

纳米半导体硫化银单层膜的自组装

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本文使用 Triton X-100 作为模板剂制备半导体硫化银纳米颗粒, 并研究了其吸收光谱的兰移特性。在金属铝或金基底上自组装有机双功能分子单层膜后, 将其浸入所制备的纳米硫化银颗粒的微乳液中, 自组装得到硫化银纳米颗粒单层膜并研究了其表面形貌特征。

关键词: 纳米颗粒 硫化银 自组装单层膜
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Formation of Self-assembled Monolayers of Silver Sulphide Nanoparticles

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Nanosize silver sulphide semiconductor particles were synthesized using the nonionic surfactant, Triton X-100. A blue shift is obtained as compared with the optical band edge of bulk silver sulphide. Onto the glass or mica slides, self-assembled monolayers (SAMs) of bifunctional organic molecule were prepared on the gold or aluminum layers. By immersing them into the microemulsion of silver sulphide, the SAMs of nanosize silver sulphide particles were acquired. Further, The surface characterization about SAMs of nanoparticles was studied.

Keywords: nanoparticles silver sulphide self-assembled monolayers

0 Introduction

It has been realized that nanosize particles have unusual optical and electronic properties differing from those of the bulk material^[1, 2]. Using self-assembled bifunctional organic monolayers as bridge compounds, semiconductor nanoparticles can be attached to metal surface. Nanoparticles will be immobilized between insulating thin films through electrostatic or covalent attachment chemistries^[3]. One of most important applications of SAMs is to fabricate self-assembled single electron tunneling devices for investigating optical and

electronic properties of semiconductor nanoparticles^[4].

Countless colloidal methods for synthesis of metal and semiconductor nanoparticles have been published^[5]. Many surfactants can be chosen to prepare for nanoparticles, such as EDTA (ethylenediaminetetraacetic acid tetrasodium salt), CTAB (cetyltrimethylammonium bromide), NP-5 (polyoxyethylene(5) nonylphenyl ether) and AOT (sulfosuccinate sodium salt)^[6-8]. Nanosize silver sulphide semiconductor particles have been prepared by reverse micellae using AOT as the surfactant^[9]. Nanoparticles, PbS, have been also obtained with Triton X-100 as the surfactant^[10].

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For the formation of SAMs of nanosize particulae, AOT is a usual choice as the surfactant. SAMs of nanosize cadmium sulphide particles have been obtained using AOT as the surfactant^[11]. However, it is still limited about self-assembly characterization of nanoparticles for single electron tunneling devices. Here, we report SAMs of nanosize silver sulphide particles that are prepared using Triton X-100 as the surfactant. Triton X-100 is a nonionic surfactant with polyoxyethylene ether structure, $\text{Me}_3\text{C}(\text{CH}_2)_4-p\text{-C}_6\text{H}_4\text{-O}-(\text{CH}_2\text{CH}_2\text{O})_{9-10}\text{H}$.

1 Experimental

A Jeol electron microscope, model JEM 100CX II was used to image nanoparticles. By placing a drop of water solution of separated nanoparticles, or microemulsion, the samples were prepared onto the surface of a copper grid coated with amorphous carbon film. Optical absorption spectra were collected at room temperature on a Shimada UV spectrophotometer. X-ray photoelectron spectroscopy (XPS) was performed on a VG ESCALAB MK-II spectrometer. The supply was operated at 300W with the $\text{Mg K}\alpha$ monochromatized X-ray source. The resolution of the spectrometer was 0.8V. The data were treated using MicroCal Origin (Version 3.0, 1991 ~ 1993 MicroCal software, Inc.). Contact mode AFM images were acquired using a Nanoscope IIIa employing Si cantilevers.

1.1 Preparation of Silver Sulphide Nanoparticles

The $0.1\text{mol} \cdot \text{L}^{-1}$ water solution of reactants, sodium sulphide and silver nitrate, was prepared in 50mL measuring flask. Injecting them respectively into solutions of surfactant, the microemulsion systems (50mL) of surfactant/solvent/water/reactants (Ag^+ and S^{2-}) were obtained in ultrasonic instrument for about one hour. Synthesis of silver sulphide (Ag_2S) nanoparticles is carried out by mixing two microemulsion systems with the same water content ($w = [\text{H}_2\text{O}]/[\text{Surfactant}]$) and then stirring vigorously about half an hour. The product was separated from solution by centrifuge for characterization. The concentrations of reactants (Ag^+ and S^{2-}) can be modified by measuring flask. The solution concentration of surfactants, Triton

X-100 or AOT, is $0.1\text{mol} \cdot \text{L}^{-1}$. The contents of water are controlled with pipette by dropping a variable volumes of reaction solution into surfactant solution. The *n*-hexanol is used as assistant solvent for Triton X-100 with their weight ratio of 2 to 3. The cyclohexane is the solvent for Triton X-100 system and the *n*-heptane is for AOT.

1.2 Preparation of Monolayers of SAMs of Silver Sulphide Nanoparticles

The metal substrate surface was prepared by thermal vapor deposition of metal onto the glass slide. We chose mercaptoacetic acid as organic bifunctional molecule. SAMs of organic molecules were formed by immersing the thin aluminum or gold layer in dilute solution of mercaptoacetic acid for 12hr with the reported method^[13, 12]. These above SAMs of organic bifunctional molecule were exposed to microemulsion of silver sulphide nanoparticles for 8hr. The microemulsion system of the solvent/surfactants/ Ag_2S nanoparticles was prepared described above. Following then, the solutions were removed by burette. The sample was rinsed by solvent for several times and then blown dry by nitrogen. Storing in the dark under vacuum desiccator, the films of samples were stable.

2 Results and Discussion

Synthesized by above method, silver sulphide nanoparticles were observed by TEM. The size of nanoparticles can be controlled by water content and the related composition concentration^[13]. The size of the Ag_2S particles increases linearly with the increase in water content. For water content equals to 5, 10, and 20, the electron microscopy photo shows an increase in the average size from 5, 6, and to 10nm, respectively. The concentrations of Ag^+ are higher than those of S^{2-} , which is important to achieve SAMs and obtain small diameter of nanosize silver sulphide particles. A picture of TEM (Fig. 1) shows Ag_2S nanoparticles synthesized using Triton X-100 as the surfactant with the equivalent concentration of Ag^+ and S^{2-} . The dispersivity was displayed in Fig. 2.

Recorded at various water contents (w), the ab-



Fig. 1 TEM photo of Ag_2S nanoparticles synthesized with $2[\text{Ag}^+] = [\text{S}^{2-}] = 0.2 \text{ mol} \cdot \text{L}^{-1}$, $w = 5$

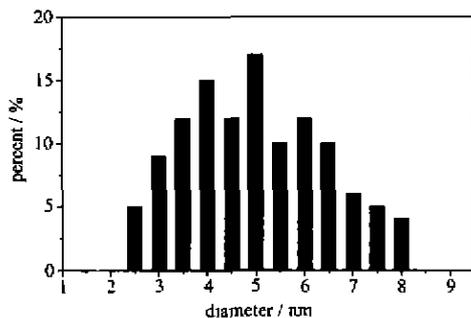


Fig. 2 Size distribution of Ag_2S nanoparticles synthesized with $2[\text{Ag}^+] = [\text{S}^{2-}] = 0.2 \text{ mol} \cdot \text{L}^{-1}$, $w = 5$

sorption spectra of Ag_2S synthesized using Triton X-100 as a surfactant are given in Fig. 3. A blue shift is obtained as compared with the optical band edge of bulk silver sulphide, which is well known to be at 1240nm (1eV).

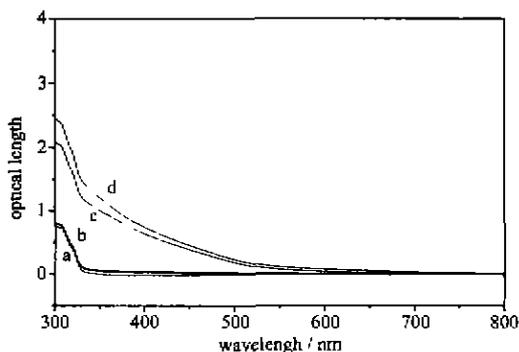


Fig. 3 Absorption spectra of Ag_2S synthesized in microemulsion system at various water contents (a) $w = 2.5$, (b) $w = 5$, (c) $w = 10$, (d) $w = 20$ In the system, Triton X-100/*n*-hexanol/cyclohexane/water, $[\text{Triton X-100}] = 0.1 \text{ mol} \cdot \text{L}^{-1}$, $[\text{Ag}^+] = [\text{S}^{2-}] = 0.0001 \text{ mol} \cdot \text{L}^{-1}$

X-ray photoelectron spectroscopy studies of these SAMs of nanoparticles show the presence of both sulfur and silver on the metal surface^[3]. Fig. 4 displays a full

survey scan which shows the presence of carbon and oxygen as well as silver, sulfur, and the underlying metal aluminum layers. The peak at 367.4eV and 373.4eV in Fig. 5 corresponds the silver in nanosize. In Fig. 6, The lower energy site at 163.7eV is indicative of a metal sulfide, while the peak at 168.8eV has been assigned to sulfur originating from surface sulfur species. In addition, the shifted peak at 162eV is signal coming from a metal sulfide and the other peak at 164eV indicates a thiol at the particle surface.

Atomic force microscopy (AFM) investigations

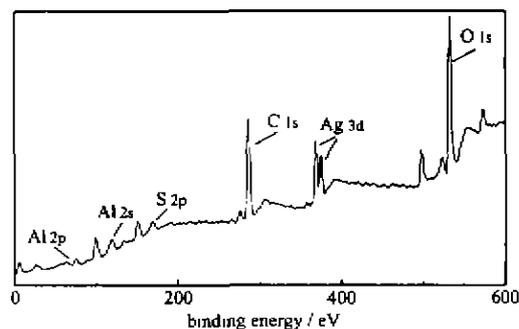


Fig. 4 XPS survey scan of SAMs of nanosize silver sulphide on the mercaptoacetic acid/aluminum surface

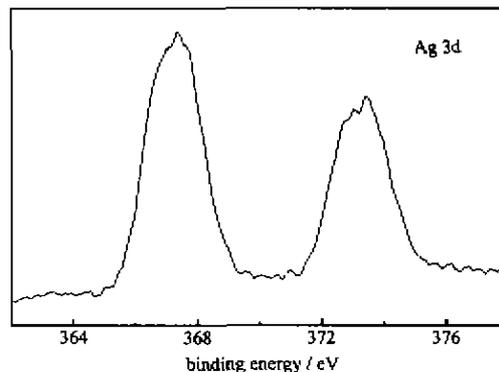


Fig. 5 XPS data of silver 3d core levels

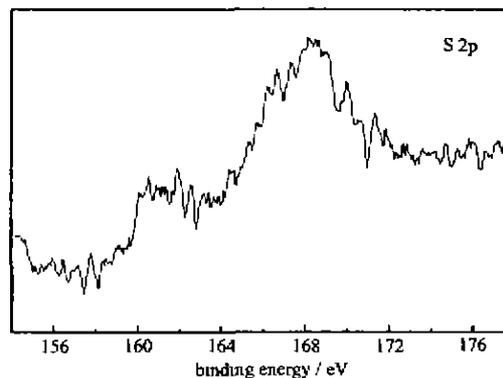


Fig. 6 XPS data of sulfur 2p core levels

can show direct surface characterization about self-assembly of nanosize particles. Aluminum film sample was acquired by thermal vapor deposition of aluminum on the plane glass. A contact mode AFM image of sample aluminum surface (Fig. 7) confirms that typical dimensions of the hillocks in this case are 150nm in diameter and 20nm in height. Fig. 8 displays a contact mode AFM image of SAMs of silver sulfide nanoparticles up to the aluminum surface of the sample. Self-assembly on the mercaptoacetic acid/aluminum surface, these silver sulfide nanoparticles have typical magnified diameter in 20nm and height in 5nm. It should be noticed that the widths of nanoparticles are in the range of 20nm, considerably larger than the value 5 nm determined from TEM measurements (Fig. 1). Such a deviation is attributed to the convolution effect of true particles with the AFM tip, which is often observed in AFM imaging. The width of nanoparticles is about 20nm, which is very different from that of thin aluminum layers with the average diameter about 80nm. It suggests that SAMs of nanosize semiconductor silver sulphide particles have been achieved.



Fig. 7 AFM images of aluminum surface
The shading is indicative of the height with black referring to the bottom of the scanned

Solution-based approaches to surface assembly of metal and semiconductor nanoparticles typically involve electrostatic or covalent binding of the particle to a surface-bound molecule. In our case, the traditional immersing time is 8hr. A contact mode AFM image of sample aluminum surface (Fig. 9) shows a sample of self-assembly of silver sulphide nanoparticles. The sample was prepared for immersing time 4hr. In the

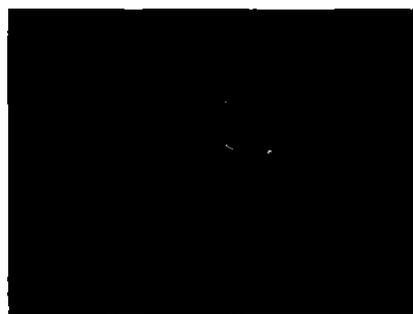


Fig. 8 AFM images of SAMs of nanosize silver sulphide on the mercaptoacetic acid/aluminum surface



Fig. 9 AFM images of SAMs of nanosize silver sulphide on the mercaptoacetic acid/aluminum surface
Immersing time is 4hr

process of self-assembly, nanoparticles tend to aggregate and precipitate, due to electrostatic interaction from nanoparticles and bifunctional organic molecules onto metal support.

AFM observation displays also that the metal support makes an effect to surface characterization of the SAMs of silver sulfide nanoparticles. Fig. 10 displays a contact mode AFM image of gold surface with many long strap units. The gold support in mica was treated at 500°C and 10^{-6} Torr. The average width of these long straps is in the size of 70nm. The micellar solution of silver sulphide/nanoparticles/AOT/



Fig. 10 AFM images of gold surface

n-heptane/water were prepared, with $2[\text{Ag}^+] = [\text{S}^{2-}] = 0.2 \text{ mol} \cdot \text{L}^{-1}$ and $w = 5$. A TEM investigation shows the size of nanoparticles is about 5nm similar to the reported^[14]. A sample with SAMs of nanoparticles was obtained by immersing SAMs of mercaptoacetic acid on the above gold support into micellar solution for 12hr. A contact mode AFM image displays that self-assembly occurs along these long straps (Fig. 11). The width of nanoparticles is in the size of 20nm.



Fig. 11 AFM images of SAMs of nanosize silver sulphide on the mercaptoacetic acid gold surface

In conclusion, the SAMs (SAM) of nanosize silver sulphide particles on the mercaptoacetic acid/aluminum surface was successfully prepared onto the glass or mica slide, using the nonionic surfactant Triton X-100. The assembly of the SAMs of silver sulfide nanoparticles depends on electrostatic interaction from nanoparticles and bifunctional organic molecules onto metal support.

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