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# Electrochemical synthesis of hierarchical $\beta$ -Ni(OH)<sub>2</sub> nanostructures on conductive textiles

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## ABSTRACT

Hierarchical and porous  $\beta$ -Ni(OH)<sub>2</sub> nanostructures (NSs) were synthesized on conductive textile (CT) substrates via a facile electrochemical deposition process. The formation of the  $\beta$ -Ni(OH)<sub>2</sub> NSs and their structural morphology strongly depended on the deposition potential. At an optimum applied cathodic voltage of  $-0.75$  V, the synthesized  $\beta$ -Ni(OH)<sub>2</sub> exhibited hierarchical and flower-like NSs and were well decorated on the CT with high porosity and good crystallinity. By varying the growth time under a proper applied cathodic voltage condition, the density of decorated hierarchical  $\beta$ -Ni(OH)<sub>2</sub> NSs on the CTs could be controlled and modified, which might have great potential for foldable electrode and electrochemical capacitor applications.

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## 1. Introduction

Nickel oxide (NiO) and nickel hydroxide (Ni(OH)<sub>2</sub>) have attracted great attention for wide application fields, such as fuel cell electrodes, electrochemical supercapacitors and gas sensors, due to their excellent capacitance, good chemical and thermal stabilities [1–3]. Recently, many efforts have focused on the fabrication of the two- or three-dimensional hierarchical NiO or Ni(OH)<sub>2</sub> nanostructures including the rod-like, flower-like and urchin-like products because the increment in the surface area to volume ratio and the quantum size effect are very important for improving the efficiency of devices [4–7]. In order to obtain such NiO or Ni(OH)<sub>2</sub> nanostructures, therefore, different fabrication techniques have been developed to be facile, fast, low growth temperature and cost-effective, e.g., the hydrothermal growth [8], sol-gel process [9], microwave assisted synthesis [10] and electrochemical deposition (ED) [11]. Among them, the ED method is considered to be one of most promising processes because it is able to readily control the morphology of nanostructures by varying the deposition potential. Indeed, the  $\beta$ -Ni(OH)<sub>2</sub> NSs which have a good stability in alkali have been widely used for positive electrode materials [12]. Meanwhile, conductive textiles (CTs) have shown an advanced feasibility including the flexible, wearable and stretchable abilities [13]. Furthermore, it can be expected to produce the largely extended surface area from the combination of micro-fiber arrays. In this work, the highly porous  $\beta$ -Ni(OH)<sub>2</sub> NSs were fabricated on CTs by a simple ED deposition

under different growth conditions. The structural and morphological properties of the  $\beta$ -Ni(OH)<sub>2</sub> NSs were investigated.

## 2. Experimental procedure

The  $\beta$ -Ni(OH)<sub>2</sub> NSs were grown on CT substrates via a simple ED method. The CT substrate was composed of woven fiber arrays, which are commercially produced with Ni plated on polyethylene terephthalate (PET). Prior to the  $\beta$ -Ni(OH)<sub>2</sub> synthesis, the CT substrates of  $3 \times 2$  cm<sup>2</sup> were prepared and cleaned by ethanol and de-ionized (DI) water. Meanwhile, 10 mM of nickel acetate tetrahydrate was dissolved in 50 mL of ethanol, and then 1 mL of sodium dodecyl sulphate was slowly dropped into the solution. After 20 min with a magnetic stirring, the ethanolic solution was changed to the transparent green colour. Then, the substrates were immersed into the ethanolic solution for 20 min and placed in oven of 130 °C for 1 h. After that, the CT substrate was dipped into the growth solution for carrying out a simple ED process. The two electrode system was utilized with a platinum mesh (counter electrode) and the CT substrate (working electrode). The growth solution was made by dissolving the 10 mM of nickel nitrate hexahydrate and 30 mM of hexamethylenetetramine in 900 mL of DI water. During the ED process, the growth solution was kept at 85 °C on a hotplate. To investigate the structural and morphological properties of  $\beta$ -Ni(OH)<sub>2</sub> NSs, a field-emission scanning electron microscope (FE-SEM, Carl Zeiss, LEO SUPRA 55) and an X-ray diffraction (XRD, Mac Science, M18XHF-SRA) were used. And the surface properties of the fabricated samples were characterized by using an atomic force microscope (AFM, XE150, PSIA).

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### 3. Results and discussion

Fig. 1 shows the top-view FE-SEM images and schematic diagram of the  $\beta$ -Ni(OH)<sub>2</sub> NSs grown on the CT substrate under a cathodic voltage of  $-0.75$  V for 40 min. At this growth condition, highly porous  $\beta$ -Ni(OH)<sub>2</sub> NSs were well decorated on the CT with good adhesion. Additionally, the woven Ni coated PET (Ni/PET) CT with  $\beta$ -Ni(OH)<sub>2</sub> NSs which were well arranged exhibited a good flexibility as shown in digital photograph as well as a largely extended specific surface area. By coating an ethanolic solution for seed layers, the hierarchical  $\beta$ -Ni(OH)<sub>2</sub> NSs were uniformly deposited over a whole surface of Ni/PET CT. In a magnified view of FE-SEM image, the large-sized ( $\sim 3$ – $5$   $\mu\text{m}$ ) and thin ( $\sim 10$ – $30$  nm) flower-like  $\beta$ -Ni(OH)<sub>2</sub> were perpendicularly aligned on the CT substrate.

Fig. 2 shows the  $2\theta$  scan XRD pattern of the  $\beta$ -Ni(OH)<sub>2</sub> NSs grown on the CT substrate under the same condition of Fig. 1. For comparison, the XRD pattern of the bare CT was also shown. Due to the woven Ni/PET CT, the broad PET peaks and Ni peaks were commonly observed in both samples. The dominant peaks and positions of Ni (111), (200) and (220) were well consistent with the standard crystallographic date (JCPDS card: 88-2326). In the low  $2\theta$  range of  $18$ – $25^\circ$ , three broad peaks of PET could be reasonably observed in good agreement with previous work [14]. For synthesized  $\beta$ -Ni(OH)<sub>2</sub> NSs, the peaks and positions corresponded to the crystalline structure of  $\beta$ -Ni(OH)<sub>2</sub> (JCPDS card: 14-0117). Furthermore, there were no XRD peaks of  $\alpha$ -Ni(OH)<sub>2</sub>, which indicates that the sample is purely composed of  $\beta$ -Ni(OH)<sub>2</sub> NSs.

Fig. 3 shows the top-view FE-SEM images of the fabricated  $\beta$ -Ni(OH)<sub>2</sub> NSs at different applied cathodic voltages of (a)  $-0.5$  V, (b)  $-0.75$  V and (c)  $-1$  V. Figs. 3(d)–(f) show the AFM surface topography images of  $2\ \mu\text{m} \times 2\ \mu\text{m}$  for the corresponding samples of (a)–(c). As the applied cathodic voltage was increased, the morphology was considerably changed from the hexagonal plate-like shape into the porous flower-like one. In general, the ED potential mainly contributes to the formation of Ni(OH)<sub>2</sub> NSs by reducing the nitrate ions and hydrogen peroxide in growth solution. This is because it supplies electrons to the surface of working samples. Hence, the hydroxide ions were produced and reacted with nickel ions, thus creating the Ni(OH)<sub>2</sub> NSs on the seed coated samples. Therefore, the growth property of Ni(OH)<sub>2</sub> NSs was strongly affected by the applied cathodic voltage. At  $-0.5$  V of applied cathodic voltage, large-sized thin hexagonal plates of  $\beta$ -Ni(OH)<sub>2</sub> NSs were formed. These thin hexagonal nanoplates had been observed in the initial formation of synthesized  $\beta$ -Ni(OH)<sub>2</sub> NSs without alignment of crystallization along the [001] axis [15]. In the same way, the applied cathodic voltage of  $-0.5$  V was not enough to align the

Ni(OH)<sub>2</sub> NSs, which leads to the shape of thin hexagonal nanoplates. Above  $-0.75$  V, however, the  $\beta$ -Ni(OH)<sub>2</sub> NSs were grown vertically and became porous. When the applied cathodic voltage was increased from  $-0.75$  to  $-1$  V, the  $\beta$ -Ni(OH)<sub>2</sub> NSs got thicker and their morphology became film-like because the growth rate was increased due to the increased amount of produced hydroxide ions and the enhanced attracting force. From the AFM images, the root-mean-square (RMS) surface roughness of  $\beta$ -Ni(OH)<sub>2</sub> NSs was significantly increased to  $115.59$  nm at the applied cathodic voltage of  $-0.75$  V. It is clear that the cathodic voltage of  $-0.75$  V provides a appropriate ED potential for synthesizing the flower-like  $\beta$ -Ni(OH)<sub>2</sub> NSs with high porosity.

Fig. 4 shows the top-view FE-SEM images of the fabricated  $\beta$ -Ni(OH)<sub>2</sub> NSs for different growth times of (a) 10 min, (b) 20 min, (c) 1 h and (d) 3 h at the applied cathodic voltage of  $-0.75$  V. The insets show the magnified images of the corresponding samples. At 10 min of growth time, the  $\beta$ -Ni(OH)<sub>2</sub> NSs were initially grown in the shape of thin hexagonal nanoplates. After 20 min, the flower-like  $\beta$ -Ni(OH)<sub>2</sub> NSs began to be aligned along the [001] axis of crystal structure from the thin hexagonal nanoplates. Then, the hierarchical flower-like  $\beta$ -Ni(OH)<sub>2</sub> NSs were densely decorated on the CT while keeping the shape with high porosity. It is noticeable that the density of the flower-like  $\beta$ -Ni(OH)<sub>2</sub> NSs can be readily controlled by varying the growth time under a proper applied cathodic voltage.

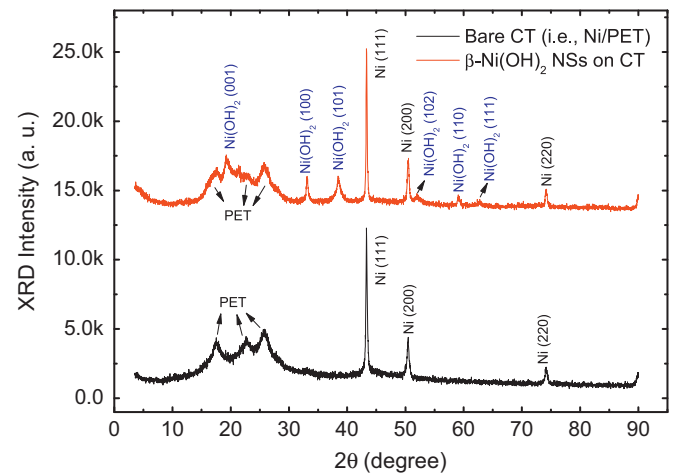


Fig. 2.  $2\theta$  scan XRD pattern of the  $\beta$ -Ni(OH)<sub>2</sub> NSs grown on the CT substrate under the same condition of Fig. 1. For comparison, the XRD pattern of the bare CT was also shown.

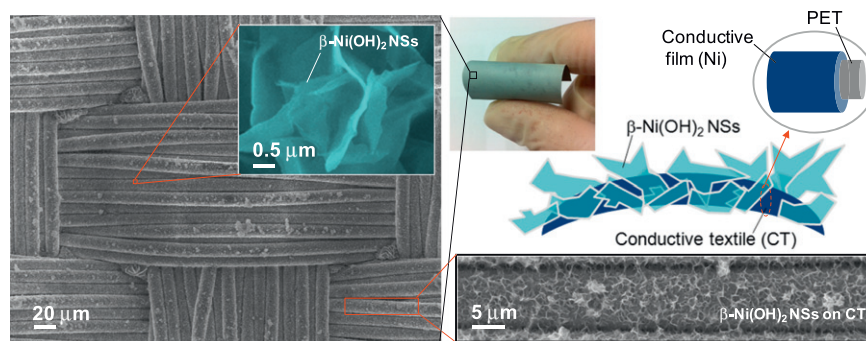
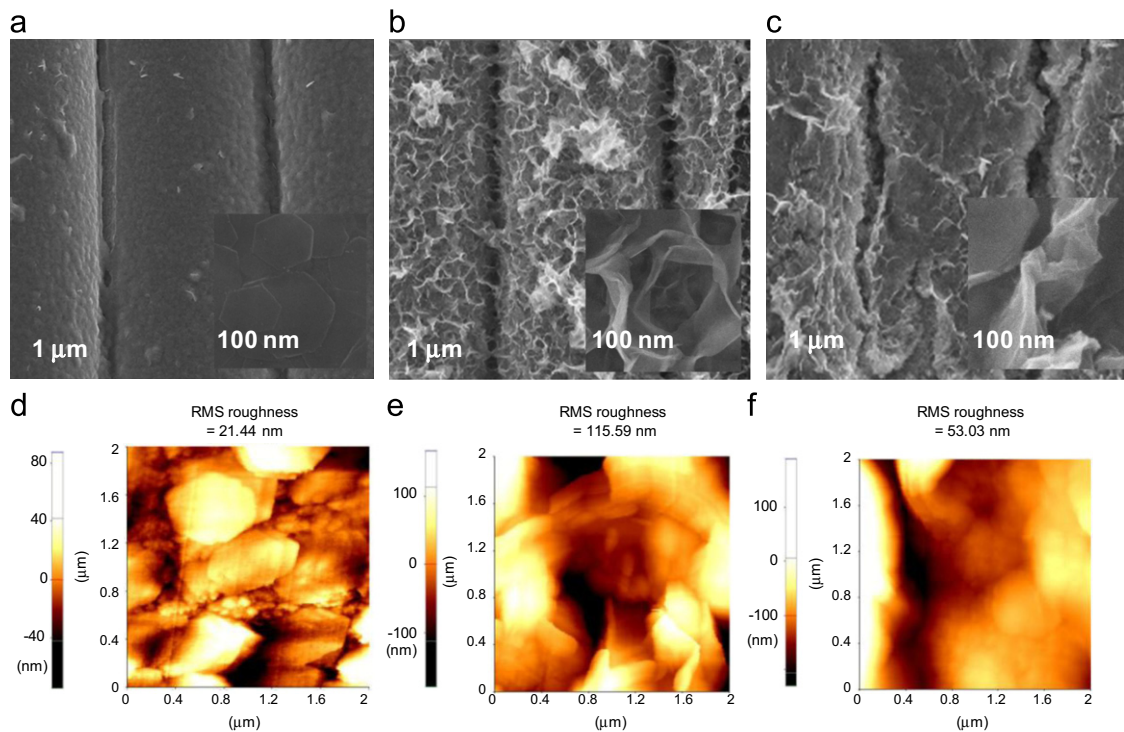
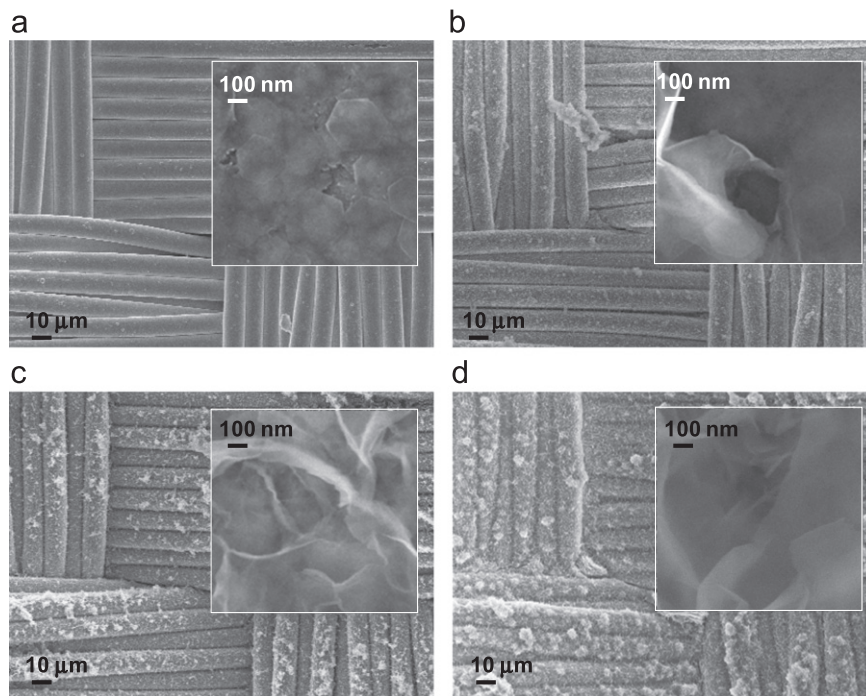


Fig. 1. Top-view FE-SEM images and schematic diagram of the  $\beta$ -Ni(OH)<sub>2</sub> NSs grown on the CT substrate under a cathodic voltage of  $-0.75$  V for 40 min. The digital photograph of the corresponding sample was also shown.



**Fig. 3.** Top-view FE-SEM images of the fabricated  $\beta$ -Ni(OH)<sub>2</sub> NSs at different applied cathodic voltages of (a)  $-0.5$  V, (b)  $-0.75$  V and (c)  $-1$  V. (d)–(f) shows the AFM surface topography images of  $2\ \mu\text{m} \times 2\ \mu\text{m}$  for the corresponding samples of (a)–(c).



**Fig. 4.** Top-view FE-SEM images of the fabricated  $\beta$ -Ni(OH)<sub>2</sub> NSs for different growth times of (a) 10 min, (b) 20 min, (c) 1 h and (d) 3 h at the applied cathodic voltage of  $-0.75$  V.

#### 4. Conclusion

Highly porous and hierarchical flower-like  $\beta$ -Ni(OH)<sub>2</sub> NSs were fabricated on the CT substrates by using the ED method. The applied cathodic voltage played an important role in forming the porous  $\beta$ -Ni(OH)<sub>2</sub> NSs. Under a proper applied cathodic voltage of  $-0.75$  V, the flower-like  $\beta$ -Ni(OH)<sub>2</sub> NSs were deposited on the CT

for a short growth time of 40 min, exhibiting a RMS surface roughness of 115.59 nm. Additionally, it is possible that the density of flower-like  $\beta$ -Ni(OH)<sub>2</sub> NSs could be controlled by changing the growth time under an optimized applied cathodic voltage. These facilely and efficiently grown flower-like  $\beta$ -Ni(OH)<sub>2</sub> NSs on CTs can be expected to be useful for various flexible electrochemical applications.

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