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Synthesis of Nickel Bowl-like Nanoparticles and Their Doping for Inducing Planar Alignment of a Nematic Liquid Crystal

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Supporting Information

ABSTRACT: Nickel bowl-like nanoparticles have first been synthesized by a magnetic self-assembly process stabilized by polyvinyl pyrrolidone (PVP) without any sphere-like materials as templates. A trace of doped bowls can induce liquid crystal (LC) molecules into a perfect planar alignment, attributable to their bowl-like shape and magnetic self-assembly into a 1D structure. It would provide a novel method of establishing LCs alignment by doping special nanostructured materials.

Many scientists focus on constructing special structures for nanomaterials to tailor their physical or chemical properties and then improving their intrinsic attributes in some applied fields.[1] Bowl-like structures have attracted much attention, as they form array films with an excellent superhydrophobicity,[2] show special phase behavior and optical properties,[3,4] and serve as efficient surface-enhanced Raman scattering (SERS) substrates.[5] However, the synthesis of the bowl-like structure still remains a big challenge. Up to now, most reported bowl-like micro/nanomaterials have been noble metals or metal oxides using the monolayer of polystyrene (PS) spheres as templates.[6] Some scientists also fabricated soft templates to prepare similar structures without PS templates,[7] but magnetic metal bowl-like nanoparticles (NPs) have not been prepared so far.

One feature of the communication is the synthesis of Ni bowl-like NPs with a magnetic self-assembly process stabilized by polyvinyl pyrrolidone (PVP) in a wet chemical route. Another feature is that we first show a remarkable effect of Ni bowl-like NPs on inducing planar alignment of liquid crystals (LCs) taking advantage of the bowl-like structure. As is known, many researchers reported a series of interesting work by doping NPs to make LCs in perfect alignment and improve LCD-related characteristics.[8] However, most doped NPs induced vertical alignment rather than planar alignment in LCs, including polyhedral oligomeric silsesquioxanes, Au NPs, and CdSe NPs.[8] All doped NPs were within several nanometers in diameter without complex structures. Differently, we studied the shape influence of Ni bowl-like NPs in constructing the planar alignment of LCs.

The scanning electron microscopy (SEM) shows the bowl-like NPs ~250 nm in diameter (Figure 1a). It is obvious that some bowls have clear edges. The inset exhibits a typical bowl with a clear edge, ~10 nm in shell thickness, three circle plates, and some small grains inside. The X-ray diffraction (XRD) pattern with broadened peaks (Figure S1, Supporting Information [SI]) also verified small particles exist with a pure chemical composition of nickel. The SEM image in Figure S2, SI, shows some undergrown bowls composed of some particles. The transmission electron microscopic (TEM) images further reveal the morphology and the crystal structure of Ni bowls (Figure 1b). Obviously, these bowls arranged themselves into chainlike structure. The inset shows the high-resolution TEM (HRTEM) image for a partial smooth edge, corresponding to the frame in Figure 1b. It is very interesting to find that the edge is well-crystalline single crystal. Another marked stripe direction indicates the inner part of the bowl has a different growth direction from the edge. The HRTEM image (Figure S3, SI) reveals polycrystalline structure for the inner part of the bowl. In Figure 1b and Figure S3, SI, all marked lattice stripes with a spacing of 0.203 nm can be indexed to the $(111)_{Ni}$ plane of cubic nickel. It could be deduced that a bowl is mainly formed by two parts, the nanoring edge and some particles.

The probable growth mechanism of Ni bowls is proposed in Figure 1c. In a similar reaction system with ethylene glycol as solvent, Ni nanochains can be easily prepared according to our published work.[9] As shown in Figure S4a, SI, the Yu group illustrated that magnetic nanorings could be fabricated by two chains joining together with opposite magnetostatic direction.[10] Also Ni rings could be produced by the chains with opposite magnetostatic direction. Meanwhile, some chains still existed because of the same magnetostatic direction (Figure S4a, SI). That is, in our system, nanorings and nanochains coexisted. As shown in Figure 1c, rings and some chains connected and formed the main structure first (proved by Figure 1b and Figures S2 and S3 [SI], showing single-crystal ring-like edges and polycrystalline inner parts). Then, many other particles with different sizes moved toward it, driven by two forces (the spontaneous aggregation for reducing the surface energy and magnetic dipole−dipole interaction). The aggregated particles gradually grew together and formed bowls. As for the two forces, they were mainly controlled by the reaction temperature and the quantity of PVP. The increasing temperature will accelerate aggregation rate of particles. The polymer PVP played a role as a stabilizer in the growth process of the product, the same as in another report.[10,11] By slightly adjusting these two factors, three other samples were obtained, and their growth explanations are illustrated in Figure S5, SI.

The crossed polarized optical microscopy (POM) was used to observe the alignment of LCs doped with 0.01 wt % Ni bowls by a polarizing optical microscope. Panels a and b of Figure 2 show the birefringent textures of the LC composite observed

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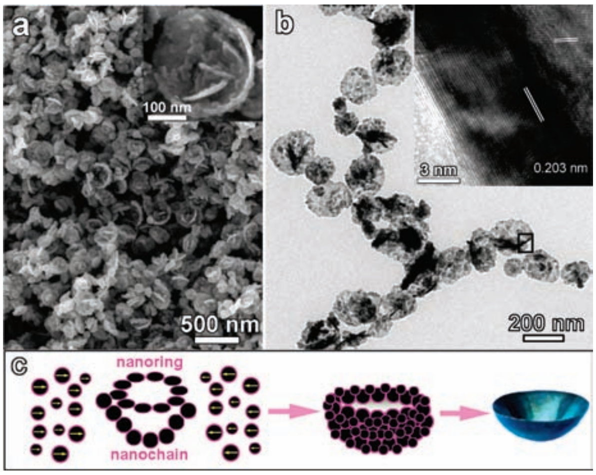

Figure 1. (a) SEM image of Ni bowls. The inset shows a typical bowl. (b) TEM image of Ni bowls with HRTEM image inserted corresponding to the marked frame in b. (c) Illustration for the growth mechanism of Ni bowls.

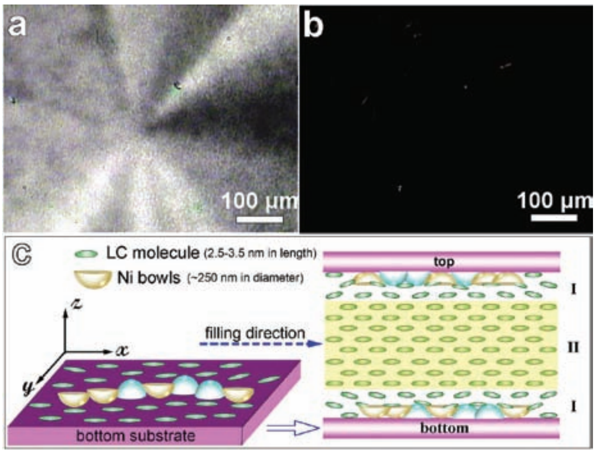

Figure 2. POM images of SLC-1717 doped with 0.01 wt % Ni bowls in bright field (a) and dark field (b). (c) The planar alignment mechanism of Ni bowls for LC molecules. (Left) Alignment on the bottom substrate (*xy* plane). (Right) LCs alignment of the cross section (*xz* plane).

at 0° and 45°. A uniform dark field in Figure 2b was obtained when the LC cell of Figure 2a was rotated by 45°, indicating that the nematic LCs obtained a planar orientation with an excellent optical quality. The POM images showed no orientation of LCs (Figure S6, SI) without doping with Ni bowls. The vertical alignment of LCs was obtained by doping with Ni flowers (sample in Figure S5a, SI) or Ni nanospheres. The results implied that the doped Ni bowls had the structure advantage in effectively inducing planar alignment of LCs.

Figure 2c exhibits how these bowls influence the arrangement of LC molecules. As the surface defects of substrates, Ni bowls were absorbed on both sides of the LC cell. Instead of stacking on top of each other as revealed by Marechal et al.,[4] the bowls tend to arrange into a one-dimensional (1D) structure (Figure 2c, similar to the chain structure in Figure 1b), attributable to the magnetic interaction among these bowls. Most 1D structures would arrange along the filling direction when the nematic LC—nanobowl composite was filled into the LC cell, which might be the result of the fluid effect.[12] In the *xy* plane (Figure 2c, left, the top substrate in the same situation), the LC molecules close to the bowls were directed by the 1D structure and aligned parallel to the substrate surface. The aligned molecules then induced neighborhood LCs along the same direction. Subsequently, all LC molecules on the substrate were oriented by direct or indirect guiding of the 1D structure. Meanwhile, the bowl-like shape provided an ideal quasi-level support for aligned LC molecules, and the aligned LCs on the substrate also induced other molecules nearby, both causing the LCs alignment in section I of the *xz* plane (Figure 2c, right). As in the *xy* plane, the aligned molecules also gradually induced neighboring LC molecules into alignment in section II (marked with yellow rectangle). Eventually, all LC molecules were induced into a perfect planar alignment because of the peculiar 1D and bowl-like structures.

To verify the alignment mechanism of Ni bowls, an organic replicating method was used. As shown in Figure S7a, SI, the LCs had the same direction with the 1D Ni bowls in a planar alignment, in accord with the proposed mechanism. Figure S7b, SI, exhibits the planar alignment of LC molecules for a larger area.

In conclusion, we synthesized Ni bowl-like NPs by a mild wet chemical method with PVP as stabilizers for the first time. A possible growth mechanism was proposed, and three other types of Ni samples were prepared under the guide of the mechanism. By doping a trace of bowls in nematic LCs, a perfect planar alignment of LCs was obtained in the cell. It could be attributable to the bowl-like shape and 1D structure self-assembled by magnetic forces. These results would provide a novel method for the synthesis of other bowl-like nanomaterials and forming LCs alignment by doping special nanostructures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details, XRD pattern, SEM images, HRTEM image, illustration images, POM image. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Mann, S.; Ozin, G. A. *Nature* **1996**, *382*, 313.

(2) Love, J. C.; Gates, B. D.; Wolfe, D. B.; Paul, K. E.; Whitesides, G. M. *Nano Lett.* **2002**, *2*, 891.

(3) (a) Liu, J.; Maaroof, A. I.; Wieczorek, L.; Cortie, M. B. *Adv. Mater.* **2005**, *17*, 1276. (b) Farcău, C.; Aştilean, S. *Appl. Phys. Lett.* **2009**, *95*, 193110.

(4) Marechal, M.; Kortschot, R. J.; Demiro, A. F.; Imhof, A.; Dijkstra, M. *Nano Lett.* **2010**, *10*, 1907.

(5) Ye, J.; Chen, C.; Lagae, L.; Maes, G.; Borghs, G.; Dorpe, P. V. *Phys. Chem. Chem. Phys.* **2010**, *12*, 11222.

(6) (a) Wang, X. D.; Graugnard, E.; King, J. S.; Wang, Z. L.; Summers, C. J. *Nano Lett.* **2004**, *4*, 2223. (b) Xia, X. H.; Tu, J. P.; Zhang, J.; Xiang, J. Y.; Wang, X. L.; Zhao, X. B. *ACS Appl. Mater. Interfaces* **2010**, *2*, 186. (c) Imura, Y.; Kato, M.; Kondo, T.; Kawai, T. *Langmuir* **2010**, *26*, 11314. (d) Wang, Y.; Chen, X.; Zhang, J.; Sun, Z.; Li, Y.; Zhang, K.; Yang, B. *Colloids Surf., A* **2008**, *329*, 184.

(7) (a) Song, Y.; Dorin, R. M.; Garcia, R. M.; Jiang, Y.-B.; Wang, H.; Li, P.; Qiu, Y.; Swol, F.; Miller, J. E.; Shelnutt, J. A. *J. Am. Chem. Soc.* **2008**, *130*, 12602. (b) Gao, P.; Chen, S.; Zhou, M. *Nanotechnology* **2006**, *17*, 320.

(8) (a) Kinkead, B.; Hegmann, T. *J. Mater. Chem.* **2010**, *20*, 448. (b) Qi, H.; Hegmann, T. *ACS Appl. Mater. Interfaces* **2009**, *1*, 1731. (c) Jeng, S.-C.; Kuo, C.-W.; Wang, H.-L.; Liao, C.-C. *Appl. Phys. Lett.* **2007**, *91*, 061112.

(9) (a) Liu, C.-M.; Guo, L.; Wang, R.-M.; Deng, Y.; Xu, H.-B.; Yang, S. *Chem. Commun.* **2004**, 2726. (b) Zhou, W.; He, L.; Cheng, R.; Guo, L.; Chen, C.; Wang, J. *J. Phys. Chem. C* **2009**, *113*, 17355.

(10) Hu, M.-J.; Lu, Y.; Zhang, S.; Guo, S.-R.; Lin, B.; Zhang, M.; Yu, S.-H. *J. Am. Chem. Soc.* **2008**, *130*, 11606.

(11) Krishna, K. S.; Mansoori, U.; Selvi, N. R.; Eswaramoorthy, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 5962.

(12) Yang, P. *Nature* **2003**, *425*, 243.