Synthesis of novel chalcogenide ‘lifebelts’ and their electrogenerated chemiluminescence

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Novel chalcogenide lifebelts have been prepared by using a simple sacrificial template method, and their electrogenerated chemiluminescence properties were studied.

To meet the demand for the fabrication of various nano-scaled electronic and optoelectronic devices, great efforts have been made to prepare these nanomaterials with various shapes and special properties. Compared with the well-studied nanotubes, nanowires, nanorods, the synthesis of ring structures is still under investigation. Nanomaterials with ring-like structures have shown unique physical and chemical properties and have promising applications. The magnetic rings 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.[1,2] It was also found that gold nanorings exhibited tunable plasmon resonances in the near infrared which were not observed for solid particles with similar size.[3] However, till now most work is focused on magnetic rings based on Fe, Co, Ni,[4–7] and only relatively few papers have reported the synthesis of nanorings besides magnetic rings. Most conventional methods for nanoparticle growth with various shapes seem not suitable for the fabrication of ring-like structures. Besides electron beam lithography (EBL) and template methods,[4,5,8–12] which are frequently used in the fabrication of magnetic nanorings, only a few methods have been developed to synthesize certain ring-like structures. Kong and Wang[13] and Leung *et al.*[14] reported the growth of ZnSe and ZnO nanorings, respectively, through thermal evaporation. Liu *et al.*[15] reported the self-assembly of CdS nanoparticles into nanoring structures. Li *et al.*[16] demonstrated a solution-based synthesis of ZnO disks and rings. Hence, it is essential to develop some simple and effective methods for the preparation of ring nanostructures, which might help to perform a detailed study for their properties.

In this communication, we have successfully synthesized novel chalcogenide ‘lifebelts’ by using a simple sacrificial template method. To our best knowledge, these novel lifebelt structures have never been reported before. Electrogenerated chemiluminescence (ECL) of the CdX hollow lifebelts was also studied. The as-prepared CdSe lifebelts showed relatively high ECL emission compared to CdS and CdTe analogues.

Fig. 1 shows the scheme of the fabrication of the lifebelts by a sacrificial template method. $Cd(OH)_2$ nanorings were used as the sacrificial templates. In the reaction, the $Cd(OH)_2$ sacrificial templates were gradually consumed, meanwhile the resultant chalcogenide formed a shell structure around the templates, inheriting the outer shapes of the sacrificial templates. When the sacrificial templates were completely consumed, the chalcogenide lifebelt structures could be obtained.

Fig. 2 shows a TEM image of the $Cd(OH)_2$ nanorings, which were readily prepared by sonication irradiation of $Cd(OH)_2$ nanoplates for 25 min according to our previous report.[17] The lifebelts have hexagonal outer shapes. The outer diameters are about 200–250 nm and inner diameters about 100–120 nm.

The chalcogenide lifebelts were readily prepared by reacting the $Cd(OH)_2$ nanorings with the corresponding chalcogenide sources. In the case of CdTe,† when the $Cd(OH)_2$ nanorings were added into NaHTe solution, Te^{2-} ions were released to react with $Cd(OH)_2$ on the surface of the template to form CdTe nuclei because CdTe has a smaller K_{sp} value than $Cd(OH)_2$.[18,19] As the reaction continued, the $Cd(OH)_2$ templates were gradually consumed and the formed CdTe nuclei grew to provide CdTe nanoparticles. Many of the CdTe nanoparticles further aggregated to form CdTe shells. Finally, when the $Cd(OH)_2$ template was completely consumed, CdTe lifebelts can be obtained. Fig. 3 shows the XRD pattern of the as-prepared CdTe products. The positions and intensities of three diffraction peaks match well with the standard diffractions of the (111), (220) and (311) planes of cubic-phase CdTe (JCPDS: 75-2086). No $Cd(OH)_2$ diffraction peaks are detected in the patterns, indicating that the $Cd(OH)_2$ templates have been completely converted into CdTe. The peaks are apparently broadened, indicating that the products are composed of small crystalline particles. The average crystal sizes are estimated to be about 4.9 nm according to the Debye–Scherrer formula.

Fig. 1 Scheme of fabrication of the lifebelts by a sacrificial template method.

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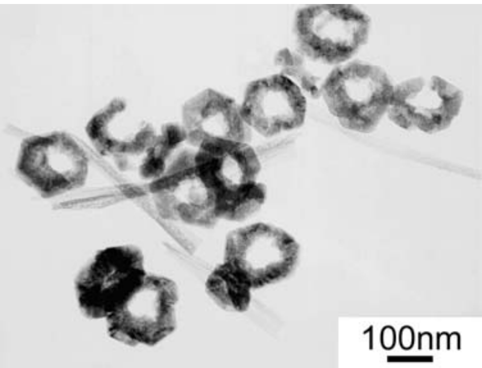

Fig. 2 TEM image of $Cd(OH)_2$ nanorings.

The TEM image (Fig. 3(b)) shows that the CdTe products can keep the original ring-like shapes of the $Cd(OH)_2$ nanorings, while the outer diameter increased to about 260 nm and the inner diameter decreased to about 70 nm. Interestingly by careful observation we see that the outer and inner rims have deeper contrast than the region between them, indicating that the rings have hollow interiors. The inset in Fig. 3(b) is an SEM image of an individual CdTe lifebelt. In the image, the hollow interior can be seen clearly from the broken part. Fig. 3(c) is a HRTEM image of an individual ring structure. The contrast difference is much clearer in the image. Thus the CdTe ring structure can be better described as nanosized inner tube, as shown in Fig. 3(e). From the HRTEM image, we can also observe that the wall is composed of small particles, which is in accordance with the XRD result. The wall thickness of the hollow ring is about 25 nm. The HRTEM image as shown in Fig. 3(d) indicated that the ring wall was well crystallized and exhibited clear lattice fringes with a *d*-spacing of 0.37 nm, which corresponds to the (111) reflection of the cubic CdTe structure.

This sacrificial template method can serve as a general method for the synthesis of chalcogenide hollow lifebelts. As we can see, following the similar steps, CdS and CdSe hollow lifebelts are also successfully prepared. XRD patterns as shown in Fig. 4(a) and (b) indicated that they were composed of hexagonal CdS and CdSe, respectively. The peaks are all broadened, indicating that the shells of the lifebelts are also composed of small particles. As shown in Fig. 4(c) and (d), CdS and CdSe lifebelts have the same hollow shape and size as the CdTe lifebelts because of the same $Cd(OH)_2$ sacrificial precursor.

The as-prepared CdSe hollow lifebelts have very high ECL emission.† Fig. 5 shows the ECL emission of CdSe lifebelts under continuous potential scanning for 18 cycles. The electrode potential was cycled between 0.1 and −1.2 V at a scan rate of 100 mV s^{-1}. Compared with the reports of Zhu and Ju on CdSe QD ECL,[20,21] it can be seen that the light emission of CdSe lifebelts shows quite good stability and relatively high intensity for QDs. This might be attributed to the aggregation of the CdSe nanocrystals and the addition of the co-reactant, which helps to overcome the poor radical anion stability.[22]

It has been reported that ECL is generated by relaxation of excited-state molecules that are produced through electron-transfer annihilation of electrogenerated anion and cation radicals.[23] As the electrode potential is made more negative, electrons are injected into the CdSe nanocrystals and the anion radicals ($CdSe^{-\bullet}$) are formed. Concurrently, $S_2O_8^{2-}$ is added as a co-reactant to produce a strong oxidant, $SO_4^{-\bullet}$, and then $CdSe^{-\bullet}$ can react with $SO_4^{-\bullet}$ to emit light in aqueous solution. the ECL mechanism is as follows:

$$\text{CdSe (nanocrystals)} + n\text{e} \rightarrow n\text{CdSe}^{-\bullet} \quad (1)$$

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^{-\bullet} \quad (2)$$

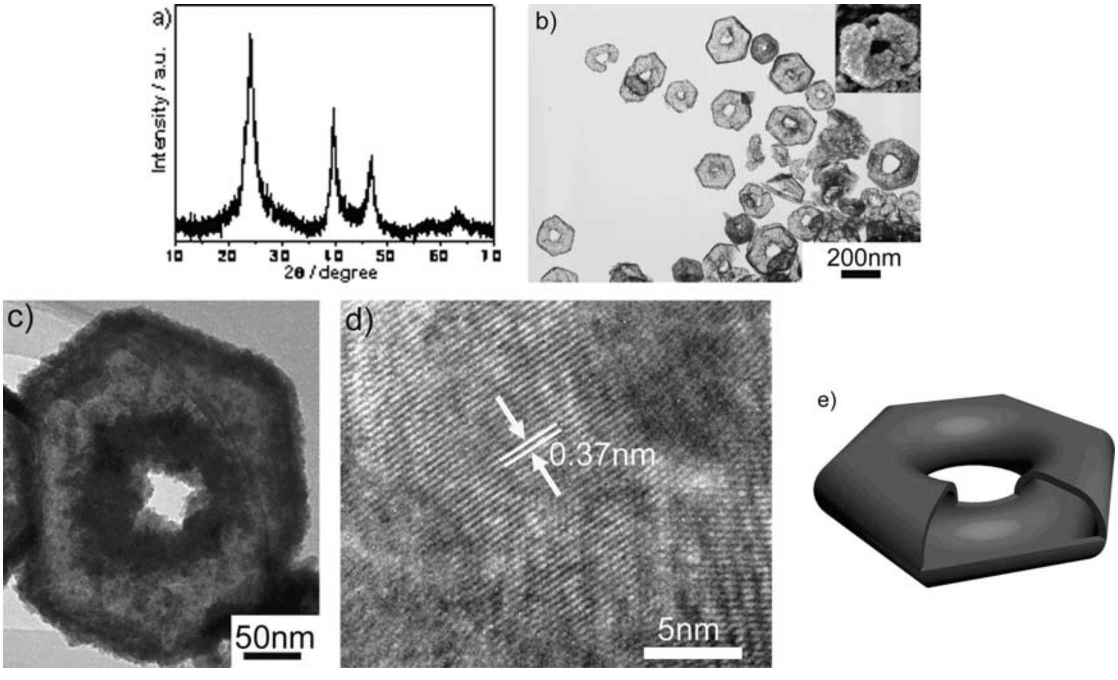

Fig. 3 XRD pattern (a) and TEM image (b) of the CdTe lifebelt product; (c), (d) are HRTEM images of an individual CdTe lifebelt; (e) is a schematic of the lifebelt.

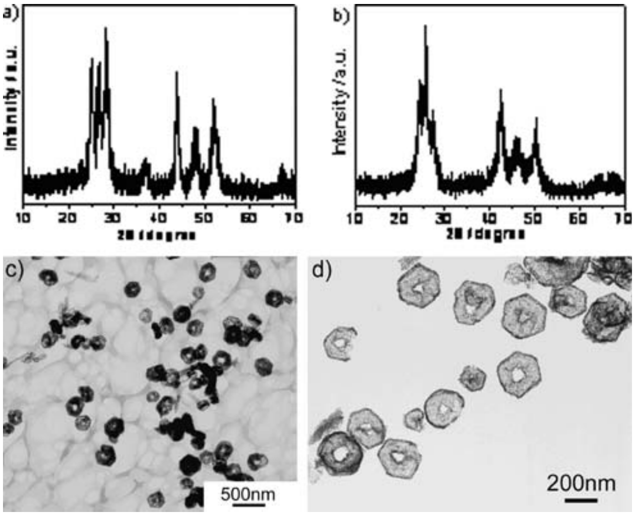

Fig. 4 XRD patterns and TEM images of CdS (a, c) and CdSe (b, d) lifebelts.

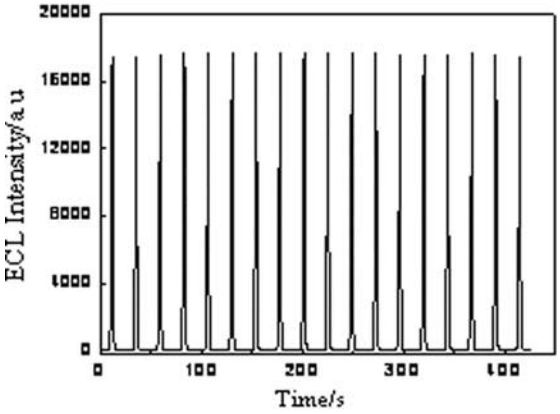

Fig. 5 ECL emission from the CdSe lifebelts in 0.1 M phosphate buffer solution (pH 7.4) containing 0.1 M KCl and 0.1 M $K_2S_2O_8$ under continuous cyclic voltammetry for 10 cycles. Scan rate: 100 mV s^{-1}.

$$\mathrm{CdSe}^{-\bullet} + \mathrm{SO_4}^{-\bullet} \rightarrow \mathrm{CdSe}^{*} + \mathrm{SO_4}^{2-} \qquad (3)$$

$$\mathrm{CdSe}^{*} \rightarrow \mathrm{CdSe} + h\nu \qquad (4)$$

Similarly, the ECL emission of CdS, CdTe lifebelts was also observed.

In summary, novel CdX (X = S, Se, Te) hollow lifebelts can be obtained by the conversion of $Cd(OH)_2$ using a sacrificial template method. The ECL emission of the CdSe lifebelts showed good stability and relatively high intensity for QDs, which has a great potential for the development of novel ECL biosensors and biological labels for ECL detection in immunoassays and nucleic acid hybridization.

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Notes and references

† *Preparation of CdTe lifebelts*: 0.22 g of the as-prepared $Cd(OH)_2$ nanorings were added to 30 ml 0.05 M NaHTe solution in a round-bottom flask, the reaction was carried out under N_2 gas protection for 15 min under sonication to ensure homogeneous dispersion of the sample, and dark brown precipitates were obtained. The precipitates were centrifuged, washed sequentially with distilled water and acetone and then dried in air. For the synthesis of CdS and CdSe lifebelts, 0.05 M TAA and Na_2SeSO_3 were used in the reaction in place of NaHTe, while other conditions were the same as the preparation of the CdTe lifebelts.
The electrochemical measurement for ECL was carried out on a CHI 812 electrochemical working station (Shanghai CH Instruments Co., China) using a three-electrode system. The electrodes were a carbon paste working electrode modified with CdX nanoparticles, a saturated calomel reference electrode (SCE), and a Pt counter electrode. The ECL emission was detected with a Model MPI-A Electrochemiluminescence Analyzer (Xi'An Remax Electronic Science & Technology Co. Ltd., Xi'An, China) at room temperature. The spectral width of the photomultiplier tube (PMT) was 200–800 nm and the voltage of the PMT was set at 800 V in the process of detection.

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