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## Three-dimensional macroassembly of chromic hydroxide

 Jiaxin Zhou  and Zhenzhao Pei \*

 Department of Chemical Engineering, School of Materials Science and Engineering, Hebei University of Engineering, Handan 056038, P.R. China  
 zhoujx713@163.com (J.Z.), peizhenzhaophd@126.com (Z.P.)

\* Corresponding author at: Department of Chemical Engineering, School of Materials Science and Engineering, Hebei University of Engineering, Handan 056038, P.R. China.

e-mail: peizhenzhaophd@126.com (Z. Pei).

### RESEARCH ARTICLE



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### ABSTRACT

Assembly of small building blocks such as atoms, molecules, nanoparticles, and microparticles into macroscopic structures has opened up new and exciting opportunities in the realm of nanotechnology and microtechnology. Here, we report a simple hydrothermal approach for assembling chromic hydroxide microscopic particles into three-dimensional chromic hydroxide with cylindrical morphology. The morphology and size as prepared samples are controlled by the concentration of  $\text{Cr}(\text{NO}_3)_3$ . Our approach provides a reliable way to successfully assemble various other types of particles into cylindrical macrostructures, realizing the shape engineering of nanoscale and microscale structures to macroscopic well-defined architectures for further applications.

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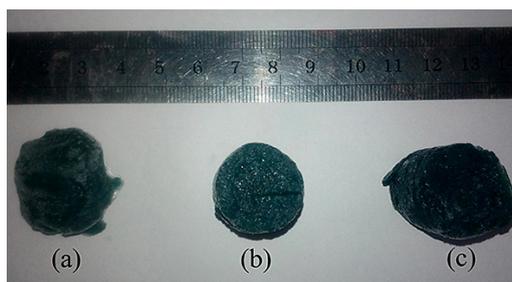
### 1. Introduction

Assemblies of metallic and inorganic particles that can translate phenomena at the nanoscale and microscale to the macroscopic level provide unique opportunities for the design of materials with collective properties and functions [1,2]. Extensive efforts thus have been directed toward the exploration of novel properties and functions that cannot be easily available without specific assembly of metallic and inorganic particles [3]. Therefore, great progress has been achieved in the self-assembly of building blocks [4], including nanoribbons [5], nanowires [6], nanofilms [7], and nanocrystals [8]. However, very few achievements have been made with three-dimensional macroscale assemblies. Therefore, the abilities to synthesize particles and to assemble particles in controllable size and shape become increasingly important [9]. Herein, we present the assembly of chromic hydroxide particles into three-dimensional macrostructures without a template to guide them, which is the spontaneous formation process in aqueous solution. We expect that our endeavor may further the research and application fields of chromic hydroxide materials.

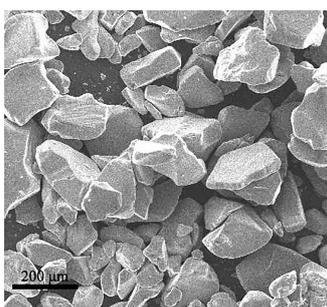
Recent advances on assembly technologies have explored various driving forces for the assembly process. Over the past few decades, layer-by-layer assembly has been of great interest owing to the ability to exert nanometer and micrometer control

over particles [10]. Control over the size, shape, and composition of these nanoscale and microscale particles has enabled the formation of macrostructures. Successful development of nanostructured and microstructured particles for assembly requires suitable methods for their fabrication. Nowadays, assembly technologies are available mainly including roll-to-roll, centrifugation, creaming, spraying, and electrodeposition [11]. Great research related to these assembly technologies is actively explored, shedding light on how these assembly technologies and underlying driving forces affect the formation and performance.

Evidence is presented in this letter for the assembly of microstructured particles. Herein, we demonstrate that the three-dimensional assembly of chromic hydroxide particles into macroscopic structures can be successfully achieved via the facile hydrothermal method. The macroscopic size of the three-dimensional chromic hydroxide can be controlled by changing the effective concentration of chromic nitrate [12]. These results exhibit that chromic nitrate can be used to assemble into complicated three-dimensional macroscopic structures [13]. Furthermore, the formation of three-dimensional macroscopic chromic hydroxide may result in some interesting properties [14,15].



**Figure 1.** Photographic images freeze-dried three-dimensional structures prepared by the macroassembly of chromic hydroxide particles via the facile hydrothermal method: (a) the front view of the sample prepared when 35 mL solution containing 0.004 mol  $\text{Cr}(\text{NO}_3)_3$  was used; (b) the front view of the as-prepared sample when 35 mL solution containing 0.006 mol  $\text{Cr}(\text{NO}_3)_3$  was used; (c) the front view of the as-obtained sample when 35 mL solution containing 0.008 mol  $\text{Cr}(\text{NO}_3)_3$  was used.



**Figure 2.** SEM image of the as-obtained sample when 35 mL solution containing 0.006 mol  $\text{Cr}(\text{NO}_3)_3$  was used.

## 2. Experimental

The facile hydrothermal method was employed to synthesize macroscopic chromic hydroxide. A certain amount of chromic nitrate was ultrasonically dissolved in 35 mL of deionized water and stirred for two minutes. Then hexamethylene amine ( $\text{C}_6\text{H}_{12}\text{N}_4$ ) was added to the solution and stirred for 15 minutes. Afterwards, the solution was hydrothermally treated at high temperature (220 °C, 5 h), the chromic hydroxide with a three-dimensional structure was successfully synthesized. A freeze-drying process was used to obtain an unchanged three-dimensional structure.

## 3. Results and discussion

Figures 1a-1c exhibited macroscopic views of the three-dimensional assembled chromic hydroxide samples. The cylindrical morphology of the as-prepared samples conformed to the morphology of the hydrothermal reaction vessel. It is found that the morphology and size as prepared samples are controlled by the concentration of  $\text{Cr}(\text{NO}_3)_3$  in the solution. When a 35 mL solution containing 0.002 mol  $\text{Cr}(\text{NO}_3)_3$  and 2 g  $\text{C}_6\text{H}_{12}\text{N}_4$  is contained in a hydrothermal reaction vessel with a volume of 50 mL, the cylindrical morphology cannot be formed and the morphology of the as-synthesized sample is a broken block solid; When 35 mL solution containing 0.004 mol  $\text{Cr}(\text{NO}_3)_3$  and 2 g  $\text{C}_6\text{H}_{12}\text{N}_4$  is placed in a hydrothermal reaction vessel with a volume of 50 mL, the cylindrical morphology can be formed, however, the bottom of the cylinder is a little broken. The diameter of the as-obtained sample is about 2 cm and the height of the cylinder is 1.8 cm (Figure 1a); when 35 mL solution containing 0.006 mol  $\text{Cr}(\text{NO}_3)_3$  and 2 g  $\text{C}_6\text{H}_{12}\text{N}_4$  is laid in a hydrothermal reaction vessel with a volume of 50 mL, the cylindrical morphology is well formed, the diameter of the as-synthesized sample is 2 cm and the height of the cylinder is 2.6 cm (Figure 1b); when 35 mL solution containing 0.008 mol  $\text{Cr}(\text{NO}_3)_3$  and 2 g  $\text{C}_6\text{H}_{12}\text{N}_4$  is placed in a hydrothermal reaction vessel with a volume of 50 mL, the cylindrical morphology also can be formed, the diameter of the as-obtained sample is 2 cm

and the height of the cylinder is 2.6 cm (Figure 1c); however, when 35 mL solution containing 0.010 mol  $\text{Cr}(\text{NO}_3)_3$  and 2 g  $\text{C}_6\text{H}_{12}\text{N}_4$  is laid in a hydrothermal reaction vessel with a volume of 50 mL, the cylindrical morphology cannot be successfully formed and the morphology of the as-synthesized sample is broken block solid. These results indicate that the morphology and size of as-prepared samples are mainly determined by the concentration of  $\text{Cr}(\text{NO}_3)_3$  in the solution. It can be concluded from the above results that when the concentration of  $\text{Cr}(\text{NO}_3)_3$  is 0.002 mol, the cylindrical morphology cannot be formed. When the concentration of  $\text{Cr}(\text{NO}_3)_3$  increases from 0.004 to 0.008 mol, the cylindrical morphology can be formed. Furthermore, when the concentration of  $\text{Cr}(\text{NO}_3)_3$  is 0.006 mol, the cylindrical morphology is formed best. However, when the concentration of  $\text{Cr}(\text{NO}_3)_3$  increases further to 0.010 mol, the cylindrical morphology cannot successfully be formed.

It can be concluded from Figure 1 that when the concentration of  $\text{Cr}(\text{NO}_3)_3$  is 0.006 mol, the cylindrical morphology is formed best. Detailed information of the as-prepared sample could be obtained from scanning electron microscopy (SEM). Figure 2 clearly shows that the cylindrical morphology is formed when the concentration of  $\text{Cr}(\text{NO}_3)_3$  is 0.006 mol. The SEM image (Figure 2) exhibits that the as-prepared chromic hydroxide sample with cylindrical morphology is assembled by small chromic hydroxide particles with smooth surface.

To investigate the mechanism of formation of these chromic hydroxide samples with cylindrical morphology, control experiments were carried out by hydrothermal treatment of  $\text{Cr}(\text{NO}_3)_3$  without  $\text{C}_6\text{H}_{12}\text{N}_4$ . When the same amount of  $\text{Cr}(\text{NO}_3)_3$  and same hydrothermal reaction temperature were used, three-dimensional macroassembly of chromic hydroxide samples was not formed and the final prepared products were usually powders, stating that  $\text{C}_6\text{H}_{12}\text{N}_4$  played a key role in the macroassembly process of chromic hydroxide. As mentioned above, when the sample was synthesized without  $\text{C}_6\text{H}_{12}\text{N}_4$ , the cylindrical morphology could not be successfully formed. It might be concluded that during the hydrothermal reaction  $\text{C}_6\text{H}_{12}\text{N}_4$  not only provided an alkaline environment, but also

acted as the template directing agent for macroassembly of the chromic hydroxide sample with cylindrical morphology.

#### 4. Conclusion

In summary, we have demonstrated that the three-dimensional macroassembly of a chromic hydroxide sample can be successfully achieved via a facile hydrothermal route. The size and microstructure of the as-prepared sample can be controlled by changing the concentration of  $\text{Cr}(\text{NO}_3)_3$  in the solution. When the concentration of  $\text{Cr}(\text{NO}_3)_3$  was low, loose agglomerates were formed, and it was not easy to form a specific shape. The viscosity was low during the reaction. When the amount of  $\text{Cr}(\text{NO}_3)_3$  was 0.004 mol, the bottom of the cylindrical shape formed was damaged because of this reason. So, the specific shape cannot be formed at low concentration. On the contrary, when the concentration of  $\text{Cr}(\text{NO}_3)_3$  was too high, a violent reaction will cause many small particles to be produced, and the reaction will not be complete. Many small particles with high activity were deposited too fast, resulting in failure to form a good cylindrical shape. Therefore, an appropriate amount of  $\text{Cr}(\text{NO}_3)_3$  was required in the reaction process to form a good cylindrical shape. Further studies will be needed for the design of materials with mechanical and electro-optical properties. Using hydrothermal method to fabricate chromic hydroxides with cylindrical morphology may provide a means for producing other materials with the same cylindrical morphology.

#### Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.

Author contributions: All authors contributed equally to this work.

Ethical approval: All ethical guidelines have been adhered. Sample availability: Samples of the compounds are available from the author.

#### ORCID

Jiixin Zhou

 <https://orcid.org/0000-0002-5049-1288>

Zhenzhao Pei

 <https://orcid.org/0000-0003-4298-7539>

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