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Poly(ethylene glycol)-Assisted Two-Dimensional Self-Assembly of Zinc Sulfide Microspheres

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A simple fabrication of two-dimensional zinc sulfide colloidal arrays with the assistance of a multihydroxy polymer is described, which can potentially be utilized in different technological fields, such as biosensor and electrooptical devices as well as a platform for studies of energy transfer between colloidal particles.

Materials with two-dimensional (2D) arrays have aroused great interest because of their unique importance in the fields of creation of integrated circuits, information storage devices, miniaturized sensors, light-harvesting structures, thin-film-display devices, etc.[1] Various methods have been developed to generate 2D arrays, including utilization of a colloidal assembly mechanism,[2] interference lithography,[3] combination of electron-beam lithography and electrochemical deposition techniques,[4] combination of self-assembly and the sol−gel technique,[5] the ion-implantation technique,[6] the serial electron-beam technique,[7] the electron-beam lithography technique,[8] and so forth. Here, we report a simple fabrication of 2D arrays of zinc sulfide (ZnS) microspheres synthesized with a biomolecule-assisted method. The material offers an approach to creating arrays of luminescent ZnS semiconductor. In our previous study,[9] we have successfully synthesized through biomolecule assistance the monodisperse wurtzite ZnS microspheres at a relatively low temperature. Herein, we report a simple fabrication of 2D self-assembly of ZnS microsphere arrays via the vertical deposition technique. The role of mono- and multihydroxy-containing compounds in the self-assembly procedure has been studied using ethanol and poly(ethylene glycol) (PEG).

ZnS, being one of the most important wide-band-gap II−VI semiconductor materials, has been extensively studied because of its valuable properties, such as photoluminescence (PL), electroluminescence, and photocatalytic properties.[10] Therefore, fabrication of 2D ZnS arrays with a simple, low-cost procedure will greatly promote its application in various fields, such as photon crystals, sensing materials, optical and electrooptical devices, and so on.

The conventional "top-down" process becomes more difficult and expensive as the size of the device features decrease. As an alternative strategy, the "bottom-up" approach based on 2D and three-dimensional (3D) self-assembly processes provides a robust solution to this challenge. Numerous methods for preparing 2D and 3D colloidal self-assembly have been reported, such as self-assembly on prepatterned substrates[11] or in the presence of various external fields.[12] However, the most promising approach is probably the vertical deposition technique.[13] This approach involves dipping vertically a substrate (such as a glass plate) into a suspension of colloidal spheres, and the ordered 2D and 3D

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(1) (a) Cho, Y.-H.; Cho, G.; Lee, J.-S. *Adv. Mater.* **2004**, *16*, 1814. (b) Geissler, M.; Xia, Y. *Adv. Mater.* **2004**, *16*, 1249. (c) Achermann, M.; Petruska, M. A.; Crooker, S. A.; Klimov, V. I. *J. Phys. Chem. B* **2003**, *107*, 13782. (d) Wang, X.; Summers, C. J.; Wang, Z. L. *Nano Lett.* **2004**, *4*, 423.

(2) Braun, P. V.; Zehner, R. W.; White, C. A.; Weldon, M. K.; Kloc, C.; Patel, S. S.; Wiltzius, P. *Adv. Mater.* **2001**, *13*, 721.

(3) Lin, S. Y.; Fleming, J. G.; Hetherington, D. L.; Smith, B. K.; Biswas, R.; Ho, K. M.; Sigalas, M. M.; Zubrzycki, W.; Kurtz, S. R.; Bur, J. *Nature* **1998**, *394*, 251.

(4) Su, Y.-W.; Wu, C.-S.; Chen, C.-C.; Chen, C.-D. *Adv. Mater.* **2003**, *15*, 49.

(5) Wang, Z.; Chumanov, G. *Adv. Mater.* **2003**, *15*, 1285.

(6) Meldrum, A.; Buchanan, K. S.; Hryciw, A.; White, W. *Adv. Mater.* **2004**, *16*, 31.

(7) (a) Lin, X. M.; Parthasarathy, R.; Jaeger, H. M. *Appl. Phys. Lett.* **2001**, *78*, 1915. (b) Valenta, J.; Juhasz, R.; Linnros, J. *Appl. Phys. Lett.* **2002**, *80*, 1070.

(8) Ferrand, P.; Egen, M.; Zentel, R.; Seekamp, J.; Romanov, S. G.; Sotomayor Torres, C. M. *Appl. Phys. Lett.* **2003**, *83*, 5289.

(9) Wu, Q. Z.; Cao, H. Q.; Zhang, S. C.; Zhang, X. R., to be submitted.

(10) (a) Fujiwara, H.; Hosokawa, H.; Murakoshi, K.; Wada, Y.; Yanagida, S. *Langmuir* **1998**, *14*, 5154. (b) Jiang, X.; Xie, Y.; Lu, J.; Zhu, L.; He, W.; Qian, Y. T. *Chem. Mater.* **2001**, *13*, 1213. (c) Yamaguchi, T.; Yamamoto, Y.; Tanaka. T.; Yoshida, A. *Thin Solid Films* **1999**, *344*, 516. (d) Leeb, J.; Gebhardt, V.; Müller, G.; Haarer, D.; Su, D.; Giersig, M.; McMahon, G.; Spanhel, L. *J. Phys. Chem. B* **1999**, *103*, 7839. (e) Falcony, C.; Garcia, M.; Ortiz, A.; Alonso, J. C. *J. Appl. Phys.* **1992**, *72*, 1525. (f) Yu, J. H.; Joo, J.; Park, H. M.; Baik, S. I.; Kim, Y. W.; Kim, S. C.; Hyeon, T. *J. Am. Chem. Soc.* **2005**, *127*, 5662. (g) Hu, J. S.; Ren, L. L.; Guo, Y. G.; Liang, H. P.; Cao, A. M.; Wan, L. J.; Bai, C. L. *Angew. Chem., Int. Ed.* **2005**, *44*, 1269.

(11) (a) Trau, M.; Yao, N.; Kim, E.; Xia, Y.; Whitesides, G. M.; Aksay, I. A. *Nature* **1997**, *390*, 674. (b) Ye, Y. H.; Badilescu, S.; Truong, V. V.; Rochon, P.; Natansohn, A. *Appl. Phys. Lett.* **2001**, *79*, 872. (c) Xia, Y. N.; Yin, Y. D.; Lu, Y.; McLellan, J. *Adv. Funct. Mater.* **2003**, *13*, 907. (d) Hoogenboom, J. P.; Rétif, C.; de Bres, E.; van de Boer, M.; van Langen-Suurling, A. K.; Romijn, J.; van Blaaderen, A. *Nano Lett.* **2004**, *4*, 205.

(12) (a) Xu, X. L.; Majetich, S. A.; Asher, S. A. *J. Am. Chem. Soc.* **2002**, *124*, 13864. (b) Abdolvand, A.; Podlipensky, A.; Matthias, S.; Syrowatka, F.; Gösele, U.; Seifert, G.; Graener, H. *Adv. Mater.* **2005**, *17*, 2983.

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colloidal crystals can be deposited on the substrate because of evaporation of the solvent. The colloidal particles are driven together by a convective transport induced by solvent evaporation and self-assembled into ordered close-packed structures derived from, to the most extent, the attractive capillary forces.[14] The thickness of the film ranging from 10 to 50 layers prepared via the vertical deposition method can be controlled through adjustment of the volume fraction and size of the colloids in a single dipping.[15]

In a typical synthesis of ZnS microspheres,[9] glutathione (0.250 g, biochemical grade, >98%) was added to a solution of $ZnCl_2$ (0.074 g dissolved in 35 mL of deionized water) with stirring, and then ethylenediamine (en; ca. 5 mL, analytical grade) was added to the mixture and stirred for 15 min. The resulting solution was transferred to and sealed in a Teflon-lined autoclave and heated to 210 °C for 10 h, and ZnS microspheres were obtained. After preparation of the ZnS arrays via the vertical deposition method,[4,6] the microslides were soaked overnight in a chromic−sulfuric acid cleaning solution, rinsed with ultrapure water, and dried in a stream of argon. A cleaned microslide was then placed vertically into a plastic tube containing a 0.5% PEG (M_w = 3350, Sigma Corp.) suspension of monodisperse ZnS microsphere colloids with an average diameter of 377 nm at a concentration of 0.5 mg/mL. The tube was then placed into a vibration-free beaker at room temperature (17 ± 1 °C). The as-prepared microsphere colloidal array was studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), and PL.

The as-prepared colloidal array was characterized by XRD. Figure 1 presents the XRD patterns of ZnS microspheres, the bare-glass microslide, and the as-prepared ZnS arrays on the substrate, respectively. Figure 1c shows a strong diffraction peak at 28.5° and two weak peaks at 47.5° and 56.4°, corresponding to the (002), (110), and (112) planes of hexagonal wurtzite-type ZnS, respectively (JCPDS Card No. 36-1450). The strong diffraction peak at 8.0° is attributed to the glass substrate background. This result confirms that the self-assembly arrays consist of monodisperse ZnS microspheres.

A typical SEM image of the as-prepared ZnS arrays is shown in Figure 2a. The image clearly shows that the ZnS microsphere arrays (ca. 22 μm × 14 μm in area) are relatively homogeneous and the microspheres are in an ordered arrangement. To study the role of multihydroxy-containing PEG in the self-assembly procedure, we also deposited the glass with the same condition except replacing PEG with monohydroxy-containing ethanol. Figure 2b shows the SEM image of the as-prepared monolayer structure when ethanol was used as the solvent. It is clear that ZnS microspheres are coagulated into close-packed clusters at different scales and form the discrete monolayer structure on the substrate.

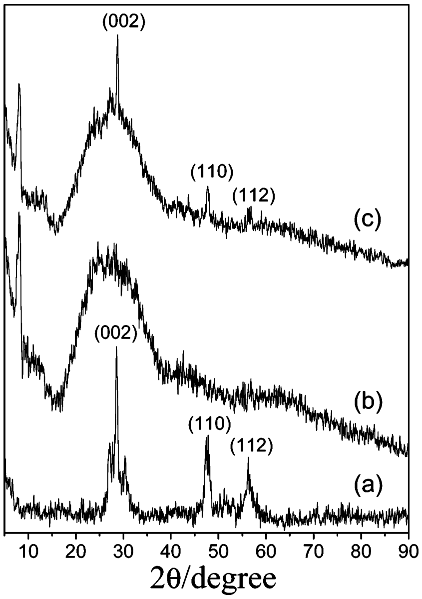

Figure 1. XRD patterns: (a) monodisperse ZnS microspheres with an average diameter of ca. 377 nm; (b) bare-glass microslide; (c) as-prepared 2D self-assembly arrays formed on a glass microslide.

It was reported that the self-assembly procedure was affected by several factors, including the colloidal size, volume fraction, relative humidity, evaporation temperature, and final drying conditions.[15,16] In the present study, the ordered 2D colloidal arrays were not formed probably because of the low volume fraction, although clusters consisting of close-packed colloids at different scales were observed in Figure 2b. In the case of PEG, the multihydroxy-containing compound can function as a stabilizer, coating the colloidal surfaces, which prevents the formation of close-packed structures. On the other hand, the larger viscosity of the PEG solution than that of the ethanol solution decreases the sediment rate induced by gravity, which favored the self-assembly procedure.

The AFM examination also shows a homogeneous surface of ZnS microsphere array self-assembled in a PEG suspension (Figure 3). Notably, slightly higher microspheres are observed in some positions that may be due to the formation of a PEG ultrathin monolayer on the substrate.[17]

There is no doubt that the environment surrounded by colloids will profoundly affect their optical characteristics. For example, particle−particle interactions resulting from the different packing densities may affect the optical properties. Therefore, the PL property of the as-prepared 2D ZnS microsphere arrays was investigated. As shown in Figure 4, a blue emission peak at ∼415 nm, accompanied by two weak peaks at ∼355 and ∼466 nm, is observed with an excitation

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(13) (a) Burmeister, F.; Schäfle, C.; Keilhofer, B.; Bechinger, C.; Boneberg, J.; Leiderer, P. *Adv. Mater.* **1998**, *10*, 495. (b) Dimitrov, A. S.; Nagayama, K. *Langmuir* **1996**, *12*, 1303. (c) Velikov, K. P.; Christova, C. G.; Dullens, R. P. A.; van Blaaderen, A. *Science* **2002**, *296*, 106. (d) Yan, Q. F.; Zhou, Z. C.; Zhao, X. S.; Chua, S. J. *Adv. Mater.* **2005**, *17*, 1917.

(14) (a) Xia, Y. N.; Gates, B.; Yin, Y. D.; Lu, Y. *Adv. Mater*, **2000**, *12*, 693. (b) Norris, D. J.; Arlinghaus, E. G.; Meng, L. L.; Heiny, R.; Scriven, L. E. *Adv. Mater.* **2004**, *16*, 1393.

(15) Jiang, P.; Bertone, J. F.; Hwang, K. S.; Colvin, V. L. *Chem. Mater.* **1999**, *11*, 2132.

(16) Kuai, S. L.; Hu, X. F.; Haché, A.; Truong, V. V. *J. Cryst. Growth* **2004**, *267*, 317.

(17) (a) Papra, A.; Gadegaard, N.; Larsen, N. B. *Langmuir* **2001**, *17*, 1457. (b) Norrman, K.; Papra, A.; Kamounah, F. S.; Gadegaard, N.; Larsen, N. B. *J. Mass Spectrom.* **2002**, *37*, 699. (c) Wang, C.; Zhang, Y. *Adv. Mater*. **2005**, *17*, 150.

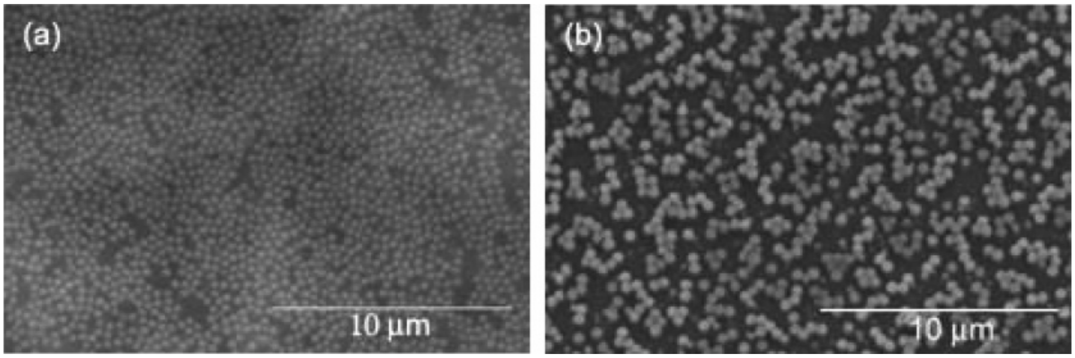

Figure 2. SEM images of self-assembly 2D ZnS arrays formed on a glass microslide in different solvents: (a) ZnS suspended in a 0.5% PEG aqueous solution; (b) ZnS suspended in ethanol.

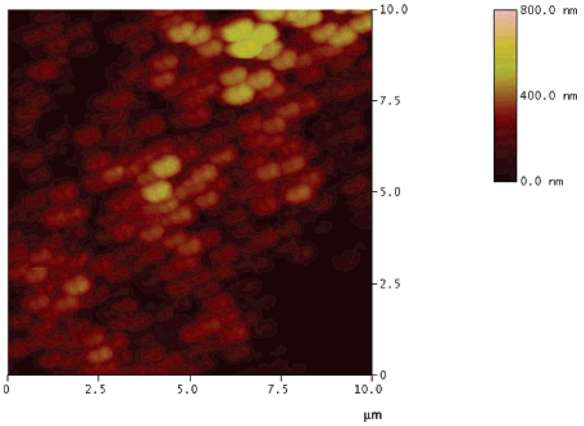

Figure 3. AFM image of self-assembly 2D ZnS arrays formed on a glass microslide in a 0.5% PEG aqueous solution.

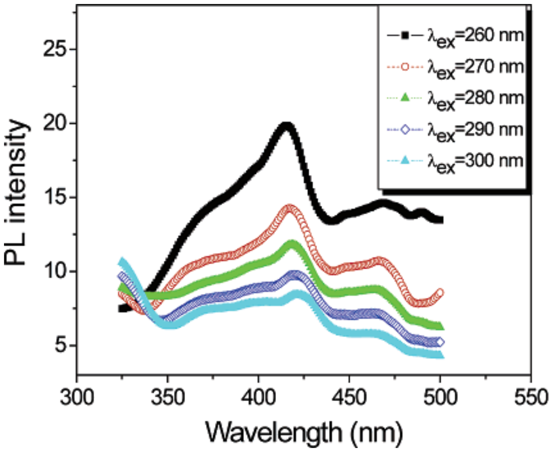

Figure 4. PL spectra of self-assembly 2D ZnS arrays formed on a glass microslide in a 0.5% PEG aqueous solution with different excitation wavelengths.

wavelength of 260 nm. Slight red shifts are observed for both emission bands, while different excitation wavelengths are employed ($\lambda_{ex} = 260$, 270, 280, and 290 nm). These shifts can be attributed to particle−particle interactions between the ZnS microspheres (i.e., energy transfer).[18] Coupling between semiconductor ZnS particles leads to electronic energy transfer from the low energy level to the high energy level and electrons in semiconductor transfer from the valence band to the conduction band, which accounts for the PL band red shift. The PL peaks of ZnS microsphere arrays have been observed to shift to lower energies (red shift) compared with the PL peaks of ZnS microspheres dispersed in solution because of dipole−dipole interdot interactions.[19] It is interesting that the PL property of an as-prepared 2D ZnS array is very similar to that of an aqueous solution.[9] However, the interaction among the ZnS microspheres in solution is weaker than that among the solid-state 2D ZnS arrays, which causes less red shifting in the solution compared with that in the solid-state 2D array. Also, the interaction among the particles in the solution is weaker than that in the solid state, which causes red-shift decrement in the solution compared with that in the solid state.[20] A phenomenon similar to that in the maxima in the emission spectra of 2D CdSe/ZnS quantum dot arrays corresponding to the emission peaks of the quantum dots in the solution was also observed by Pacifico and co-workers.[21] However, it is apparent that 2D ZnS microsphere arrays are more useful than ZnS particles in the solution for use as building block materials in optoelectronic devices.

In summary, the results presented in this Communication providing a simple and template-free fabrication approach of 2D ZnS colloidal arrays may find uses as biosensor and electrooptical devices as well as a platform for studies of energy transfer between colloidal particles.

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(18) Babayan, Y.; Barton, J. E.; Greyson, E. C.; Odom, T. W. *Adv. Mater.* **2004**, *16*, 1341.

(19) (a) Kagan, C. R.; Murray, C. B.; Nirmal, M.; Bawendi, M. G. *Phys. Rev. Lett.* **1996**, *76*, 1517. (b) Kagan, C. R.; Murray, C. B.; Bawendi, M. G. *Phys. Rev. B* **1996**, *54*, 8633.

(20) Xu, B. S., Eds. *Nanomaterials and Application Technology*; Chemical Industry Press: Beijing, China, 2004.

(21) Pacifico, J.; Gómez, D.; Mulvaney, P. *Adv. Mater.* **2005**, *17*, 415.