Note

Construction of CdS Nanoparticle Chain on DNA Template

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Salmon sperm DNA was used as template to assembly and nucleate CdS nanoparticles. Transmission electron microscopy (TEM) images showed that the CdS nanoparticles formed unique nanostructure which present regular and parallel chains along DNA molecular chain. The width of every chain was about 3 nm. Raman and X-ray photoelectron energy spectroscopy (XPS) confirmed that the nucleation sites of CdS nanoparticles were phosphate acid groups of DNA.

Keywords DNA, CdS, nanoparticle chain

Introduction

The formation of nanostructured materials using biological molecules as template is currently an active field attracting international endeavor. The study of such biomineralization processes offers valuable insights into the scope and nature of materials chemistry at the inorganic-organic interface.[1-8] Biological templates, such as protein cages,[9] biolipid sylinders,[10] bacterial rhapidosomes,[11] s-layer[6] and DNA[12,13] present definite nucleic sites for mineral deposition on the surface of organized biological macromolecules, in which the structure, size, shape, orientation, texture and constituents of the minerals can be precisely controlled. DNA is the quintessential building block for materials synthesis. Recently, many exciting works focus on the DNA-based methodology for preparing nanocluster circuits, arrays and diagnostic materials.[14-16]

Use of DNA as template to synthesize semiconductor particles and ordered arrays of particles has also been the strategies for many synthetic chemists and materials chemists. Coffer and his co-workers are the first to utilize calf thymus DNA as a stabilizer/template to form both CdS nanoparticles and their mesoscopic aggregates.[17-19] This approach provides many possibilities for syntheses of mesoscale structure. In this work, we present the assembly and nucleation of CdS nanoparticles on the surface of salmon sperm DNA. With DNA molecular chain as template, the growth and assembly of CdS can be well controlled. Transmission electron microscopy (TEM) observations show that the CdS nanoparticles are arranged as unique chain-like structure along the DNA molecules. The Raman and XPS spectral results confirm that the nucleation sites of CdS are phosphate acid groups of DNA.

Experimental

Sample preparation

Salmon sperm DNA (300—2000 b.p.) was purchased from Sigma. Cadmium chloride was analytical grade and recrystallized before use. Water with a conductivity of 18 MΩ·cm was used in the whole experiment. 5 mg of salmon sperm DNA was dissolved in 500 mL of water containing 1 mol/L NaCl. $CdCl_2$ was dissolved in another 500 mL of water with the concentration of 3×10^{-5} mol/L. Then the DNA solution and $CdCl_2$ solution were mixed and stored for 2 d to ensure complete interaction between DNA and Cd^{2+}. The mixed solution was exposed to an appropriate amount of H_2S gas that was obtained from the hydrolysis of thioacetamide (CH_3CSNH_2) in water for 24 h.[20] In this case, H_2S was produced gradually in order to define the growth of CdS nanoparticles. The resulting mixed solution was precipitated by adding ethanol and centrifuged to obtain DNA-linked CdS powder.

Apparatus

Transmission electron microscopy (TEM) was taken on a Hitachi H-8100 IV electron microscopy. Raman spectra were recorded on a Bruker RFS-100 FT-Raman spectrometer equipped with liquid nitrogen-cooled Ge detector and a 1064 nm CW ND/YAG laser as excitation source. X-Ray photoelectron energy spectroscopy (XPS) was obtained by using a VG Scientific ESCALAB Mark II spectrometer referenced to

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C_{1s} at 284.6 eV.

Results and discussion

Morphological structure investigation of CdS *nanoparticle chain on* DNA *template*

Figs. 1a and 1b are the large-scale TEM images of an aliquot of DNA-linked CdS solution dropped on copper grid covered by Formvar film. It reveals the formation of large, spherical clusters with diameters about 200 nm. Fig. 1a shows a single sphere cluster and Fig. 1b shows two interconnected spheres. The electron diffraction (ED) pattern of the CdS cluster (Fig. 1c) shows some circles that illustrates the CdS nanoparticles have the polycrystalline phase and the calculated *d* values are in consistent with those of CdS with hexagonal structure. The enlarged images of the labelled regions in Figs. 1a and 1b are shown in Figs. 1d and 1e, respectively. The formation of regular and parallel nanoparticle chains inside every spheres can be seen. The width of every chain is about 3 nm, which is slightly larger than that of a single DNA double helix. It means that every sphere is composed of CdS nanoparticle chains that are uniform and parallel to each others. For interconnected spheres (Fig. 1b), it shows that the CdS nanoparticle chains are also interconnected to extend into interior of another sphere. The UV-visible spectral measurement confirms the formation of CdS nanoparticles. From the edge of the absorption band at about 350 nm, it can be estimated that the size of the CdS nanoparticles is about 1 nm.[21] Generally, DNA chain can be considered as a kind of linear polymer containing repeated polyanions-phosphate acid groups. Therefore, if there is lack of enough salt ions in aqueous solution, DNA molecule chain can not be well extended. It tends to be curled and entangled into sphere structure, as obtained in Figs. 1a and 1b. In each sphere, CdS nanoparticles are formed and arranged along the DNA molecule chain to present chain shape. The defined growth and regular shape of CdS nanoparticle chain demonstrates the important role that DNA plays in the process of inorganic nano-material synthesis. It can act as an excellent steric and electrostatic protector of the particles to define the growth of CdS. So the configuration of DNA molecule existed in different environment can direct the inorganic nanoparticles with controllable nanostructures.

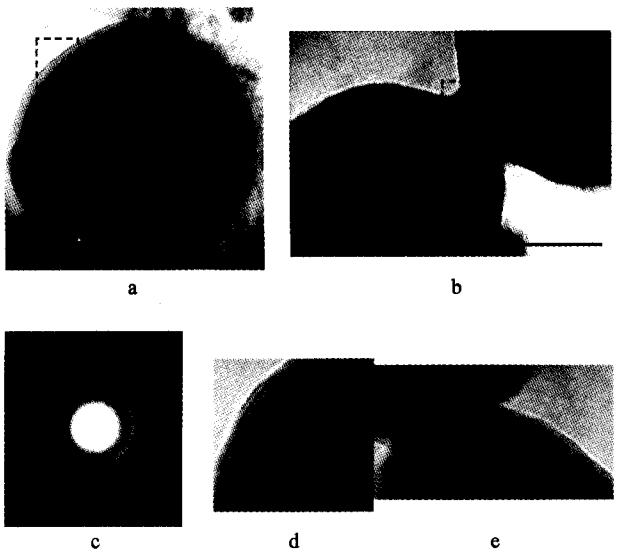

Fig. 1 TEM images of CdS nanoparticle chain formed using DNA as template dropped on copper grid. (a) Single sphere structure, (b) interconnected two spheres, scale bars = 100 nm, (c) electron diffraction pattern of the CdS nanoparticle, (d) enlarged TEM image of the labelled region in (a), (e) enlarged TEM image of the labelled region in (b).

Study on the CdS *nucleation sites on* DNA *template*

DNA is a kind of linear polymer containing repeated pattern of charged phosphate acid groups. Therefore, in principle, this functionality should offer nucleation site for surface-controlled inorganic nanoparticle deposition. The coordination interaction between phosphate acid group of DNA and CdS is confirmed by Raman and XPS spectroscopy. Fig. 2 is the XPS of P_{2p} for DNA in NaCl solution and the mixture of DNA and $CdCl_2$. For DNA in NaCl solution, there is only one P_{2p} peak at 132.00 eV. After coordinated with Cd^{2+}, the P_{2p} bind energy split into two peaks, one at 131.9 eV and

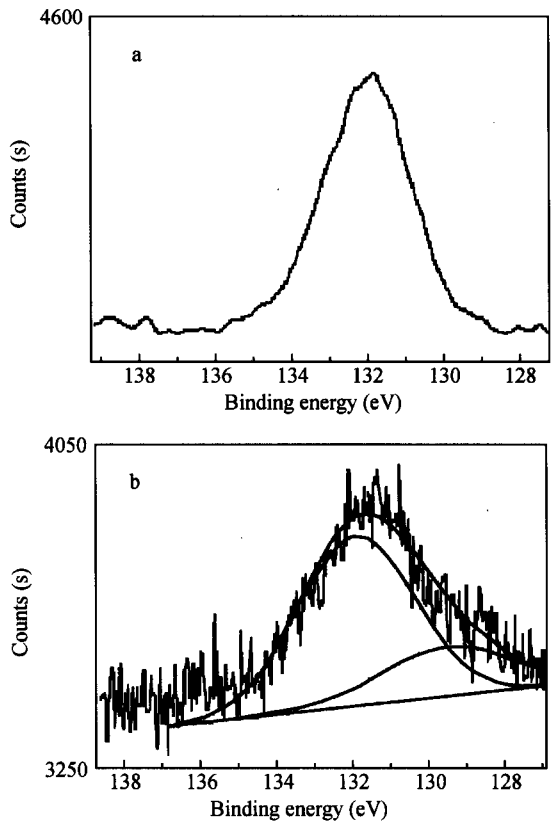

Fig. 2 XPS of P_{2p} for (a) DNA in NaCl solution and (b) the mixture of DNA and $CdCl_2$ dropped on Si substrate.

another at 129.5 eV. It shows that the coordination of Cd^{2+} decreases the bind energy of P_{2p}. Fig. 3 gives the Raman spectra of DNA in NaCl solution and the mixture of DNA and $CdCl_2$. Raman bands originating from in-plane C—C and C—N stretching vibrations of the base residues are expected to dominate in the spectral range of 1100—1700 cm^{-1}.[22,23] The bands around 1101.5 cm^{-1} are assigned to the symmetric O—P—O stretching vibration of the nucleic acid phosphodioxy (PO_2^-) group.[24] It can be seen that the intensity of the band is obviously weakened after linked by Cd^{2+}. The spectrum of DNA shows a strong PO_2^- scissor vibration at 494 cm^{-1}.[24] This band disappears in the spectrum of DNA/Cd^{2+} complex. These are the direct certification of the coordination interaction between phosphate acid group and Cd^{2+}. At the same time, the bands at 781.4 and 729.3 cm^{-1} associated with ring breathing of C and A are also weakened due to the coordination of DNA with Cd^{2+}. Both the Raman and XPS spectra reveal that the phosphate acid groups of DNA provide the nucleation site for the growth of CdS nanoparticles.

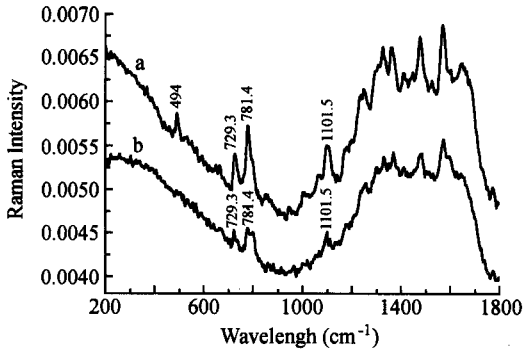

Fig. 3 Raman spectra of DNA in NaCl solution and DNA-linked Cd^{2+} solution dropped on Si substrate. (a) DNA in NaCl solution, (b) the mixture of DNA and $CdCl_2$.

Conclusions

In this study, double-stranded salmon sperm DNA was used as template to construct CdS nanoparticle chains. As biological macromolecule DNA provides definite nucleic sites and natural linear shape on which the growth of inorganic material with special structure can be well controlled and directed. It is expected that the use of biomolecules as template can provide more chances to synthesize inorganic nanoparticles or their assembly with specific shapes and properties.

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