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DNA-Templated Formation of Needle-like CdS Nanoparticles in Langmuir-Blodgett Film

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Monolayer film of octadecylamine (ODA) and DNA-Cd^{2+} complex was co-transferred onto substrates by Langmuir-Blodgett (LB) technique. Needle-like CdS nanoparticles were formed by exposing the LB film to H_2S. It is shown that DNA template plays important role in directing the formation of the needle-like CdS nanoparticles.

Keywords CdS; DNA; Langmuir-Blodgett film; template

INTRODUCTION

Methods for syntheses of inorganic nanoparticles by using biological molecules as template have attracted great attentions in recent years[1]. Biological templates, such as protein cages[2], biolipid sylinders[3], bacterial rhapidosomes[4], DNA [5] etc., have been used to direct deposition, assembly and syntheses of inorganic nanoparticles. Here, we report formation of needle-like CdS nanoparticles by using monolayer LB film of salmon sperm DNA-Cd^{2+} complex and ODA as

template.

EXPERIMENTAL

Salmon sperm DNA was purchased from Sigma. Chloroform was redistilled twice before use. Cadmium chloride was recrystallized before use. Water with a conductivity of 18 MΩ·cm was used to prepare the subphases. The surface pressure-area isotherms were recorded on a Mayer-Fein technic Langmuir trough with a compression speed of 3 $cm^2 \cdot min^{-1}$. ODA monolayers were spread from a chloroform solution of 5×10^{-4} $mol \cdot L^{-1}$ onto water subphase containing 10 $\mu g \cdot ml^{-1}$ DNA and $CdCl_2$ (3×10^{-5} $mol \cdot L^{-1}$) subphase containing 10 $\mu g \cdot ml^{-1}$ DNA. The monolayers were transferred onto silicon or copper grid covered by Formvar film by the vertical dipping method at a surface pressure of 30 $mN \cdot m^{-1}$ and deposition speed of 18$cm \cdot min^{-1}$. Transmission electron microscopy (TEM) was taken on a Hitachi H-8100 IV electron microscopy.

RESULTS AND DISCUSSION

Figure 1 shows surface pressure-surface area (π-A) isotherms of ODA on subphase of pure water, water subphase containing DNA and $CdCl_2$ subphase containing DNA. From the isotherms, it can be seen that both the areas per molecule of ODA on the subphase containing DNA and the subphase containing both DNA and Cd^{2+} ions are larger than that of ODA on pure water subphase. When ODA was spread onto subphase containing DNA, the increased area per molecule suggests that there may exist interactions between the amine groups of ODA and the phosphate groups of DNA. This makes the DNA mole-cules are absorbed at air/solution interface and lead to the rearrangement of the monolayer[6]. When ODA was spread onto subphase containing DNA

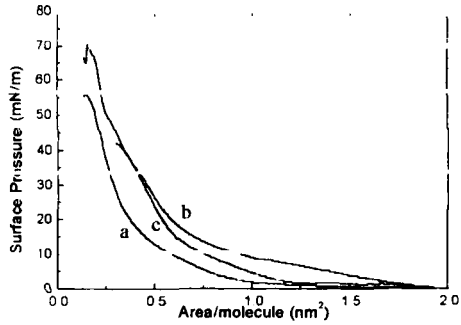
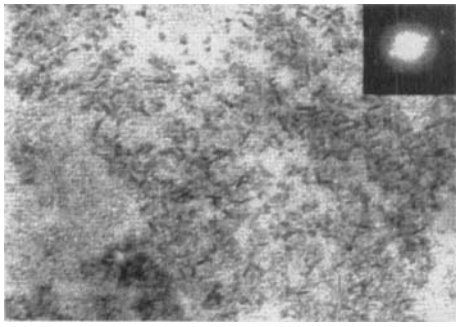


FIGURE 1. π-A isotherms of ODA on subphases of (a) pure water, (b) containing DNA and (c) $CdCl_2$ (3×10^{-5} mol·L^{-1}) containing DNA.

and Cd^{2+} ions, the area per molecule is a little smaller than that on subphase containing only DNA. It can be expected that there may exist interactions between Cd^{2+} ions and phosphate groups of DNA, which results in the formation of DNA-Cd^{2+} complex. This makes the amine groups of ODA have fewer chances to interact with the phosphate groups of DNA and the amount of DNA absorbed at the interface is decreased. The formation of DNA-Cd^{2+} complex is further confirmed by XPS measurements. XPS spectrum of DNA-ODA monolayer film shows P 2p peak at 132.0 eV. When $CdCl_2$ is contained in the subphase, this peak will shift to 129.5 eV and a new Cd $3d_{3/2}$ peak could be observed at 411.6 eV. The same conclusion can also be drawn from our Raman spectral measurements[7].

After the Langmuir films of ODA on subphase containing DNA and Cd^{2+} ions was transferred onto copper grids covered by Formvar film and then the monolayer film was exposed to H_2S gas, TEM observation shows that a kind of needle-like CdS nanoparticles are obtained (Figure 2). Electron diffraction pattern indicates that the formed CdS nanoparticle is a single crystal and the axis (growth direction) of the needle-like CdS nanoparticles is [002][8]. XPS spectrum of the DNA-Cd^{2+} and ODA LB film shows Cd $3d_{3/2}$ peak at 411.6 eV, after



100 nm

FIGURE 2 TEM image of the needle-like CdS nanoparticles. Insert shows their electron diffraction pattern.

exposing it to H_2S, this peak shifts to 410.4 eV, indicating the formation of CdS nanoparticles. If only $CdCl_2$ solution was used as subphase, after ODA monolayer was trans-ferred onto copper grid and exposed to H_2S, no CdS nanoparticles with defined shape could be observed. This means DNA template play vital important role in directing the formation of needle-like CdS nanoparticles. The phosphate groups of the DNA provide nucleation sites for the growth of the CdS nanoparticles. The observation of the needle-like morphology indicates that the nucleation and growth are well controlled by the monolayer LB film containing DNA as template.

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