Vertically-aligned Co(OH)$_2$ Nanosheet Films for Flexible All-solid-state Electrochemical Supercapacitor

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Abstract. Vertically-aligned Co(OH)$_2$ nanosheets were cathodically electrodeposited on a piece of gold coated polyethylene terephthalate (Au-PET) as an electrode material for supercapacitor. The Co(OH)$_2$ electrode showed a high capacitance of 2695 F g$^{-1}$ at 8 A g$^{-1}$ in 1 M KOH aqueous electrolyte. Besides, the films were employed to assemble symmetric all-solid-state supercapacitors with PVA/LiCl gel served as solid electrolyte. The device exhibits an areal capacitance of 50.5 μF cm$^{-2}$ at the current density of 2 μA cm$^{-2}$ accompanied by excellent cycle stability.

1. Introduction
As fast growing of consumer electronics market, the supercapacitor has attracted tremendous attention as a promising energy storage device owing to its high power density and superior cycling stability [1]. In addition, the all-solid-state flexible supercapacitor enjoys great popularity for its flexibility and lightweight [2]. Moreover, the electrode material plays an important role in supercapacitor, transition metal oxides/hydroxides have been studying heartily for their high capacitances and energy densities [3]. Among various materials, Co(OH)$_2$ is attractive because of its high specific capacitance and low cost [4].

In present work, we synthesized vertically-aligned Co(OH)$_2$ nanosheet films using a simple and controllable electrodeposition method. The Co(OH)$_2$: films were tested to observe their morphological and electrochemical characterizations. In three electrodes test, the Co(OH)$_2$: reached a high specific capacitance up to 2695 F g$^{-1}$ at 8 A g$^{-1}$ in 1 M KOH aqueous solution. And we also made the all-solid-state symmetric supercapacitors (ASS-SCs) by assembling two pieces of the as-made electrodes. The capacitance of the device remained 105% of its original value after 10,000 charge/discharge (CD) cycles at 2 μA cm$^{-2}$.

2. Experimental section

2.1. Electrodeposition of Co(OH)$_2$ Nanosheet Films.
The Co(OH)2 nanosheets were grew on the Au-PET employing electrodeposition method. In the three-electrode cell, an Au-PET plate (1*3 cm²), a platinum sheet and a saturated calomel electrode (SCE) were used as working electrode, counter electrode and reference electrode, respectively. The electrolyte solution was composed of 0.1 M Co(NO₃)₂ and 0.1 M KNO₃ without adjusting its PH. During the deposition, the suitable potential was -0.7 V and the temperature was about 30℃. After 20 minutes’ electrodeposition, the working electrode was taken out from the electrolyte, rinsed with distilled water and dried in the air.

Fig 1. (a) top-view and (b) side-view SEM images of the Co(OH)2 films (c) the corresponding SAED pattern (d) HRTEM image.

2.2. Assembly of ASS-SCs.
PV A/LiCl gel was indispensable to work as solid electrolyte. In detail, 6 g of LiCl and 6 g of polyvinyl alcohol (PVA) were added into 60 mL of distilled water, and stirring up the mixture until it became transparent under 85℃. Two pieces of Co(OH)₂ nanosheet films were soaked by the gel and then assembled tightly with a cellulose separator in between. The device was sealed up by plastic adhesive tape after dried in oven for 24 hours at 50℃.

2.3. Material Characterization and Electrochemical Measurement.
The morphologies and microstructures were characterized with a scanning electron microscopy (SEM,
Quanta 200) and a transmission electron microscopy (TEM, Tecnai F20). Electrochemical measurements including cyclic voltammetry (CV) curves and galvanostatic discharge (GD) curves were conducted on an electrochemical workstation (CHI 660D). The electrochemical performance of Co(OH)$_2$ electrode was measured in a three-electrode system and the performance of the ASS-SC was tested in a two-electrode system, respectively.

3. Results and Discussion

3.1. Morphological and Structural Characterizations.

Figure 1a, b show the top-view and side-view SEM images of the Co(OH)$_2$ films, respectively. From above, the Co(OH)$_2$ interlaced sheets with pores and channels, which would accelerate electrochemical reactions and provide short diffusion paths for ions [5]. From the side view, Co(OH)$_2$ nanosheets stood vertically on the substrate and have a thin thickness of about 1.5 μm. The corresponding selected area electron diffraction (SAED) and High-resolution TEM (HRTEM) images were given for qualitative phase analysis. From figure 1c, the lattice spacing was calculated as 0.23 nm and 0.15 nm corresponding to the (002) and (111) planes, which well indexed to the Co(OH)$_2$ phase (JCPDS 74-1057). In figure 1d, the lattice fringe spacing was measured to be 0.23 nm, confirming the existence of single-crystal Co(OH)$_2$ ultriorly [6].

Fig 2. (a) Comparative CV curves of Au-PET substrate and Co(OH)$_2$ electrode (b) CV curves of the Co(OH)$_2$ electrode at various rates (c) GD curves and (d) the corresponding capacitance of the Co(OH)$_2$ electrode.

3.2. Electrochemical Characterization.

1 M KOH electrolyte was used in the three-electrode system to perform the electrochemical characterizations of the Co(OH)$_2$ films. Figure 2a shows the CV curves of Au-PET substrate and Co(OH)$_2$ film CV at a scan rate of 100 mV s$^{-1}$ in a potential window of -0.1 V to 0.6 V vs SCE.
Compared with the Co(OH)\textsubscript{2} film, the curve of Au-PET substrate nearly comes to be a line shape and have a rather small area, illustrating that the contribution of substrate to the total electrochemical capacitance can be neglected [7]. Figure 2b shows the CV curves of the Co(OH)\textsubscript{2} film at different rates of 50 mV s\textsuperscript{-1}, 100 mV s\textsuperscript{-1}, 150 mV s\textsuperscript{-1}, 200 mV s\textsuperscript{-1}. They keep similar rectangular-like shapes, indicating good capacitance and high-rate capability [8]. It’s hard to charge the cell to 0.6 V and the discharge curve have a sharp decline between 0.4 V and 0.6 V, which is agreement with the results on other substrates [9]. Hence Figure 2c presents the GD curves at different current densities of 4 A g\textsuperscript{-1}, 8 A g\textsuperscript{-1}, 16 A g\textsuperscript{-1}, 32 A g\textsuperscript{-1} with a specific potential window of -0.1 V to 0.4 V. The Co(OH)\textsubscript{2} electrode formed by electrodeposition have a tiny mass density of about 0.06 mg cm\textsuperscript{-2}, which perhaps lead to the mass specific capacitance as high as 2695 F g\textsuperscript{-1} at 8 A g\textsuperscript{-1}. The corresponding capacitances are shown in Figure 2d, measured as 2526 F g\textsuperscript{-1} (4 A g\textsuperscript{-1}), 2695 F g\textsuperscript{-1} (8 A g\textsuperscript{-1}), 2344 F g\textsuperscript{-1} (16 A g\textsuperscript{-1}), 1952 F g\textsuperscript{-1} (32 A g\textsuperscript{-1}).

ASS-SCs were assembled by using Co(OH)\textsubscript{2} films as the electrodes and examined in a two-electrode system to perform its electrochemical properties. Figure 3a shows the CV curves of the devices at various rates measured between 0 and 0.8 V with the PVA/LiCl gel severed as the solid electrolyte. With the scan rates increasing from 50 mV s\textsuperscript{-1} to 200 mV s\textsuperscript{-1}, the CV curves behave similarly in shape, indicating the ability of the SCs to conduct electrons at high rates [10]. Figure 3b shows the typical GD curves of the optimal device at different densities of 2 \(\mu\)A cm\textsuperscript{-2}, 4 \(\mu\)A cm\textsuperscript{-2}, 6 \(\mu\)A cm\textsuperscript{-2}, 10 \(\mu\)A cm\textsuperscript{-2}. A good liner relation of the discharge potentials with time was fond, illuminating a rapid I-V response [11]. The corresponding areal specific capacitances were calculated as 50.5 \(\mu\)F cm\textsuperscript{-2} (2 \(\mu\)A cm\textsuperscript{-2}), 44 \(\mu\)F cm\textsuperscript{-2} (4\(\mu\)A cm\textsuperscript{-2}), 42 \(\mu\)F cm\textsuperscript{-2} (6\(\mu\)A cm\textsuperscript{-2}), 38.8 \(\mu\)F cm\textsuperscript{-2} (10 \(\mu\)A cm\textsuperscript{-2}), respectively. The solid supercapacitor avoided the exfoliation of active materials and thus capacitance kept quite stable with the rates increasing. Although the areal capacitance doesn’t achieve an excellent value, the cycle performance is really outstanding as shown in Figure 3d. The cycle stability of the ASS-SC was performed by GCD
tests at the current density of 2 μA cm\(^{-2}\). The capacitance rose up 5% at the first 250 cycles, and subsequently it kept quite stable without any decay until 10000 cycles. The initial increase in specific capacitance is due to the slow diffusion of the electrolyte ions with the electrode materials [12]. The very high capacitance retention of the ASS-SC is associated with its unique flexible interconnected sheet network [13].

4. Conclusion
In summary, the vertically-aligned Co(OH)\(_2\) nanosheet films were synthesized by cathodic electrodeposition technique. The morphology was observed by SEM and the phase was confirmed by HRTEM. Electrochemical tests of films showed the pretty good capacity, citing the high capacitance of 2695 F g\(^{-1}\) at 8 A g\(^{-1}\). An ASS-SC was fabricated by two Co(OH)\(_2\) film electrodes, and the flexible device exhibited an excellent stability.

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