Published in final edited form as:

Chemistry. 2016 August 01; 22(32): 11143–11147. doi:10.1002/chem.201600906.

A facile process for the preparation of three-dimensional (3D) hollow Zn(OH)₂ nanoflowers at room temperature

Ren Cai^a, Dan Yang^c, Liqing Zhang^a, Liping Qiu^b, Hao Liang^b, Xigao Chen^a, Sena Cansiz^a, Zuxiao Zhang^a, Shuo Wan^a, Kimberly Stewart^a, Prof. Qingyu Yan^c, and Prof. Weihong Tan^{a,b}

^aCenter for Research at Bio/Nano Interface, Department of Chemistry and Department of Physiology and Functional Genomics, Shands Cancer Center, UF Genetics Institute and McKnight Brain Institute, University of Florida, Gainesville, Florida 32611-7200, United States

^bMolecular Science and Biomedicine Laboratory, State Key Laboratory for Chemo/Bio-Sensing and Chemometrics, College of Biology, College of Chemistry and Chemical Engineering, and Collaborative Research Center of Molecular Engineering for Theranostics, Hunan University, Changsha 410082, China

^cSchool of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

Abstract

A facile strategy has been developed to synthesize double-shelled Zn(OH)₂ nanoflowers (DNFs) at room temperature. The nanoflowers were generated via conversion of Cu₂O nanoparticles (NPs) using ZnCl₂ and Na₂S₂O₃ by a simple process. Outward diffusion of the Cu²⁺, produced by an oxidation process on the surface of NPs, and the inward diffusion of Zn²⁺ by coordination and migration, eventually lead to a hollow cavity in the inner NPs with a double-shelled 3D hollow flower shapes. The thickness of the inner and outer shells is estimated to be ~20 nm, and the thickness of nanopetals is about 7 nm. The nanoflowers have large surface areas and excellent adsorption properties. As a proof of potential applications, the DNFs exhibited an excellent ability to remove organic molecules from aqueous solutions.

Graphical Abstract

Correspondence to: Weihong Tan.

Supporting information for this article is available on the WWW under <http://www.chemeurj.org/> or from the author.

The double-shelled $\text{Zn}(\text{OH})_2$ nanoflowers show uniform size and hollow double-shell features. The thickness of the inner and outer shells is estimated to be ~ 20 nm, and the thickness of nanopetals is about 7 nm. As a proof of potential applications, the DNFs exhibited an excellent ability to remove organic molecules from aqueous solutions

Keywords

Cu_2O ; double-shelled nanoflower; adsorption; recyclability

It is well established that morphologies of complex nanostructures play a critical role in determining the properties and corresponding applications of inorganic nanomaterials.¹ In particular, flower-like nanostructures have demonstrated attractive applications in a variety of areas, including drug delivery,² catalysis,³ Raman-active tags for *in vivo* applications,⁴ battery electrodes,⁵ gas sensors,⁶ and live cell imaging.⁷ So far, fabrication of flower-like nanostructures has required stringent control. For example, multifunctional DNA nanoflowers were prepared through rolling circle replication.⁸ $\text{Au}@\text{MnO}$ nanoflowers were obtained by the decomposition of manganese acetylacetonate in diphenyl ether in the presence of preformed Au NPs.⁹ Using copper (II) ions as the inorganic component and various proteins as the organic component, hybrid organic-inorganic nanoflowers were also prepared by a precipitation process.¹⁰ These examples all represent successful fabrication of flower-like nanostructures. Nevertheless, these methods are time-consuming, costly, and pose a risk to the environment.

To address these limitations, including the requirement for high temperature, we herein report a facile process for the preparation of three-dimensional (3D) hollow $\text{Zn}(\text{OH})_2$ nanoflowers at room temperature. These $\text{Zn}(\text{OH})_2$ nanoflowers, which have double shells, were synthesized through conversion of Cu_2O nanoparticles (NPs) using polyvinylpyrrolidone (PVP), ZnCl_2 and $\text{Na}_2\text{S}_2\text{O}_3$ (Scheme 1). This process involves two steps. First, with the addition of the surfactant PVP, passivation layers are formed on the

surface of the solid Cu_2O particles by adsorbed PVP. Second, two distinct reactions occur, including 1) outward diffusion of Cu^{2+} produced by an oxidation process on the surface of NPs, and 2) the inward diffusion of Zn^{2+} by coordination and migration. These two reactions eventually lead to the formation of a hollow cavity in the inner NPs, such that these nanoparticles present a double-shelled 3D hollow flower-like shape, or 3D double-shelled nanoflowers (DNFs). As confirmed by treatment with rhodamine B, a typical organic molecule, these DNFs exhibit high adsorption capacity with excellent recyclability for removal of organic pollutants in waste water.

Thus, the Cu_2O nanoparticles (Figure S1, Supporting Information (SI)) served as precursor for hollow $\text{Zn}(\text{OH})_2$ nanoflowers,¹¹ the end product generated within 10 minutes after sequential addition of ZnCl_2 and aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (see Experimental Section in SI). The field emission scanning electron microscopy (FESEM) image shows flower-like architectures with each flower composed of dozens of flake-like nanopetals (Figure 1a). Such morphology can be attributed to hexagonal $\text{Zn}(\text{OH})_2$ (JCPDS: 07-0155) with no impurities, as detected by X-ray diffraction (XRD) pattern (Figure 3d). Energy dispersive X-ray spectroscopy (EDX) results also confirmed $\text{Zn}(\text{OH})_2$ nanoflowers as the end product (Figure S3, SI). The hollow feature is shown by transmission electron microscopy (TEM) image (Figure 1b), and Figure 1c shows several typical nanoflowers, clearly demonstrating their twin thin shells. The diameter of the inner hollow spheres is ~ 250 nm, and the length of the outer petals is ~ 350 nm. The thickness of the inner and outer shells is estimated to be ~ 20 nm. The observed lattice fringes of $d = 0.237$ nm and 0.245 nm in the high-resolution TEM (HRTEM) image (Figure 1d) correspond to the d spacing of the (205) and (116) lattice planes of the hexagonal $\text{Zn}(\text{OH})_2$ structure, respectively. This is consistent with the XRD result. The selected-area electron diffraction (SAED) pattern (inset in Figure 1d) indicates that the petals are polycrystalline. Z-contrast scanning TEM analysis further confirms the double-shelled nanoflower structure (Figure S2a, SI). The intensity profile, along with a cross-sectional line, shows clear dips in the shell regions, corresponding to the void space between the inner and outer shells. Shell thickness, as estimated by the distance between two dips, is $20 \sim 25$ nm, which agrees with the TEM observation (Figure 1d). Nitrogen adsorption-desorption isotherms of these DNFs are shown in Figure S2b (SI). The specific surface area of the DNFs, as estimated by the Brunauer-Emmett-Teller (BET) method, was measured as $261.5 \text{ m}^2\text{g}^{-1}$.

To understand mechanisms underlying the formation of DNFs (see experimental section, SI), intermediate products were collected (Figure 2). Starting with the solid Cu_2O NPs as precursor (Figure 2a–b and Figure 3a), yolk-shell structures were observed within 30 seconds stirring (Figure 2c–d and Figure 3b). Meanwhile, some petals had already formed on the yolk-shell structures. The void space continued to expand toward the inner solid parts, and after 1 minute, the interior of the solid particles became void, and the second shell was formed (Figure 2e–f and Figure 3c). Further extension of the reaction time to 10 minutes led to complete disappearance of the inner solid parts (Figure 2g–h and Figure 3d), with only the two shells preserved to generate nanoflowers with double-shelled hollow interiors. As a result, uniform nanoflowers with double shells and hollow interiors were generated.

Based on the above observations (Figure 2), the formation of DNFs appears to result from the outward diffusion of ions to the solution and the inward diffusion of vacancies into the solid, as shown in Scheme 1. The detailed formation procedure is proposed as follows: The following six steps provide a detailed summary of DNF formation. (1) PVP molecules adsorbed on the surface of solid Cu_2O particles form a protective layer and stabilize the structures.¹² (2) After addition of ZnCl_2 aqueous solution, hydrolysis reactions occur. First, the hydrolysis product of ZnCl_2 ($\text{ZnCl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}[\text{Zn}(\text{OH})\text{Cl}_2]$) reacts with Cu_2O to form a soluble $\text{Cu}[\text{Zn}(\text{OH})\text{Cl}_2]$ complex ($\text{Cu}_2\text{O} + 2 \text{H}[\text{Zn}(\text{OH})\text{Cl}_2] \rightleftharpoons 2\text{Cu}[\text{Zn}(\text{OH})\text{Cl}_2] + \text{H}_2\text{O}$).¹³ This process, in combination with Cu^+ oxidation, leads to partial dissolution of the Cu_2O particle surface ($2\text{Cu}^+ + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{Cu}^{2+} + 2\text{OH}^-$) (See standard electrode potentials, SI).¹⁴ (3) Then, $\text{Na}_2\text{S}_2\text{O}_3$ reacts with Cu_2O to generate OH^- : $\text{Cu}_2\text{O} + x\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \rightarrow [\text{Cu}_2(\text{S}_2\text{O}_3^{2-})_x]^{2-2x} + 2\text{OH}^-$; $\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HS}_2\text{O}_3^- + \text{OH}^-$.¹³ (4) The OH^- released from reaction (3) facilitates the precipitation of $\text{Zn}(\text{OH})_2$ ($[\text{Zn}(\text{OH})\text{Cl}_2]^- + \text{OH}^- \rightarrow \text{Zn}(\text{OH})_2 + 2\text{Cl}^-$).¹⁵ Therefore, when reaction (3) occurs, $\text{Zn}(\text{OH})_2$ is precipitated synchronously, and the as-generated shell structure tends to deposit around the etched interface of Cu_2O , where the local concentration of OH^- is highest (Figure 2c–d). Further evolution of $\text{Zn}(\text{OH})_2$ into 2D petals may be attributed to the presence of $\text{S}_2\text{O}_3^{2-}$ in the solution. According to a previously reported work, anions, such as sulfate, can block some active sites on the ZnO surface and suppress growth along the $[001]$ direction, thereby resulting in growth of a 2D structure.¹⁶ Formation of a $\text{Zn}(\text{OH})_2$ shell at the interface separates the inner Cu_2O and the outer soft base ($\text{S}_2\text{O}_3^{2-}$).^{16–17} Driven by the concentration gradients,¹⁸ Cu^{2+} , Zn^{2+} and $\text{S}_2\text{O}_3^{2-}$ can freely diffuse across the shells through vacancy exchange. (5) For the remaining inner solid Cu_2O (Figure 2c–d and Figure 3b), the outward diffusion of Cu^{2+} is much faster than the simultaneous inward diffusion of Zn^{2+} , leading to rapid corrosion and, hence, void formation in the inner solid Cu_2O , gradually generating the second shell (Figure 2e–f and Figure 3c). (6) Finally, given sufficient reaction time (10 min), double-shelled nanoflowers are formed upon complete outward diffusion of Cu^{2+} and inner diffusion of Zn^{2+} via vacancy exchange in the reaction (Figure 2g–h and Figure 3d).¹⁸ The entire process was monitored by XRD. Figure 3b–c demonstrates diffraction peaks of both Cu_2O and $\text{Zn}(\text{OH})_2$, which clearly indicate the decreasing intensity of Cu_2O . As shown in Figure 3d, the peak of Cu_2O has completely disappeared, and the peaks can be indexed to $\text{Zn}(\text{OH})_2$. When XRD was performed, a pattern of phase change from Cu_2O to $\text{Zn}(\text{OH})_2$ could be observed along the gradient of continuing synthesis (Figure 3 and Figure 2). These results are consistent with the variation of the Cu content in EDX (Figure S3–S5, SI). Although the two shells form at different stages (Figure 2c–h), it is interesting to note that the thickness of both $\text{Zn}(\text{OH})_2$ shells is in the narrow range of 20–25 nm (Figure 1c and Figure 2h). This can be attributed to PVP passivation and precipitation of $\text{Zn}(\text{OH})_2$ on the Cu_2O surface, which effectively hinder the inward diffusion of the soft base ($\text{S}_2\text{O}_3^{2-}$), generating thin shells at the interface layers.

These unique nanostructures with 2D petals and double-shelled hollow interior are expected to exhibit large surface areas and many active sites for adsorption of organic waste. Accordingly, rhodamine B (RhB), a typical organic molecule, was selected for a proof-of-concept demonstration.¹⁹ When the initial concentration of RhB (pink solution) in water was 10 mg/L, the DNFs could quickly load about 98.1% RhB within 60 minutes, and the color of

the RhB solution changed from pink to colorless, as shown by the photo and UV/Vis absorption curves in Figure 4a–b. Adsorption efficiency was found to be 99.1%, 98.3%, and 82% with initial RhB concentrations of 50, 100, and 200 mg/mL, respectively (Figure 4c). Maximum RhB adsorption capacity was estimated to be 232 mg/g, which is 30 times higher than that of the solid Cu₂O precursor (Figure S6, SI). To demonstrate the reverse process, the DNFs with adsorbed RhB were collected and added to ethanol, which resulted in a reversal from colorless to light pink (Figure 4a) and then dark pink within 30 minutes, indicating that RhB could be reversibly released from the DNFs. RhB could completely removed after repeated washing with ethanol. This excellent adsorption/desorption feature of the DNFs may be partially attributed to their unique structure. It has been suggested that the relatively large surface area and double-shelled hollow interior may contribute to a strong tendency for the dye to migrate and relocate to the flower petals, thereby improving the adsorption.²⁰ Considering their low cost, highly efficient adsorption and excellent recyclability, DNFs have great potential for treatment of polluted water.

In summary, we have designed a facile route to synthesize 3D double-shelled nanoflowers at room temperature. The diameter of the inner hollow spheres was ~250 nm, and the length of the outer petals was ~350 nm. The unique double-shelled hollow interior resulted from simultaneous diffusion of Zn²⁺ inward and Cu²⁺ outward through the passivation layers in the reaction process. Benefiting from the unique morphology of this hybrid nanostructure, a high RhB adsorption capacity of 232 mg/g could be achieved from these DNFs, but this process could be just as easily reversed by ethanol washing. We expect that this simple and novel strategy can be further extended to the synthesis of other functional nanostructures for more intriguing applications.

Experimental Section

Synthesis of double-shelled Zn(OH)₂ nanoflowers (sizes of ~350 nm)

In a typical experiment, Cu₂O (10.5 mg), DI-water (5.4 mL), and ethanol (6 mL) were added sequentially to a 25 mL flat-bottom flask. After ultrasonication for 10 min, 340 mg PVP (molecular weight 24 000) was added to the solution. The solution was vigorously stirred for 15 min, after which 0.6 mL of ZnCl₂ (7.4 mg) aqueous solution was added. The mixture was stirred for an additional 10 min. Then, 4 mL of 1M Na₂S₂O₃ aqueous solution were added dropwise (drop/2s) to the above mixture. Finally, the mixture was stirred for 10 min. The yellow mixture gradually changed to transparent gray, and the products were collected by centrifugation and washed with acetone and methanol three times. The hydrodynamic diameters of as-prepared products were determined by dynamic light scattering (DLS) (Microtrac Nanotrac Ultra) (Figure S2c, SI).

Water Treatment Experiment

A50 mg sample of the DNFs was added to 2 mL RhB solution (10 mg/L) while slowly shaking at 25 °C until the absorbance at 554 nm no long changed. To demonstrate the reverse (desorption process), the DNFs samples containing RhB were collected by removing the colorless solution, and slowly added to 2 mL ethanol. With shaking, the adsorbed RhB gradually desorbed from the DNFs samples, which changed from colorless to light pink and

then dark pink within 30 minutes, indicating that RhB could be reversibly released from the DNFs. RhB can be removed completely after repeated washing with ethanol several times. To recycle the DNFs, the DNFs were repeatedly washed with ethanol until the ethanol was colorless, the DNFs samples was dried by vacuum for repeated use.

An adsorption kinetics test was performed with 7 mL of RhB solution with an initial concentration of 200 mg/L. These adsorption experiments were carried out in a bottle (20mL) containing as-obtained DNFs (50mg) under stirring throughout the test. In each run, 200 μ L of the solution were removed and diluted by a factor of 600. An equilibrium adsorption isotherm was also determined for RhB by a concentration variation method. The quantitative determination of the RhB concentration in solution at different time intervals was performed by measuring the absorbance at 554 nm using a Cary Bio-100 UV/Vis spectrometer.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

The authors are grateful to Dr. Kathryn Williams for her critical comments during the preparation of this manuscript. This work is supported by grants awarded by the National Institutes of Health (GM079359 and CA133086). This work is also supported by the National Key Scientific Program of China (2011CB911000), NSFC grants (NSFC 21221003 and NSFC 21327009) and the China National Instrumentation Program (2011YQ03012412).

References

1. a) Auyeung E, Li TING, Senesi AJ, Schmucker AL, Pals BC, de la Cruz MO, Mirkin CA. Nature. 2014; 505:73–77. [PubMed: 24284632] b) Liu G, Young KL, Liao X, Personick ML, Mirkin CA. J. Am. Chem. Soc. 2013; 135:12196–12199. [PubMed: 23905761] c) Ke Y, Ong LL, Shih WM, Yin P. Science. 2012; 338:1177–1183. [PubMed: 23197527]
2. Hu R, Zhang X, Zhao Z, Zhu G, Chen T, Fu T, Tan W. Angew. Chem., Int. Ed. 2014; 53:5821–5826.
3. Mohanty A, Garg N, Jin R. Angew. Chem., Int. Ed. 2010; 49:4962–4966.
4. Xie J, Zhang Q, Lee JY, Wang DI. ACS Nano. 2008; 2:2473–2480. [PubMed: 19206281]
5. Zhu J, Yin ZY, Yang D, Sun T, Yu H, Hoster HE, Hng HH, Zhang H, Yan QY. Energy Environ. Sci. 2013; 6:987–993.
6. Huang J, Yu K, Gu C, Zhai M, Wu Y, Yang M, Liu J. Sens. Actuators, B. 2010; 147:467–474.
7. Teng Y, Song LX, Ponchel A, Yang ZK, Xia J. Adv. Mater. 2014; 26:6238–6243. [PubMed: 25100221]
8. Zhu G, Hu R, Zhao Z, Chen Z, Zhang X, Tan W. J. Am. Chem. Soc. 2013; 135:16438–16445. [PubMed: 24164620]
9. a) Schladt TD, Shukoor MI, Schneider K, Tahir MN, Natalio F, Ament I, Becker J, Jochum FD, Weber S, Köhler O, Theato P, Schreiber LM, Sönnichsen C, Schröder HC, Müller WEG, Tremel W. Angew. Chem., Int. Ed. 2010; 49:3976–3980. b) Ocsóy I, Gulbakan B, Shukoor MI, Xiong X, Chen T, Powell DH, Tan W. ACS Nano. 2012; 7:417–427. [PubMed: 23211039]
10. Ge J, Lei J, Zare RN. Nat. Nanotech. 2012; 7:428–432.
11. Zhang J, Liu JF, Peng Q, Wang X, Li YD. Chem. Mater. 2006; 18:867–871.
12. Shahmiri M, Ibrahim NA, Shayesteh F, Asim N, Motallebi N. J. Mater. Res. 2013; 28:3109–3118.
13. a) Rich, R. Inorganic Reactions in Water. Springer; 2007. b) Emeléus, HJ., Sharpe, AG. Advances in inorganic chemistry and radiochemistry. Vol. 17. Academic Press; 1964. p. 120

14. Palomar-Pardave, M., Gonzales, I., Romero-Romo, M., Oropez, T. MES 23: Electrochemistry, Nanotechnology, and Biomaterials. Electrochemical Society; 2008.
15. Pung S-Y, Lee W-P, Aziz A. Int. J. Inorg. Chem. 2012; 2012:1–9.
16. Huang M, Tso E, Datye AK, Prairie MR, Stange BM. Environ. Sci. Technol. 1996; 30:3084–3088.
17. Alyea HN. J. Chem. Educ. 1969;46, A34.
18. a) Cai R, Liu H, Zhang W, Tan H, Yang D, Huang Y, Hng HH, Lim TM, Yan Q. Small. 2013; 9:1036–1041. [PubMed: 23239602] b) An K, Kwon SG, Park M, Bin Na H, Baik SI, Yu JH, Kim D, Son JS, Kim YW, Song IC, Moon WK, Park HM, Hyeon T. Nano Lett. 2008; 8:4252–4258. [PubMed: 19367964]
19. a) Liu SP, Liu ZF, Luo HQ. Anal. Chim. Acta. 2000; 407:255–260. b) Wu T, Liu G, Zhao J, Hidaka H, Serpone N. J. Phys. hem. B. 1998; 102:5845–5851.
20. Faust, SD., Aly, OM. Adsorption processes for water treatment. Elsevier; 2013.

Figure 1. Double-shelled $\text{Zn}(\text{OH})_2$ nanoflowers: a) FESEM images; b) low-magnification and c) high-magnification TEM images; d) HRTEM image. (Inset is the SAED pattern).

Figure 2. TEM images of time-dependent evolution of double-shelled interior for fabrication of $\text{Zn}(\text{OH})_2$ nanoflowers. The samples were collected by TEM at a) and b) 0s; c) and d) 30s; e) and f) 1 min; g) and h) 10 min.

Figure 3.
XRD patterns of time-dependent evolution of double-shelled interior for fabrication of $\text{Zn}(\text{OH})_2$ nanoflowers. The samples were collected at a) 0s (Cu_2O); b) 30s; c) 1 min; d) 10 min (DNFs).

Figure 4.

(a) Photographs and (b) absorption spectra of 2 mL of 50 mg/mL RhB solution in the presence of 20 mg of DNFs for 1) 0 min, 2) 1 min, 3) 20 min, and 4) 60 min, respectively; then 5) 15 min and 6) 30 min after addition of fresh ethanol. (c) Time-dependent profiles of RhB removal from solution, with initial RhB concentrations ranging from 50 to 200 mg/L.

Scheme 1.

Schematic illustration of 3D double-shelled nanoflowers formed from Cu_2O nanoparticles.