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Growth and quantum confinement in AgI nanowires

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Abstract

Silver iodide nanowires were synthesized in W/O microemulsions by using cyclohexane/Triton X-100/*n*-pentanol system. Most likely, surfactants form rod-like aggregates that can serve as template for growth of two dimensional nanomaterials. It was found that the length of the AgI nanowires increases as a function of aging time, while the diameter decreases. Final length of the AgI nanowires is several microns, while the diameter is smaller than 3 nm. Morphological changes are accompanied by optical and structural changes. Large blue shift of excitonic peak from bulk value at 420 to 326 nm was observed as a consequence of the size quantization effect. Decrease of diameter is followed by the amorphization of AgI nanowires.

Keywords: AgI; Nanowires; Size quantization effect; Nanomaterials; Semiconductors; Microemulsions

1. Introduction

Compared to bulk materials, nano-scale materials exhibit large specific surface area and size-dependent quantum confinement effects. Nano-scale materials often have distinct electronic, optical, magnetic, catalytic and thermal properties. Over the past few years, significant efforts have been made in order to synthesize various 0D, 1D and 2D nano-scale materials, i.e., quantum dots, wires and wells [1–9]. Above mentioned structures have attracted considerable attention due to the promising fundamental properties for utilization in electronic and photonic applications [10,11]. On the other hand, the recent availability of semiconductor nanocrystals with anisotropic properties (rods and wires) has renewed interest in understanding how shape affects their electronic and optical properties [12,13]. Systematic research of dots, rods and wires provides possibility to explore the transition from simple 3D to 2D confinement, over quantum rods, i.e., anisotropic quantum dots. The synthesis of uniform nanorods and nanowires (NWs) and their assembly into well defined structures are currently a major challenge.

So far, AgI quantum dots have been prepared in acetonitrile using polybrene as a stabilizer [14,15], and in aqueous solution using poly(ethyleneimine) to inhibit particle growth [16]. Recently, Xu et al. [17,18] synthesized AgI NWs in reverse micelles, but unfortunately they did not investigate their optical properties. Their work was a starting point for the further investigations described in this paper. We used a synthetic procedure described in Ref. [17] and in addition followed morphological, structural and optical changes upon aging. We found that the length of the AgI NWs increased as a function of aging time, while, on the other hand, the diameter became smaller reaching the quantum size domain. Those changes are accompanied by optical changes. We observed a large blue shift of the excitonic peak from bulk value at 420 to 326 nm due to the size quantization effect. To the best of our knowledge this is the first example of 2D confinement in the case of AgI nanoparticulates. Also, decrease in diameter is accompanied by the amorphization of AgI NWs.

2. Experimental

All chemicals (silver nitrate, potassium iodide, cyclohexane, Triton X-100, *n*-pentanol and ethanol) were of the highest purity available, and they were used without further purification. The AgI NWs were prepared by rapid mixing of two separate microemulsions containing $AgNO_3$ or KI, as described elsewhere [17]. Briefly, each microemulsion contained 0.46 g of

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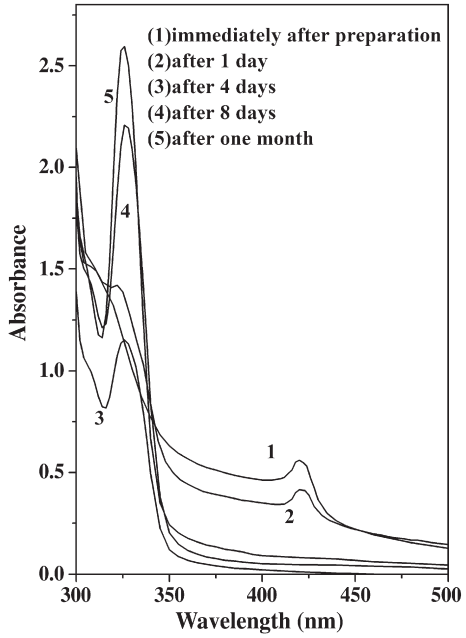

Fig. 1. Absorption spectra of AgI NWs in W/O microemulsion as a function of aging time (0.01 M AgI; $[I^-]/[Ag^+]=3$).

n-pentanol, 3.37 g of Triton X-100, 7.64 g of cyclohexane and 1 g of water, and consequently the molar ratio between water and surfactant was $\omega=[H_2O]/[\text{Triton X-100}]=11$. Molar ratio between iodide and silver ions was constant in all experiments ($[I^-]/[Ag^+]=3$) while concentrations of iodide and silver ions were in the range from 0.009–0.03 M to 0.003–0.01 M, respectively. Silver and iodide concentrations were calculated per aqueous phase. For the sake of clarity, we kept the molar ratio between reactants and composition of W/O microemulsion as in Ref. [17], while the initial concentrations of the reactants were different.

Absorption spectra of AgI NWs in W/O microemulsions were measured using a Perkin Elmer Lambda 5 UV–VIS Spectrophotometer.

Microstructural characterization of AgI NWs at different aging times was performed by transmission electron microscopy (TEM) using Philips EM 400 microscope operated at 120 kV. The samples for TEM measurements were prepared by dissolving one droplet of microemulsion in 2 ml of ethanol. The obtained samples were placed on C-coated Cu grids.

The X-ray diffraction (XRD) measurements were carried out on a BRUKER D8 ADVANCE diffractometer in theta/theta reflection geometry with parallel beam optics achieved by multilayer Göbel mirror, which is suitable for the examination of liquid samples. Diffraction data for structure analysis were collected in 2θ range from 10° to 80° with steps of 0.05° and 10 s counting time per step.

3. Results and discussion

When two separate W/O microemulsions containing $AgNO_3$ and KI were mixed together an appearance of yellowish color due to the formation of AgI can be observed. The obtained mixture becomes clearer with aging. Absorption spectra of the AgI in W/O microemulsion (0.01 M AgI, $[I^-]/[Ag^+]=3$) as a function of aging time are shown in Fig. 1.

Immediately after preparation absorption spectrum showed typical features of bulk AgI with the excitonic peak at 420 nm [19]. Aging of AgI sample induced blue shift of excitonic peak from its bulk position at 420 to 326 nm. The excitonic peak at 326 nm became more pronounced as a function of aging time and it stopped to change after approximately one month. It is important to emphasize that samples with lower concentration of AgI (0.003 and 0.005 M AgI) showed completely the same optical behavior (spectra not shown). The only difference is longer time needed to reach equilibrium when the excitonic peak at 326 nm stops to change; thus, the lower the concentration of Ag^+ and I^- precursor ions in W/O microemulsions, the longer the time to reach equilibrium. The increase of band gap energy of 0.85 eV can be attributed to the size quantization effect that arises from the confinement of charge carriers in the finite volume of small AgI particles.

So far, an increase of band gap energy for AgI quantum dots has been observed by Mićić et al. [14,15] and Mulvaney [16], as well as by Meisel et al. [20] in pulse radiolysis study. They reported position of the excitonic peak at 303 [14], 315 [15], 323 [16] and 334 nm [20] for AgI quantum dots with average diameter of 25, 23, 30 and 32 Å, respectively. Knowing from TEM measurements (see further in the text) that prepared AgI nanoparticulates are in the form of NWs and using effective mass approximation model for 2D confinement we estimated that the diameter of AgI NWs which corresponds to the excitonic peak at 326 nm should be 23.6 Å. It should be pointed out

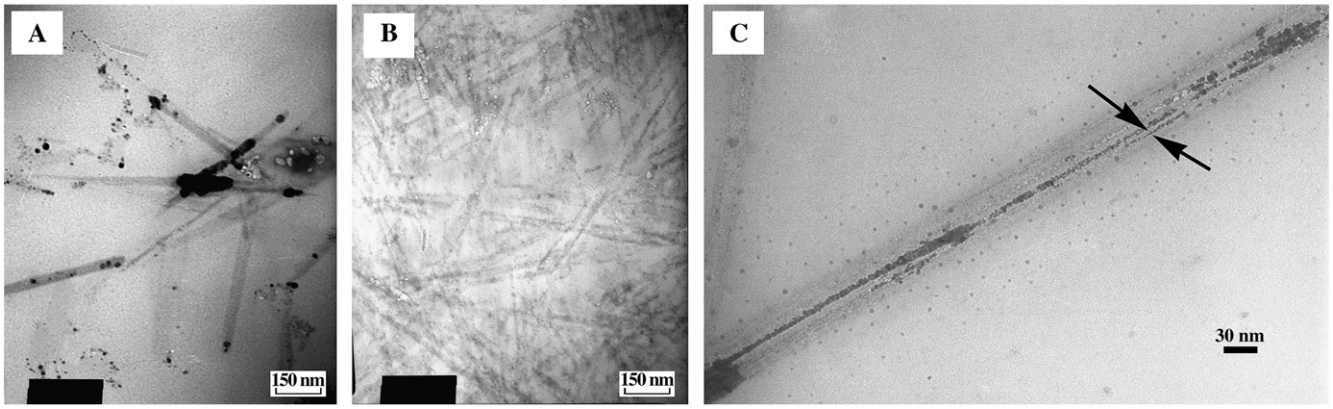

Fig. 2. Typical TEM images of the AgI NWs (0.01 M AgI; $[I^-]/[Ag^+]=3$) synthesized in W/O microemulsion: (A) immediately after preparation, and (B and C) after one month of aging.