

Fabrication of Cd(OH)₂ nanorings by ultrasonic chiselling on Cd(OH)₂ nanoplates†

Jian-Jun Miao,^a Rui-Ling Fu,^a Jian-Min Zhu,^b Ke Xu,^a Jun-Jie Zhu*^a and Hong-Yuan Chen^a

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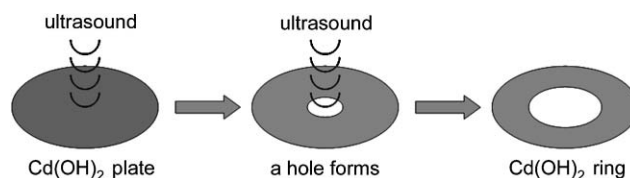
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Cd(OH)₂ nanorings were successfully fabricated from Cd(OH)₂ nanoplates by ultrasonic chiselling, a unique effect of the sonochemical process that has never been reported before.

Due to their unique size- and shape-dependent physical effects, various nanoscaled materials, such as nanoparticles, nanotubes (nanorods, nanowires) and nanoplates, have been developed as functional building blocks for fabricating complex nanoscaled electronic or optoelectronic devices. Recently, ring structures as building blocks have attracted intense research interest because of their novel properties and promising applications. For example, magnetic nanorings can maintain stable vortex states and hold the potential for information storage in two chiralities of the circulating magnetization which made them promising candidates for high-density magnetic random access memory (HDRAM).^{1,2} Gold nanorings have shown enhanced localized electromagnetic fields in their ring cavities.³ Persistent currents in metal rings and superconducting rings have been studied.^{4,5} However, most conventional methods for the growth of nanoparticles with various shapes may be useless in the fabrication of ring structures due to their unique structural features. The fabrication of ring structures is almost limited to electron beam lithography (EBL) or template techniques,^{6–12} which involve relatively complex operations. Only recently has Wang *et al.*¹³ demonstrated a solution-based synthesis of ZnO disks and rings, and Liu and Zeng¹⁴ fabricated semiconductor rings with the self-assembly of nanocrystals. It is a challenge for chemists or materials scientists to fabricate ring structures.

In recent years, ultrasonic irradiation has been extensively used in the synthesis of nanomaterials.^{15,16} The effects of high intensity ultrasound result primarily from acoustic cavitation:¹⁷ the formation, growth, and implosive collapse of bubbles in liquids. During the acoustic cavitation process, very high temperatures (>5000 K), pressures (>20 MPa), and cooling rates (>10¹⁰ K s⁻¹) can be achieved upon the collapse of the bubble, which provides a unique platform for the growth of nanostructures from 0D nanoparticles, 1D nanotubes (nanorods, nanowires), to 2D nanoplates, and even mesoporous and hollow structures.^{15,18,19}



Scheme 1 Fabrication process of the ring.

Here, we report a convenient sonochemical method for the fabrication of single-crystalline Cd(OH)₂ nanorings in aqueous solution. The fabrication process is illustrated in Scheme 1. Cd(OH)₂ nanoplates were used as the precursor. Upon exposure to ultrasonic irradiation, a hole is developed gradually at the center of each individual nanoplate, resulting in the formation of Cd(OH)₂ nanorings. To the best of our knowledge, in this process, the high-speed liquid microjets induced by ultrasonic irradiation served as nanoscale chisels, a unique effect of the sonochemical process that has never been observed or investigated.

The morphology and crystal structures of all the products were studied by using XRD, TEM and HRTEM. The powder XRD pattern of the Cd(OH)₂ nanoplates is shown in Fig. 1a. The diffraction peaks can be indexed to the pure monoclinic phase of Cd(OH)₂ (JCPDS 40-0760). Fig. 2a is a typical TEM image of the Cd(OH)₂ nanoplates. The plates have hexagonal outer shapes with diameters in the range of 200–250 nm. The arrow indicates two nanoplates standing vertically on the copper grid. The thickness of the plates is about 50 nm. The SAED pattern (inset in Fig. 2a) of an individual plate shows the single-crystalline nature. Fig. 2b is a representative HRTEM image of the single-crystalline nanoplate, which exhibits clear lattice fringes. The lattice fringes are all parallel to one side of the hexagon and the interplanar spacing is measured to be about 0.283 nm, which is in good agreement with the [200] crystalline plane of the monoclinic system of Cd(OH)₂.

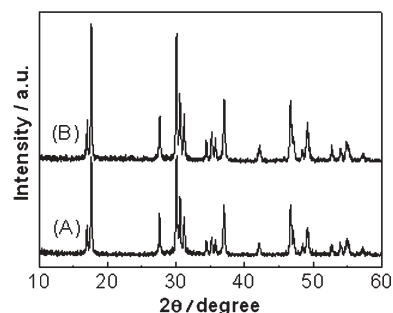


Fig. 1 Powder XRD patterns of the as-prepared Cd(OH)₂ nanoplates (A) and nanorings (B).

^aKey Lab. of Analytical Chemistry for Life Science, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, P. R. China. E-mail: jjzhu@netra.nju.edu.cn; Fax: +86-25-8359-4976; Tel: +86-25-8359-4976

^bNational Lab. of Solid Microstructure, Nanjing University, Nanjing, 210093, P. R. China

† Electronic supplementary information (ESI) available: TEM image and XRD pattern of Cd(OH)₂ nanowires, TEM images of CdS, CdSe and PbF₂ rings. See DOI: 10.1039/b604688f

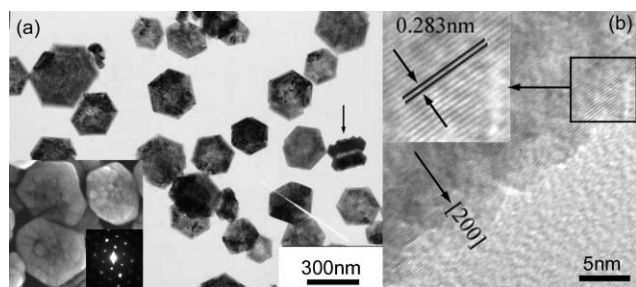


Fig. 2 TEM (a) and HRTEM (b) images of the as-prepared Cd(OH)₂ nanoplates; insets in (a) are an SEM image of the nanoplates and a representative SAED of a single nanoplate.

The nanoplates were readily transformed into nanoring structures upon ultrasonic irradiation. As shown in Fig. 3a, after 10 min of ultrasonic irradiation, holes with diameter about 40 nm could be seen in the center of the hexagonal plates, indicating the formation of ring structures. The SEM image of the inset in Fig. 3a clearly shows a hexagonal ring structure. When the irradiation was prolonged to 20 min, the holes enlarged to more than 100 nm, as shown in the TEM image (Fig. 3b). However, the hexagonal outer shapes of the nanoplates are still preserved.

It is interesting that such sono-chiselling effects do not change the single-crystalline nature of the Cd(OH)₂ nanorings. As shown in Fig. 1b, inset in Fig. 3b and Fig. 3c respectively, the nanorings exhibit almost the same XRD pattern, SAED pattern and high resolution lattice fringes as the nanoplates, which indicates the nanorings are also single-crystalline Cd(OH)₂ of monoclinic phase.

Besides the nanorings, we also obtained wire-like byproducts composed of monoclinic Cd(OH)₂ (JCPDS 40-0760) (Fig. S1, ESI[†]) at the top of the beaker. The wires occurred simultaneously with the formation of the Cd(OH)₂ nanorings, and with a longer time of ultrasonic irradiation the yield and length of the wires increased, which indicated that the wires were formed from the chiselled fragments of Cd(OH)₂.

The above results clearly proved that the Cd(OH)₂ ring structures were fabricated *via* a hole formation and enlargement process based on the Cd(OH)₂ nanoplates as shown in Scheme 1, accompanied by a simple chemical process of dissolution and recrystallization of Cd(OH)₂. Wang *et al.*¹³ prepared ZnO rings from ZnO disks *via* a similar process by heating rather than ultrasonic irradiation. A high density of defects at the center of the disk results in a high local reaction/etching rate under heating, which leads to the formation of a hole. However, in our

experiments, when ultrasonic irradiation was replaced by heating at the boiling point of the solution, no morphological changes of the pristine nanoplates were observed, indicating that such chiselling effects could not be induced by thermal processes. In addition, unlike the regular hexagonal ZnO holes defined by the {10 $\bar{1}$ 0} facets at the center the holes,¹³ the holes in Cd(OH)₂ nanorings are irregular, as shown in Fig. 3d and f. These results indicated that ultrasonic irradiation played a key role in the formation of the ring structures. A few intermediate ring structures were observed as shown in Fig. 3e and g. The Cd(OH)₂ in the center is not entirely etched. The edge of the remaining Cd(OH)₂ is irregular but smooth, in analogy to the etching by impingement of water jets. As is well known, in a liquid–solid system, high-speed microjets of liquid are produced near solid surfaces by implosive collapse of bubbles during ultrasonic irradiation.²⁰ These microjets can reach velocities of hundreds of meters per second. Impingement of the high-speed jets on the solid surface creates localized etching, which has been used in ultrasonic cleaning and heterogeneous reactions. Similarly, when a suspension of Cd(OH)₂ nanoplates is under ultrasonic irradiation, the produced high speed jets would etch the Cd(OH)₂ nanoplates by impingement to form a ring structure. Although it is not very clear how the impingement effect works, a preliminary explanation can be addressed as follows. It can be assumed that because the Cd(OH)₂ plates are suspended in the solution, the movement of the plates is readily changed by the impingement. When the impingement acts on the edge of a nanoplate, the plate turns by a rotation moment, and the impinging effect is greatly decreased. When the impingement acts at the center of a plate, it is another case. The plate cannot turn, but is forced to move along the direction of impinging, trying to decrease the impinging effect. However, the liquid resistance would greatly prevent the movement. So the center receives much more impinging effect than the edge, and is etched faster, so a hole is first “chiselled” at the center by the microjets. With longer impinging time, the hole size gradually increases, forming a ring structure. Additionally, as indicated by the SEM image in Fig. 2a(inset), the surface of the nanoplates is not smooth, especially in the central part, so the roughness may also facilitate the central part absorbing more of the impinging effect and be etched first.

In conclusion, we have fabricated single-crystalline Cd(OH)₂ nanorings from Cd(OH)₂ nanoplates in aqueous solution. The ultrasonic irradiation effect comes from high-speed micro-jets of liquid produced by implosive collapse of bubbles during ultrasonic irradiation, which chiselled holes on Cd(OH)₂ nanoplates to obtain the ring structures. By using the prepared Cd(OH)₂ nanoring as

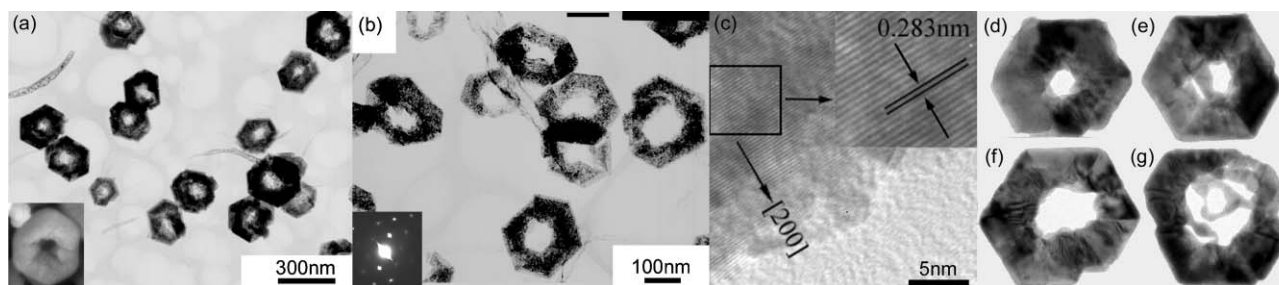


Fig. 3 Morphologies of the nanoring products. (a) TEM image of nanorings with 15 min ultrasound irradiation. Inset in (a) is an SEM image of a single nanoring. (b) TEM and (c) HRTEM images of nanorings with 25 min ultrasound irradiation. Inset in (b) is a SAED of a single nanoring. (d–g) TEM images with higher resolution showing the detailed morphologies of the rings.

template, we have prepared CdS and CdSe nanorings (Fig. S2, ESI†), which will be reported in a forthcoming paper. Moreover, in our recent work a similar chiselling effect of ultrasonic irradiation was also observed in the synthesis of PbF₂ nanoplates (Fig. S3, ESI†), which indicated that the present work might be of certain generality and contribute to the machining of nanostructures. The more detailed mechanism is under further investigation. We would like to acknowledge the support by the National Natural Science Foundation of China (Grant Nos 20325516, 90206037 and 20521503).

Notes and references

‡ In a typical procedure, 0.5 g CdCl₂·2.5H₂O and 2.0 g poly(*N*-vinyl-2-pyrrolidone) (PVP) were dissolved in 50 ml distilled water. Ammonia (30%) was added drop by drop to the solution until it became transparent. Distilled water (60 ml) was added into the solution to obtain precipitate A (nanoplates). Then the solution with precipitate A was irradiated with a high-intensity ultrasonic horn (Xinzhì Co., China, Ti-horn 20 kHz, 60 W cm⁻²) under ambient air for a certain time. Precipitate B (nanorings) at the bottom of the beaker was separated by decantation. The precipitate was centrifuged, washed sequentially with distilled water and acetone and then dried in air for characterization.

- 1 J. G. Zhu, Y. F. Zheng and G. A. Prinz, *J. Appl. Phys.*, 2000, **87**, 6668–6673.
- 2 J. Rothman, M. Klauí, L. Lopez-Díaz, C. A. F. Vaz, A. Bleloch, J. A. C. Bland, Z. Cui and R. Speaks, *Phys. Rev. Lett.*, 2001, **86**, 1098–1101.

- 3 J. Aizpurua, P. Hanarp, D. S. Sutherland, M. Kall, G. W. Bryant and F. J. G. de Abajo, *Phys. Rev. Lett.*, 2003, **90**, 57401.
- 4 E. M. Q. Jariwala, P. Mohanty, M. B. Ketchen and R. A. Webb, *Phys. Rev. Lett.*, 2001, **86**, 1594–1597.
- 5 K. A. Matveev, A. I. Larkin and L. I. Glazman, *Phys. Rev. Lett.*, 2002, **89**, 96802.
- 6 U. Welp, V. K. Vlasko-Vlasov, G. W. Crabtree, J. Hiller, N. Zaluzec, V. Metlushko and B. Ilic, *J. Appl. Phys.*, 2003, **93**, 7056–7058.
- 7 Y. G. Yoo, M. Klauí, C. A. F. Vaz, L. J. Heyderman and J. A. C. Bland, *Appl. Phys. Lett.*, 2003, **82**, 2470–2472.
- 8 M. Steiner and J. Nitta, *Appl. Phys. Lett.*, 2004, **84**, 939–941.
- 9 F. Q. Zhu, D. L. Fan, X. C. Zhu, J. G. Zhu, R. C. Cammarata and C. L. Chien, *Adv. Mater.*, 2004, **16**, 2155–2159.
- 10 F. Yan and W. A. Goedel, *Nano Lett.*, 2004, **4**, 1193–1196.
- 11 H. Xu and W. A. Goedel, *Angew. Chem., Int. Ed.*, 2003, **42**, 4696–4700.
- 12 K. L. Hobbs, P. R. Larson, G. D. Lian, J. C. Keay and M. B. Johnson, *Nano Lett.*, 2004, **4**, 167–171.
- 13 F. Li, Y. Ding, P. X. X. Gao, X. Q. Xin and Z. L. Wang, *Angew. Chem., Int. Ed.*, 2004, **43**, 5238–5242.
- 14 B. Liu and H. C. Zeng, *J. Am. Chem. Soc.*, 2005, **127**, 18262–18268.
- 15 A. Gedanken, *Ultrason. Sonochem.*, 2004, **11**, 47–55.
- 16 M. M. Mdleleni, T. Hyeon and K. S. Suslick, *J. Am. Chem. Soc.*, 1998, **120**, 6189–6190.
- 17 K. S. Suslick, *Science*, 1990, **247**, 1439–1445.
- 18 J. Geng, W. H. Hou, Y. N. Lv, J. J. Zhu and H. Y. Chen, *Inorg. Chem.*, 2005, **44**, 8503–8509.
- 19 R. K. Rana, Y. Mastai and A. Gedanken, *Adv. Mater.*, 2002, **14**, 1414–1418.
- 20 K. S. Suslick and G. J. Price, *Annu. Rev. Mater. Sci.*, 1999, **29**, 295–326.