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# 玫瑰花状氢氧化钴的结构和浸润性

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**摘要**:在没有任何表面活性剂条件下,通过简单的方法首次合成了玫瑰花状$\beta$-Co(OH)$_2$微晶。玫瑰花状$\beta$-Co(OH)$_2$微晶宽3~5 μm,厚2~3 μm,是由平均厚度为15 nm的纳米片所组成。玫瑰花状$\beta$-Co(OH)$_2$组成的薄膜的接触角为158.5°±1.2°,表面处于任意的角度,水滴都不会滴落。

**关键词**:晶体结构;微观结构;玫瑰花状氢氧化钴;表面;粘附力
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# Structure and Wetting Properties of Rose-Like Cobalt Hydroxide

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**Abstract:** Rose-like cobalt hydroxide [$\beta$-Co(OH)$_2$] microcrystals were synthesized by a facile route without any surfactants. The rose-like $\beta$-Co(OH)$_2$ microcrystals, 3~5 μm in width and 2~3 μm in thickness, are composed of nanosheets with an average thickness of 15 nm. The water contact angle (CA) of the rose-like $\beta$-Co(OH)$_2$ film is 158.5°±1.2° and the water droplet is firmly pinned on the surfaces without any movement at any tilted angles.

**Key words:** crystal structure; microstructure; rose-like cobalt hydroxide; surfaces; adhesion

## 0 Introduction

Physical and chemical properties of materials are largely affected by their micro-/nano- structures, thus, it is a feasible way to improve the intrinsic performance of materials by designing and constructing special micro-/nano- structures, which has attracted considerable attention in recent years[1-6]. Especially, due to the unique catalytic, magnetic and electrochemical properties of cobalt hydroxides, synthesis of nanostructured cobalt hydroxides with various sizes, shapes and dimensions have been widely studied until now[7-9]. To date, a variety of cobalt hydroxide crystals with different nanostructures have been obtained[1-4], as example, rose-like nanostructured cobalt hydroxides can be synthesized by hydrothermal route with the addition of surfactants[3]. Although some strategies have been developed to achieve nanostructured cobalt hydroxide crystals, the exploitation of rose-like $\beta$-Co(OH)$_2$ microcrystals in facile reaction condition by a

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controlled mode still remains a big challenge.

In this study, rose-like cobalt hydroxide ($\beta$-$Co(OH)_2$) microcrystals are realized and their "petal effect" wettability is investigated., A facile avenue is developed to synthesize rose-like $\beta$-$Co(OH)_2$ microcrystals without any surfactants in a wet chemical route and rose-like $\beta$-$Co(OH)_2$ microcrystal films exhibit superhydrophobic high adhesion property (petal effect) which resembles the real rose petal. We expect our effort may provide an effective and versatile route for the fabrication of other nanostructured hydroxides with appropriate properties.

## 1 Experimental

### 1.1 Preparation of $\beta$-$Co(OH)_2$

All chemicals used were analytical grade and were used without further purification. In a typical synthesis, 0.250 3 g of Co $(CH_3COO)_2\cdot 4H_2O$ (99.5%) and 1.699 3 g HMT (99%) (hexamethylene-tetramine, $C_6H_{12}N_4$) were first dissolved in 200 mL of a 1:9 ($V/V$) mixture of ethanol and deionized water in a beaker at room temperature. Then the solution was heated to 90 ℃ at 2 ℃$\cdot$min$^{-1}$ in a water bath under magnetic stirring, maintained for 45 min. After being cooled down to ambient temperature, the suspension containing pink particles was filtered and thoroughly washed by distilled water and ethanol several times, and then dried at room temperature before further characterization. Cobalt hydroxide thin films were fabricated according to the literature[10].

### 1.2 Materials characterizations

X-ray powder diffraction (XRD) analyses were carried out on an X-ray powder diffraction (XRD) using a Rigaku Dmax2200 X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda$=0.154 16 nm). The sample was used for XRD analysis in the $2\theta$ range from 10° to 80°, and the applied current and voltage were 40 mA and 40 kV, respectively. Morphological studies were conducted using a field-emission scanning electron microscope (Hitachi S-4800, 5 kV). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) investigations were performed using a JEOL JEM-2100F microscope. The water contact angles were measured using a Dataphysics OCA20 contact-angle system at ambient temperature. Water droplets (5 μL) were dropped carefully onto the surface of samples. The average contact angle was obtained by measuring at five different positions of the same sample.

## 2 Results and discussion

The XRD pattern of the as-prepared powder is depicted in Fig.1. All of the diffraction peaks are consistent with those of the $\beta$-phase hexagonal cobalt hydroxide (PDF 74-1057). It can be observed that the peak intensity of the $\beta$-$Co(OH)_2$ is the strongest, indicative of its highly crystalline nature. The main reason for forming the high crystalline is the homogeneous precipitation process utilizing the slower hydrolysis of HMT. Moreover, it can be seen that XRD pattern of the product exhibits a sharp diffraction peak at 0.465 3 nm, which can be assigned to the (001) reflection.

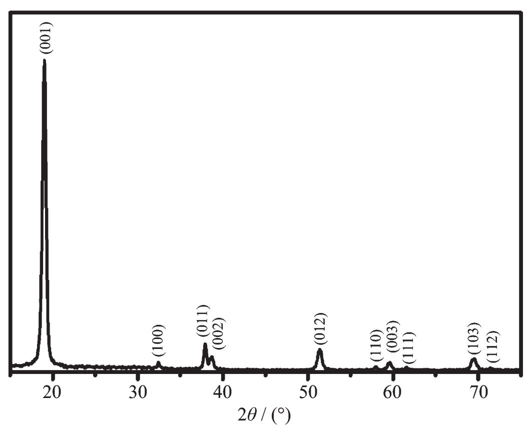


Fig.1 Powder XRD pattern of the as-synthesized sample

As shown in the scanning electron microscopy (SEM) images of the particle (Fig.2a), $\beta$-$Co(OH)_2$ exhibits well-defined rose-like microcrystals which are uniform and distribute homogenously in whole vision with a diameter of 3~5 μm and thickness of 2~3 μm. The high-magnification SEM images (Fig.2b, Fig.2b1, 2b2 and 2b3) reveal that each rose-like structure is composed of a network of nanosheet building blocks with thickness of about 15 nm. These blocks could not be broken up into individual nanosheet by ultrasonic, which are much more stable than the reported doughnut-shaped micrometer-sized aragonite particles[11]. It

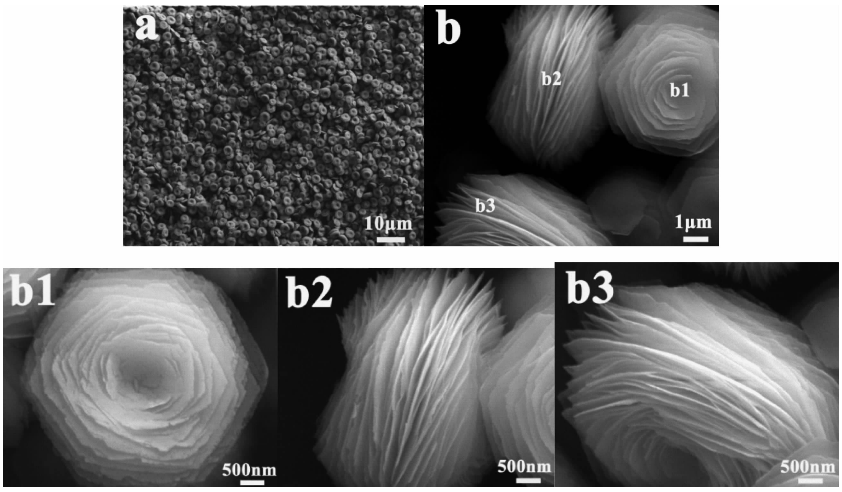


Fig.2 (a), (b) Typical FE-SEM images of $\beta$-$Co(OH)_2$ sample at lower and higher magnifications, respectively; (b1-b3) Enlarged images

also shows a highly oriented growth behavior and fairly high aspect ratios (~260), which may improve their physicochemical properties, thus enhancing their practical applications[12].

Fig.3 shows TEM and HRTEM images of the samples. An overview of the samples in Fig.3a is consistent with the SEM images in Fig.2. The TEM image of a single rose taken from the samples is shown in Fig.3b, which further verifies rose-like morphology and also shows distinct contrast between the center and outer parts. The observation of magnified image reveals that the outer part is quite thick, whereas the central part is thin (Fig.3b). High-resolution Fig.3c and 3d are TEM (HRTEM) images on the thin edges of a single rose. The results show that the rose-like structure is composed of multilamellar overlapped nanosheets, which demonstrates that proper reaction conditions without any surfactant can result in very stable and well-defined rose-like superstructure. In Fig.3d, the marked lattice stripes with 0.234 nm match the (002) plane of $\beta$-phase hexagonal cobalt hydroxide, which also exhibits that the thickness direction of $\beta$-$Co(OH)_2$ is along the fixed [001] direction ($c$ axis of hexagonal $\beta$-$Co(OH)_2$). It could be deduced that a rose-like superstructure is mainly formed by self-assembling nanosheets along the $c$ axis direction. The above results demonstrate that the rose-like $\beta$-$Co(OH)_2$ microcrystals can be produced by this simple one-step route.

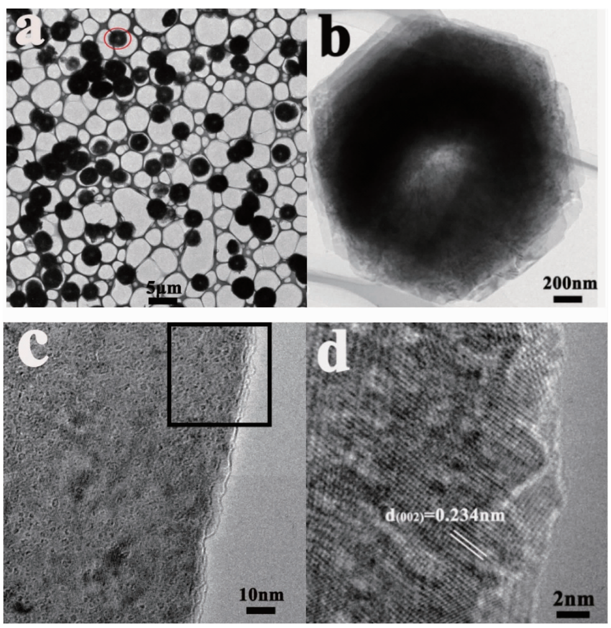


Fig.3 (a) Low-magnification TEM image of $\beta$-$Co(OH)_2$ sample viewed from the broad plane, (b) Magnified TEM image taken from the marked area of the (a), (c) HRTEM image of $\beta$-$Co(OH)_2$ sample (d) Magnified image of the region marked by the black square in c

Fig.4a shows SEM images of the rose-like film. It can be seen that the rose-like microcrystals arrange well on the substrate with their front face orienting outside. It is worth noting that the film can not be wetted by water. Fig.4b shows the optical picture of a 5 μL water droplet on the rose-like film surface. The water droplet on the rose-like film surface is sphere shape, demonstrating good hydrophobicity. Further-more, the water contact angle was measured to investigate wettability of the film. As can be seen in Fig.4c, the water CA on the rose-like film is 158.5°±1.2°, showing superhydrophobicity. Interestingly, water droplet pins firmly on the substrate and can not roll away from the surface at any tilt angle even when the film is turned upside down (Fig.4d, e). This result indicates strong adhesive force between water and the film.

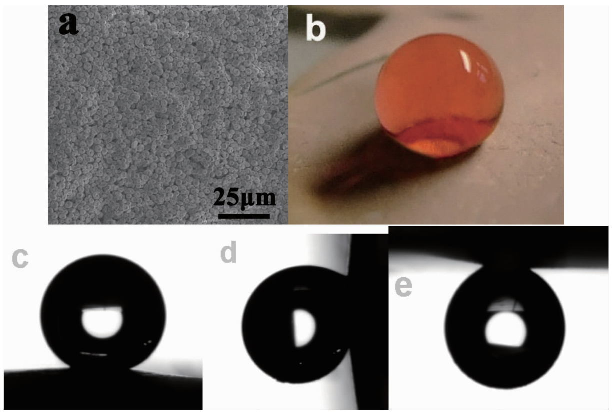


Fig.4 (a) Low magnification SEM image of the surface structures on the rose-like $\beta$-$Co(OH)_2$ film; (b) Picture of a 5 μL water droplet on the rose-like $\beta$-$Co(OH)_2$ film surface; (c~e) Static contact angle measurement of a 5 μL water droplet on the rose-like $\beta$-$Co(OH)_2$ film surface with different tilt angles: 0°, 90° and 180°

Material wettability can be dramatically enlarged by introducing micro-/nano- structures into it[13]. In our experiment, micro/nano composite structured $\beta$-$Co(OH)_2$ lowers the surface energy of the film, thus exhibiting superhydrophobicity. In general, there are two possible states for superhydrophobicity: Wenzel's state and Cassie's state, which can be explained by the following equation, respectively,

$$\cos\theta_w = r\cos\theta \quad (1)$$

$$\cos\theta_w = f_1\cos\theta_1 + f_2\cos\theta_2 \quad (2)$$

where $\theta_w$ stands for water contact angle (CA) of rough surface, $\theta$ means the intrinsic CA of smooth material, $r$ is the ratio of the actual area to the apparent area wetted by water. $\theta_1$ and $\theta_2$ are the water CA of two different components on the surface, while $f_1$ and $f_2$ represent the corresponding area ratio of the two components separately.

For the Wenzel's state, water attaches the solid surface, showing high hysteresis, while water in Cassie's state embodies low hysteresis. Considering the high water hysteresis here, we speculate that water stays in Wenzel's state on rose-like $\beta$-$Co(OH)_2$ film. As illustrated in Fig.5, water enters the micro-interspace between rose-like microcrystals, but can not impregnate the gap between nanosheets on individual microcrystal. This state is called superhydrophobic Cassie impregnating wetting state, just the same with real rose petal reported by Feng et al[14].

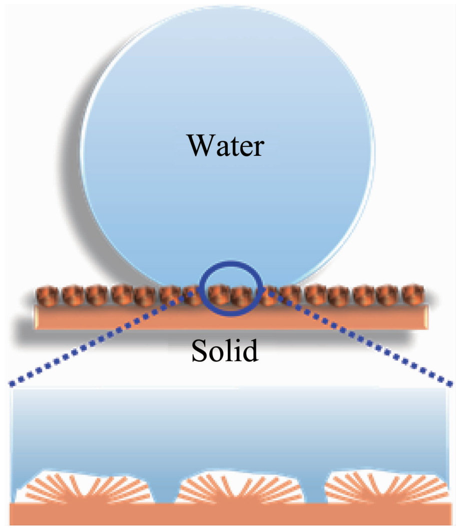


Fig.5 Schematic illustration for a drop of water in contact with the film composing of roses (the Cassie impregnating wetting state)

## 3 Conclusions

In conclusion, we synthesized rose-like $\beta$-$Co(OH)_2$ microcrystals by a mild wet chemical method without any surfactant for the first time. It is the first finding that these micro- and nanostructure provide sufficient micro-/nano- composite roughness for superhydrophobicity and yet at the same time maintains a high adhesive force between water and the film, which may have the potential applications of the rose-like $\beta$-$Co(OH)_2$ film in environmental protection in the future.

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