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# Enhanced supercapacitor performance using hierarchical $TiO_2$ nanorod/$Co(OH)_2$ nanowall array electrodes

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ABSTRACT

We report novel hierarchical $TiO_2$ nanorod (NR)/porous $Co(OH)_2$ nanowall array electrodes for high-performance supercapacitors fabricated using a two-step process that involves hydrothermal and electrodeposition techniques. Field-emission scanning electron microscope images reveal a bilayer structure consisting of $TiO_2$ NR arrays with porous $Co(OH)_2$ nanowalls. Compared with the bare $TiO_2$ NRs, the hierarchical $TiO_2$ NRs/$Co(OH)_2$ electrodes showed improved pseudocapacitive performance in a 2-M KOH electrolyte solution, exhibiting an areal specific capacitance of 274.3 mF $cm^{-2}$ at a scan rate of 5 mV $s^{-1}$. The electrodes exhibited good stability, retaining 82.5% of the initial capacitance after 4000 cycles. The good pseudocapacitive performance of the hierarchical nanostructures is mainly due to the porous structure, which provides fast ion and electron transfer, a large surface area, short ion diffusion paths, and a favourable volume change during the cycling process.



## 1. Introduction

In recent years, energy has become one of the major issues facing the world. To help mitigate growing energy costs, energy storage devices are required for future high-power applications. Supercapacitors are a new class of energy storage device, which have become the subject of much recent research interest because of the high power density, long cycle life, short charging time, and safe operation compared with lithium-ion batteries and conventional dielectric capacitors [1–3]. Supercapacitors have a number of potential applications, including electric vehicles, hybrid electric vehicles, and mobile electronics [4–7].

It is well known that capacitance and the energy storage performance of supercapacitors depends on the electrode materials. Therefore, much research has been carried out in recent years to improve the performance of supercapacitors by developing new electrode materials [8–12]. Hydrous ruthenium oxide has shown the greatest specific capacitance and has excellent reversibility; however, the toxicity, scarceness and high cost of the Ru limits its commercial application [13,14]. Therefore, much effort has been devoted to searching for alternative electrode materials. Metal oxides and hydroxides are inexpensive and environmentally friendly with good electrochemical performance, and those that possess multiple oxidative states or structures and can facilitate redox reactions are of particular interest [15].

Titanium dioxide ($TiO_2$) and cobalt hydroxide ($Co(OH)_2$) are considered to be two of the most promising materials due their low cost, natural abundance, low toxicity, and relatively small environmental impact [16–18]. These materials have a wide range of existing and potential applications, including supercapacitors, lithium-ion batteries, gas sensors, electrocatalysts, and magnetic devices [16,19,20]. $Co(OH)_2$ has a high theoretical capacitance and excellent redox activity [21,22], and $TiO_2$ is an electrochemically stable semiconductor and is commonly used as electrodes in electrochemical devices [23]. However, these materials may not provide high specific capacitance at higher current densities, and therefore much attention has been paid to improving the specific capacitance, structural stability, and electrochemical stability at high current densities.

One of the most promising approaches is to construct complex nanoscale architectures with a combination of two types of materials and/or structures on a conducting substrate as binder-free electrodes for high-performance supercapacitors. Hierarchical nano-architectures possess a large specific surface area and can exploit synergetic properties of materials and short ionic and electronic diffusion paths, which can lead to faster kinetics, more

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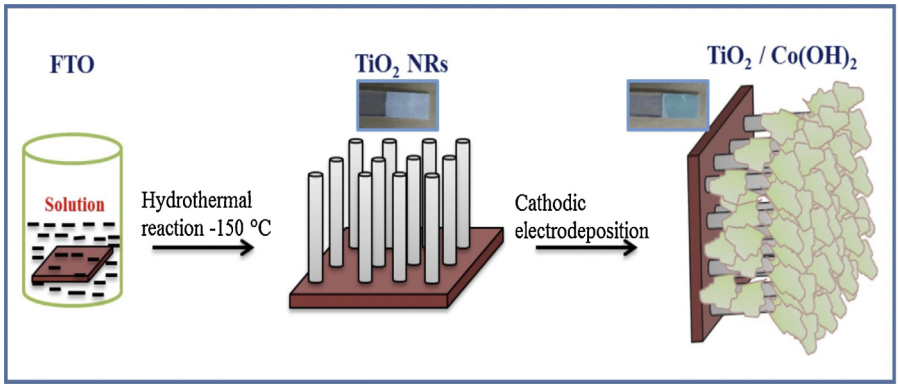


**Scheme 1.** Schematic diagram showing the $TiO_2/Co(OH)_2$ hierarchical nanostructure growth process.

efficient contacts with the electrolyte ions, and more electroactive sites for Faradaic energy storage, resulting in high specific capacitance at high current densities [7,24,25]. Therefore, designing suitable electrodes with a suitable nanostructure is of much interest, and recently much effort has been devoted to the synthesis of advanced hierarchical nano-architectures that combine two materials that exhibit improved electrochemical performance [26–30].

Here, we describe a simple method to prepare $TiO_2$ nanorods (NRs)/porous $Co(OH)_2$ nanowall bilayer hierarchical nanostructures on fluorine-doped tin oxide (FTO) substrates. This synthetic approach is based on the combination of hydrothermal synthesis (the $TiO_2$ NR sub-structure) and electrodeposition methods (the $Co(OH)_2$ nanowall superstructure), which results in the unique structure and morphology. Compared with bare $TiO_2$ NR array electrodes, the bilayer hierarchical nanostructured electrode exhibited markedly improved electrochemical performance with a higher areal specific capacitance as well as better cycling stability. This hierarchical architecture provides a large surface area and large number of active sites to facilitate ion and electron transfer, which leads to the larger specific areal capacitance than the single-layer structure.

## 2. Experimental methods

### 2.1. Preparation of $TiO_2/Co(OH)_2$ hierarchical nanostructure

All reagents used in these experiments were of analytical grade and were used directly without further purification. $TiO_2$ NRs were grown on FTO substrates using a hydrothermal deposition method, as described in Ref.[31] $Co(OH)_2$ nanowalls were grown over the $TiO_2$ NRs by cathodic electrodeposition. Briefly, the electrolyte for electrodeposition was obtained by dissolving 6 g of $Co(No_3)_2$ and 0.85 g of $NaNO_3$ in 100 mL of distilled water. Electrodeposition was carried out in a standard three-electrode system. The $TiO_2$ NRs were coated on the FTO substrate as the working electrode, Ag/AgCl was used as the reference electrode, and a platinum foil was used as the counter electrode. Electrodeposition was carried out using a cyclic voltammetry (CV) system with an applied potential in the range of–0.4 to–1 V at a scan rate of 10 mV $s^{-1}$ over four cycles. The deposited samples were removed and rinsed with distilled water, and then samples were dried in an oven for 1 hour at 60 °C. The mass of the $TiO_2/Co(OH)_2$ hierarchical nanostructure was calculated from the difference in weight of the before and after deposition measured with a highly sensitively balance with precision down to 10 μg. The loading mass of the $TiO_2/Co(OH)_2$ hierarchical nanostructure was 0.55 mg/$cm^2$.

### 2.2. Structure, morphology, and composition

The crystal structure of the samples was investigated using a Rigaku powder X-ray diffraction (XRD) machine operated at 40 kV and 40 mA with $Cuk_\alpha$ radiation. The morphology of the samples was observed using a field-emission scanning electron microscope (FE-SEM) (JSM-6700F, JEOL Ltd). The chemical composition and the oxidation state of elements present in the outermost part of the sample were characterised using X-ray photoelectron spectroscopy (XPS) with a Theta Probe AR-XPS System, Thermo Fisher Scientific (U.K).

### 2.3. Electrochemical characterization

All the electrochemical measurements were performed using an Autolab PGSTAT302 N in a standard three-electrode system consisting of the $TiO_2/Co(OH)_2$ hierarchical nanostructured electrode as the working electrode, a saturated calomel electrode as the reference electrode, and a platinum counter electrode in a 2-M KOH electrolyte. The electrochemical behaviour of the as-prepared electrodes was characterised using CV and galvanostatic charge–discharge tests. The CV was carried out in a potential range of −0.1 to +0.5 V at a range of scan rates. Constant-current charge–discharge tests were carried out at different current densities within a potential range of −0.1 to +0.5 V.

## 3. Results and discussion

### 3.1. Synthesis and characterisation

Our approach to fabricate the $TiO_2/Co(OH)_2$ hierarchical nanostructures involved two steps, as shown in Scheme 1. First, the sub-structure of vertically aligned $TiO_2$ NR arrays was grown on the FTO substrate using the hydrothermal method. Second, the superstructure of $Co(OH)_2$ nanowalls was deposited onto the tip surface of the $TiO_2$ NRs using electrodeposition.

The crystal structure of the $TiO_2/Co(OH)_2$ hierarchical nanostructure was examined using XRD measurements. Fig. 1 shows a typical XRD pattern of the $TiO_2/Co(OH)_2$ hierarchical nanostructure. It can be clearly seen that the $TiO_2/Co(OH)_2$ hierarchical nanostructure exhibited a tetragonal rutile phase of $TiO_2$ NRs and α-phase of the $Co(OH)_2$ nanowall. The peaks represented by diamond symbols in the figure correspond to the FTO substrate. Figs. 2a shows cross-sectional field-enhanced scanning electron microscope (FE-SEM) images, and Fig. 2b shows plan view FE-SEM images of the $TiO_2$ NRs. It can be clearly seen that the as-prepared $TiO_2$ NRs had a tetragonal structure, were highly uniform, and formed a densely packed array of vertically aligned NRs. The average