A dry method to synthesize dendritic Ag$_2$Se nanostructures utilizing CdSe quantum dots and Ag thin films

Lian Hu$^{1,2}$, Bingpo Zhang$^1$, Tianning Xu$^3$, Ruifeng Li$^1$ and Huizhen Wu$^1$

$^1$Department of Physics and State Key Laboratory of Silicon Materials, Zhejiang University Zheda road 38, Hangzhou 310027, People’s Republic of China
$^2$School of science, Jiangnan University, 1800 Lihu Avenue, Wuxi 214122, Jiangsu, People’s Republic of China
$^3$College of Science, Zhejiang University of Technology, Hangzhou, Zhejiang 310024, People’s Republic of China

E-mail: hzwu@zju.edu.cn

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Abstract

Dendritic Ag$_2$Se nanostructures are synthesized in a dry environment by UV irradiating the hybrids composed of CdSe quantum dots (QDs) and silver (Ag). UV irradiation on CdSe QDs induces a photooxidation effect on the QD surface and leads to the formation of SeO$_2$ components. Then SeO$_2$ reacts with the Ag atoms in either Ag film or QD layer to produce the Ag$_2$Se. The growth mechanism of Ag$_2$Se dendrites on solid Ag films is explored and explained by a diffusion limited aggregation model in which the QD layer provides enough freedom for Ag$_2$Se motion. Since the oxidation of the CdSe QDs is the critical step for the Ag$_2$Se dendrites formation this dry chemical interaction between QDs and Ag film can be applied in the study of the QD surface chemical properties. With this dry synthesis method, the Ag$_2$Se dendrites can also be facilely formed at the designed area on Ag substrates.

Keywords: CdSe quantum dots, dry chemical reaction, dendrites, silver

1. Introduction

Semiconductor–metal coupling structures have attracted wide attentions since the compensatory properties of both components [1–6]. For example, the CdSe quantum dots (QDs)–Ag coupling structure has a unique luminescence tuning character caused by exciton–plasmon interaction [5]. Besides the physical interaction between the CdSe QDs and Ag components, the chemical interactions in the CdSe QDs–Ag hybrid structure are also worth being studied. The cation exchange between the CdSe QDs and Ag$^+$ in colloid dispersions was well studied by several groups [7–10]. But the chemical reaction between the CdSe QDs and Ag in solid state is not investigated before.

Dendritic crystal structures, the products of the hierarchal self-assembly at non-equilibrium conditions, can reflect the anisotropy of crystal growth concretely. Thus the preparation of dendritic structures with different material attracts attentions of many researchers. In general, dendritic crystal structures are usually obtained by wet-chemical method in a solution environment or a vapor deposition method [11–16]. It is preferred to assume that dendritic crystals can hardly grow in solid state medium because dry ambient can’t provide enough freedom for nucleation and growth of dendritic crystals.
In this paper, we studied the chemical reaction between CdSe QDs and Ag in solid states. The dendritic Ag₂Se nanostructures are obtained on an Ag film substrate at designed area by irradiating the CdSe QDs/Ag hybrid structure with UV light. Different from other approaches of dendrite growth, the Ag₂Se dendrites in this work were grown in solid state CdSe QDs. This simple method can be executed at room temperature and designed area in a completely dry environment.

2. Experiment sections

2.1. Preparation CdSe QDs capped with Oleic acid

Cadmium oxide (CdO, 99.95%), selenium powder (Se, 99.999%), tri-n-octyl phosphine (TOP, 90%), oleic acid (90%), 1-octadecane (ODE, 90%), were purchased from Alfa Aesar. All reagents were used as received. The oleic acid capped CdSe QDs were synthesized as our previous work. Typically, 0.2585 g (2 m mol) CdO powder, 6 ml oleic acid, and 30 ml ODE were loaded in a 50 ml three-neck flask. Then the mixture was heated to 300°C under the argon atmosphere till the transparent Cd precursor was formed. Then the heater was removed to lower down temperature of Cd precursor. When the temperature of the Cd precursor dropped to 240 °C, 1.2 ml stock Se precursor solution TOP-Se (Se powders dissolved in TOP with 2 M concentration) was quickly injected into the flask. The flask was cooled off in air. Then the QDs in ODE phase was mixed with double volume of ethanol and centrifuged at 4000 rpm. Finally, the precipitate was re-dispersed in toluene.

2.2. Preparation of Ag₂Se dendritic structures

Figure 1(a) schematically illustrates the preparation procedure of a QDs/Ag structure. 60 nm Ag film was thermally evaporated on a solid substrate (silicon wafer or glass slide). CdSe QDs dispersed in toluene was dropped directly on the Ag film. The QDs/Ag sample was dried naturally and then irradiated by a 365 nm UV light (20 W) to grow Ag₂Se dendritic crystals. When UV light is irradiated on the QDs/Ag sample the interaction between CdSe QDs and Ag can be ignited [5]. To selectively form Ag₂Se crystals on a designed area of the Ag film a metallic mask plate with stripe hollows was covered on the surface of the QDs/Ag sample and UV light irradiated the sample through the hollows as shown in figure 1(a). After 24 h UV irradiation, black stripes can arise at the irradiated area of the QDs/Ag structure. After removal of the mask plate, the sample was then cleaved to two pieces for characterizations. One piece was washed in chloroform to remove the QDs from the Ag film while the other one was not washed.

2.3. Characterizations

Steady state photoluminescence measurement was carried out with Edinburgh FLS920 system with the excitation line of 325 nm from a xenon lamp. A Hitachi S-4800 scanning electron microscope was used to measure the surface morphology of the samples. High resolution TEM images were scanned by a Tecnai G2 F20 S-TWIN transmission electron microscope.

3. Results and discussion

3.1. Structural and optical characteristics

Figures 1(b) and (c) show a TEM image of the QDs and a SEM image of the surface of the as-deposited Ag film, respectively. The TEM image reveals that the size of the CdSe QDs is approximately 5 nm. The SEM image shows that the as deposited Ag film is composed of dense and small Ag grains with size of ~30 nm.

Figure 1(d) is the photos of the two pieces of the cut sample illuminated by indoor light (top part is the sample after washing off the QD layer; bottom part is the sample without washing), which shows that the UV irradiation induced black stripes on the Ag film. Figure 1(e) shows the photos of the two pieces of the cut sample by 405 nm light excitation. In the washed sample (top part in figure 1(e)) the UV irradiated stripes become blue due to the scattering of incident light while the non-irradiated part is dark. In the sample without washing (bottom part in figure 1(e)) the UV irradiated stripes is bright yellow while the non-irradiated part is dark brown. These phenomena indicate that the UV irradiation changes the optical properties of the CdSe QDs/Ag structure thus the luminescence pattern is formed with the mask plate. The expected intensity enhancement and blue shift of the luminescent emission of the QDs with UV irradiation are observed due to the photoactivation effect [17–22]. The oxidation of QD surface induced by UV irradiation passivates the dangling bonds and reduces the density of surface defect states, which results in the enhancement of the luminescence emission. Adequate oxidation of QD surface can also reduce the effective size of the QDs, which makes the blue shift of bandedge emission peak as observed in the PL spectra [5]. As shown in figure 1(f), the luminescent peak of the QDs without UV irradiation locates at 566 nm. After UV irradiation, the luminescent peak of the QDs blue shifts to 520 nm and the integrated luminescent intensity is about 20 times of that of the QDs without UV irradiation. Here, the influence of the formed Ag₂Se on the QDs PL peak positions shown in figure 1(f) can be excluded as Ag₂Se has a very narrow bandgap (Eg≈0 eV) [14].

The SEM images of the ‘black area’ on Ag film are shown in figures 2(a)–(d). The morphology of black area is so different from that of the as-deposited Ag film shown in figure 1(c): well assembled 3D dendritic structures with 1–2 μm in length are observed on the Ag film substrate. In most of the dendrites, three branches are symmetrically grown around a main trunk and the angle between the main trunk and side branches is about 70°. The period of the branches is ~50 nm. The energy dispersive x-ray spectroscopy (EDS) characterization of the black area indicates that the Ag and Se elements have the ratio of 2–1, which asserts that this black
The crystal product is the compound of Ag and Se: Ag₂Se. The XRD pattern of the dendrites in figure 3 further confirms that the crystalline dendrites are β-Ag₂Se with orthorhombic phase \[11–13\]. A few dendrites are collected for HRTEM observation as shown in figures 2(e) and (f).

The XRD patterns of the ‘black’ dendrites are shown in figure 3. The XRD patterns of a QD layer and an Ag film are also separately shown for reference. Apparently, the XRD pattern of Ag₂Se dendrites present sharp diffraction peaks at 22.9, 37.0, 40.0 and 46.8 which are indexed to the (002), (013), (031) and (004) diffraction planes of β-Ag₂Se with orthorhombic phase (JCPDS card, #24-1041, space group P2₁2₁2₁). The (002) diffraction peak of the Ag₂Se crystal dominates the XRD pattern, indicating that the
Figure 2. (a)–(d) SEM images of the Ag$_2$Se dendrites with different magnifications. (e), (f) TEM images of Ag$_2$Se dendrites.

Figure 3. XRD patterns of the CdSe QD layer (bottom), Ag film (middle) and the ‘black’ Ag$_2$Se dendrites (top).

Diagram 1. The schematic of the possible reaction for the formation of Ag$_2$Se dendrites.
dendrites have preferential growth orientation along [001] direction.

3.2. The mechanism of the Ag₂Se dendrites formation

From the data of the XRD shown in figure 3, we can conclude that the element Se and Ag in the Ag₂Se dendrites originate from the covering CdSe QDs and underneath Ag film, respectively. But, questions remain unanswered: How do the CdSe QDs and Ag react to form the Ag₂Se dendrites? What’s the role of the UV irradiation? To answer these questions we add more experiments and mechanism discussions.

3.2.1. Is the photoactivation of QDs relevant to the formation of Ag₂Se dendrites? For the dry growth of the dendrites here, UV irradiation impact on the CdSe QDs/Ag structure is very significant. In the process of UV irradiation, both photoactivation effect of CdSe QDs and dendrite growth occur. Is the photoactivation of the QDs related to the growth of Ag₂Se dendrites? We know that the oxygen in air plays a critical role in the photoactivation process on QDs, thus the photoactivation of QDs is also called photooxidation because UV irradiation provokes oxidation of QD surface which modifies the density of the QD surface states. The Se atoms on the CdSe QD surface are oxidized to form SeO₂ during UV irradiation [19–21], which results in the evident enhancement of PL intensity as observed in figure 1(f).

Our previous work showed that the UV irradiation can hardly influence on the QDs in a vacuum environment since no oxidation occurs on QD surface [17]. When the CdSe QDs/Ag structure was irradiated with the UV light for 24 h in a vacuum vase, again no black dendrite products were observed. We found that the dendrite formation always accompanies the oxidation of CdSe QDs, which indicates that oxygen is critical for the Ag₂Se dendrite formation during the UV irradiation. We also found that longtime UV irradiation on the Ag film does not favor the dendrite formation. Since the oxygen is important in the formation both of SeO₂ and Ag₂Se dendrites, we can conclude that the SeO₂ is a pivotal intermediate product for Ag₂Se dendrite growth.

It is known that there exist H₂O molecules besides the oxygen in air ambient. A previous study showed that H₂O molecules can participate in the photoactivation process [22]. We repeated the photo-induced growth of Ag₂Se dendrites in dry air, consequently the black products were still seen and the PL intensity enhancement by photoactivation was still observed. So we can further conclude that H₂O molecules are not the essential factor for photoactivation of QDs and growth of Ag₂Se dendrites. But we can’t exclude that the H₂O is an impetus for the photoactivation process (supporting information). A possible reaction route for the formation of Ag₂Se dendrites is proposed in diagram 1.

To observe the dendrite structure more clearly a 30 nm Ag film were deposited on a Si substrate and then proceeded with thermal annealing at 180 °C for half an hour in air. Annealing of the Ag islands leads to the diffusion of Ag atoms, and consequently the well-known Ag island morphology formed as a dewetting phenomenon [23–26]. By depositing a suitable thickness of Ag film, the Ag islands with round exteriors can be obtained (figure 4(a)). A QD layer was then coated on the
Ag islands and the sample was stored for three weeks in common indoor environment with natural light. Interestingly, the dendrites on the Ag islands were still observed (figure 4(c)), which indirectly confirms that the oxidation of CdSe QDs can occur in common indoor light. We also found that no evident black products emerge on the Ag film under the CdSe QD layer if the sample was stored in dark environment (the sample was stored for four weeks), which indicates that the oxidation on CdSe QDs is very slow without the photoactivation. Comparing the dendrites in figures 4 and 2, the dendrites in figure 2 are evidently denser than those in figure 4, which indicates that UV irradiation can substantially accelerate the formation of SeO2 in the coated QD layer.

3.2.2. Diffusion limited aggregation (DLA) model for explaining the dendrite growth. The growth of dendritic structure is usually explained by the DLA model and the orientated attachment model [27, 28]. In previous studies the dendrite growths usually occurred in a liquid or vapor environment [11–16]. In a liquid environment, the ions or the precursor particles were orientedly deposited on nuclei and therefore the hierarchical structures form step by step. But in our case, the Ag2Se dendrites grew at the interface between the solid Ag film and CdSe QD layer rather than in liquid phase materials. The solid QD layer here acts as liquid for the migrating and combining of Ag atoms and SeO2 molecules. Since QDs have a core and ligand structure, the QD layer is not so compact that enough motion freedom for dendrite precursors can be reached.

The Ag atoms can detach from the Ag film and diffuse into the QD layer due to thermal motion. The Ag atoms then interact with SeO2 molecules in the QD layer to form the Ag2Se monomers or particles. Comparing figures 4(a) and (b), the dense, regular and smooth Ag islands become loose and irregular ones after the growth of dendrites. The dendrites at different growth stage can be seen in figures 4(c) and (d). The bright tips with ∼20 nm size on Ag are the initial Ag2Se dendrites; the SeO2 reacts with the Ag atoms on the surface of the Ag film to form the Ag2Se nuclei, then the oriented attachment of Ag2Se monomers or particles around on them occurs for dendrite growth. The dendrite growth prefers along [001] direction. The mechanism for the oriented attachment of Ag2Se particles can be confirmed by the SEM images shown in figure 5. The irregular particles appear at the terminals of the branches of the relatively big dendrites (the sizes are usually larger than 3 μm) because the ‘ripe’ Ag2Se particles grown in the QD layer could attach to the dendrite branches.

4. Conclusions

Dendritic Ag2Se nanostructures are synthesized in a dry environment by UV irradiating the hybrids composed of CdSe QDs and Ag. The mechanism of the chemical reaction between CdSe QDs and Ag film in solid state is revealed. The UV irradiation on the CdSe QDs can speed up the oxidation of QD surface then the oxidation product reacts with Ag to form the Ag2Se dendrites. The solid QD layer promises the motion freedom of SeO2 molecules and Ag atoms for their reaction. We further find that the Ag2Se dendrites can grow even in air ambient without UV irradiation. Beyond the exciton-plasmon interaction in the CdSe-Ag structure, the chemical reaction between CdSe QDs and Ag can’t be ignored. The Ag2Se dendrites can be formed at the designed area on Ag substrates with this simple and low cost ‘dry method’. Since the oxidation of the CdSe QDs is the critical step for Ag2Se dendrites formation this dry chemical interaction between QDs and Ag film can also be applied in the study of the QD surface chemical properties.

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