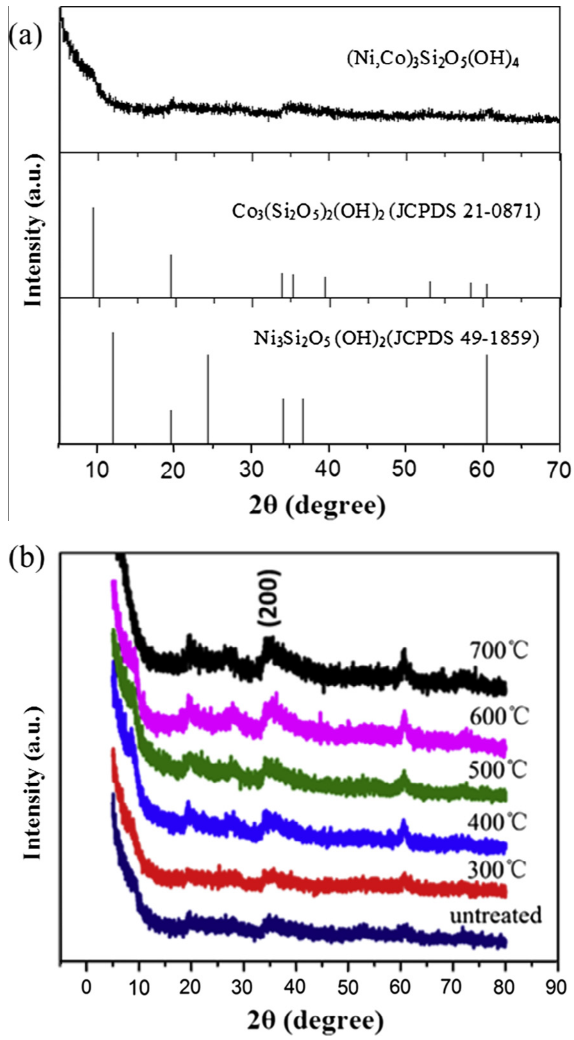

Fig. 1. (a) XRD pattern of (Ni, $Co)_3Si_2O_5(OH)_4$ nanospheres; and (b) XRD patterns of (Ni, $Co)_3Si_2O_5(OH)_4$ annealed at different temperatures.

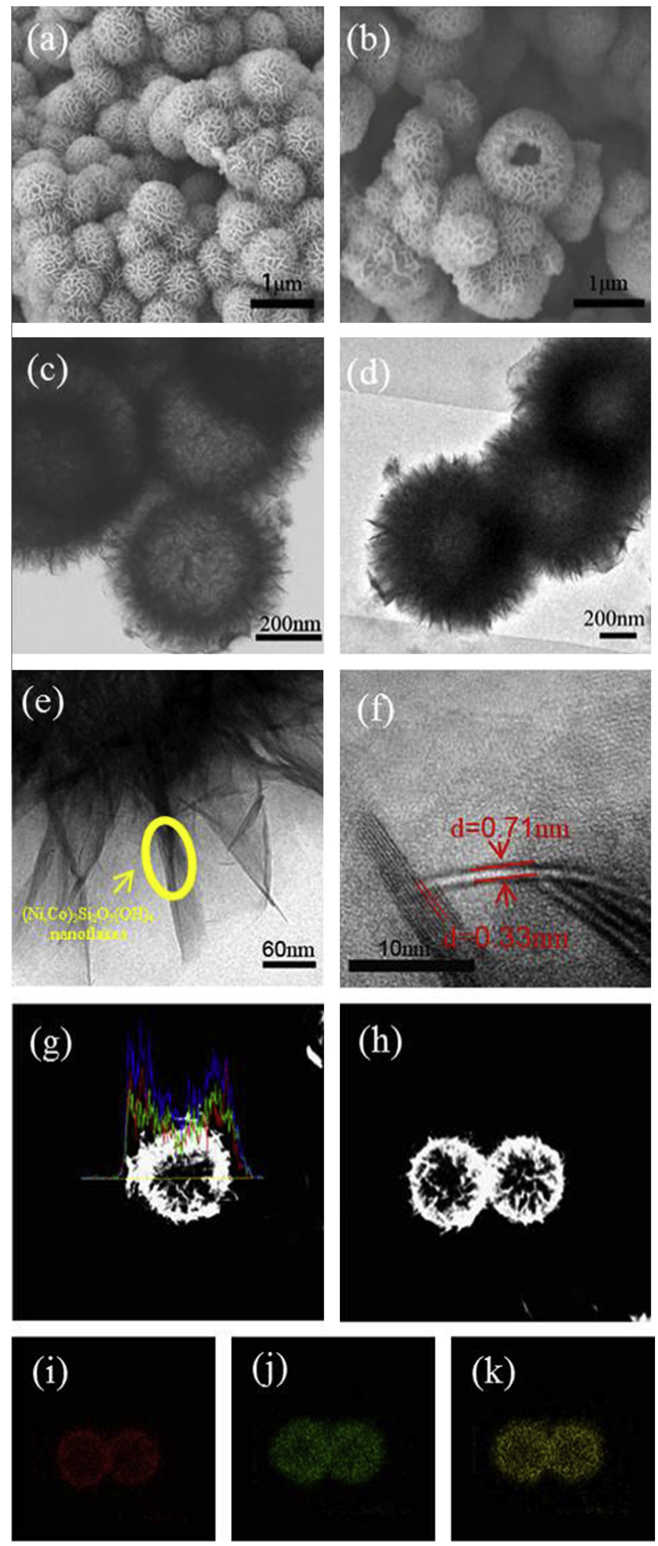

Fig. 2. SEM images before (a) and after (b) annealing at 600 °C, TEM images before (c) and after (d) annealing at 600 °C, (e, f) HRTEM images of the nanospheres, (g, h) elemental line profiles and the related elemental mapping images of (i) Co, (j) Ni and (k) Si.

So far, many efforts have been aimed at improving the cycling stability of the cobalt and nickel compounds. A common strategy is to combine transition-metal oxides into composites with carbon, which is both lightweight and electronically conducting, offering high specific capacitance and stability for the pesudocapacitor [11,19]. In addition, improving the stability of the single component compound itself is also an important approach. Synthesizing materials with new morphology and appropriate phase is an effective way to increase the stability [15]. Some studies have shown that layered double hydroxide or oxide such as Ni_xCo_{1-x}LDH and $NiCo_2O_4$ exhibited increased capacity and improved cycle stability, compared with pure $Ni(OH)_2$ [20]. Despite of the valuable progresses, the cycle performance for the single component electrode materials is unsatisfactory yet. Hence, it is of great importance to develop new strategies that could greatly enhance the long-term cycling stability of the materials.

Silicate hydroxides with porous structure and tunable composition have found many applications [21–23]. As the members of this family, nickel silicate hydroxides, especially the $Ni_3Si_2O_5(OH)_4$ nanotubes, and cobalt silicate hydroxides, have been studied due to their layered structures and special properties. Their excellent electrochemical performance has been extensively investigated [22–24]. However, their stability issue has not been well explored. Therefore, in this work, a novel and ultra-stable layered Co–Ni silicate hydroxide hollow nanosphere was synthesized by using a facile one-step hydrothermal method with SiO_2 spheres as the template and its application for supercapacitor was also explored. Its excellent stability was demonstrated. In this way, a facial method was established to improve the stability of layered cobalt or nickel compounds as supercapacitor materials and promote the