

Synthesis and Properties of Hybrid Colloidal Au-CdSe Nanoparticles

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The communication is devoted to the synthesis procedure and properties of hybrid nanoparticles of colloidal gold with cadmium selenide. Optical and morphological characteristics of the above-mentioned particles, as well as the formation mechanisms, are discussed.

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1. INTRODUCTION

Interest to hybrid colloidal nanoparticles which contain metal and semiconductor components has considerably increased during the last decade. Structures of such type, as a rule, contain II-VI semiconductor due to the simplicity of synthesis and cheapness of precursors and metal (partially or completely inert and, as a rule, noble) for removal of the probable oxidation of metal cluster. FePt₃-CdSe (CdS, ZnS, PbS) [1], Ag-ZnO [2], Ag-CdSe [3], Hg-HgS [4], and other structures [5] are the most studied in this context. Structures of colloidal gold with cadmium selenide (sulphide) [5-9] are of greatest interest. Such structures are characterized by different morphologies and properties which depend, mainly, on the succession and duration of injections of the corresponding precursors. In the present work, we propose the technique for obtaining hybrid nanoparticles of the type Au core/set of CdSe nanobars.

2. EXPERIMENTAL TECHNIQUE

2.1 Precursors and synthesis procedure

Synthesis was realized in an atmosphere of flowing nitrogen. Three-necked flask was placed in the heating element; one neck was connected with the condenser; another one – with the temperature controller (thermocouple). Slightly modified (with substitution of octadecylphosphonic acid (ODPA) by the corresponding one with less length of carbon chain) method from [10] was used for the synthesis of CdSe nanocrystals. Formation of the core of colloidal gold was performed according to the modified (by injection duration) procedure from [8].

Cadmium precursor was prepared from cadmium oxide (CdO, 99,5%, Sigma-Aldrich, 0,2054 g, 1,6 mM), tetradecylphosphonic acid (TDPA, CH₃(CH₂)₁₃PO(OH)₂, 99%, PCI Synthesis, 0,713 g, 2,56 mM), and trioctylphosphine oxide (TOPO) (CH₃(CH₂)₇)₃PO, 99% Sigma-Aldrich, 3,93 g, 10,17 mM) which were placed into flask (50 ml). In an atmosphere of flowing nitrogen mixture was heated up to 320 °C and exposed at this temperature until all cadmium oxide will react to the formation of the corresponding phosphonates (visually, dark red solution was turned into colorless one). Duration of the reaction was 1-2 hours.

Precursor of selenium was prepared at the room temperature, 0,063 g (0,8 mM) of Se powder (99%, Sigma-Aldrich) was dissolved in tributylphosphine (TBP,

(CH₃(CH₂)₃)₃P, 99%, Sigma-Aldrich, 0,31 ml, 0,253 g, 1,25 mM; mass fraction of selenium is 25%) with addition of 1,14 ml (0,947 g, 2,56 mM) of trioctylphosphine (TOP, (CH₃(CH₂)₇)₃P, 97%, Sigma-Aldrich); 0,35 ml (0,3 g, 3,26 mM) of anhydrous toluene (C₆H₅CH₃, 99,5%, Sigma-Aldrich), and 0,178 g (0,64 mM) of TDPA and was exposed by mechanical-ultrasonic mixing till decoloration of the initially dark-grey solution.

Synthesis of CdSe nanobars: cadmium precursor was heated up to 320 °C in flowing N₂. At this temperature, selenide precursor was rapidly injected into cadmium one. Nanocrystals were grown during 8 min at 300 °C, and then flask was removed from heater. When flask reached the temperature of 100 °C, 5 ml (47 mM) of toluene were injected into the obtained solution for non-admission of TOPO crystallization. Obtained solutions had optical characteristics typical for nanobars of the length of about 15 nm and length/diameter ratio of 5. Further, CdSe nanoparticles were used for the formation of micelles on the colloidal gold cores.

Precursor of gold: 5 ml of toluene solution (47 mM), which contained gold trichloride (AuCl₃, 99%, Sigma-Aldrich, 12 mg, 0,03 mM), didodecylmethylammonium bromide (DDAB, (CH₃(CH₂)₁₁)₂N(CH₃)₂Br, 98%, Sigma-Aldrich, 40 mg, 0,086 mM), and dodecylamine (DDA, CH₃(CH₂)₁₁NH₂, 98%, Sigma-Aldrich, 70 mg, 0,38 mM), was exposed by ultrasonic mixing (5 min) and rapidly (4-5 s) injected into suspension of CdSe nanobars (in the ratio of 1:30) at mixing in flowing nitrogen. The samples, both CdSe nanobars and Au-CdSe hybrids, were cleaned using several cycles: deposition by anhydrous methanol-centrifugation (15 min at 2000 min⁻¹)-dissolution in anhydrous toluene.

2.2 Measurement techniques

For optical investigations, solutions of the samples were placed in a quartz cell of the thickness of 1 mm. Photoluminescence spectra (PL) were obtained at room temperature using fluorescent spectrometer Jobin-Yvon Fluorolog-3 which contained xenon lamp as a source of excitation of the emission, double monochromator and CCD detector operated by software Horiba J-Y. Spectra of the UV-visible absorption were obtained by Agilent 8453 multidiode absorption spectrometer. Transmission electron microscopy (TEM) was studied on the electron microscope JEOL JEM 3010 in the transmission mode and electron energies of 300 keV. For the TEM investi-

gations, standard copper grid with carbon coating was dipped into solution of nanoparticles, and then it was dried at 50 °C in an atmosphere of flowing nitrogen.

3. RESULTS AND DISCUSSION

In Fig. 1 we present the absorption spectra of cadmium selenide nanobars before and after injection of gold precursor. They illustrate active interaction of the obtained CdSe particles with rapidly injected colloidal gold that considerably changes the behavior of the UV-visible absorption of solutions. Spectrum of the directly synthesized solution of CdSe nanobars essentially resembles the spectrum of the corresponding particles synthesized using ODPAs as passivating and stabilizing ligands [10, 11] and corresponds to the nanobars with linear sized of 3×15 nm. These nanobars have sharp absorption bands and narrow luminescence band (see Fig. 2) that implies the absence of deep carrier traps, sufficient monodispersity and surface quality. In particular, absorption bands at 603 nm and 495 nm are clearly distinguishable, and band is slightly diffuse at 574 nm. These bands belong to the exciton transitions $1\sigma_b - 1\sigma_n$, $1\pi_b - 1\pi_n$ та $2\sigma_b - 2\sigma_n$, respectively. The line of background is close to 0,1 in the units of optical density (OD) characterizing small light scattering loss (in particular, according the Rayleigh mechanism), and therefore, aggregated nanoparticles loss.

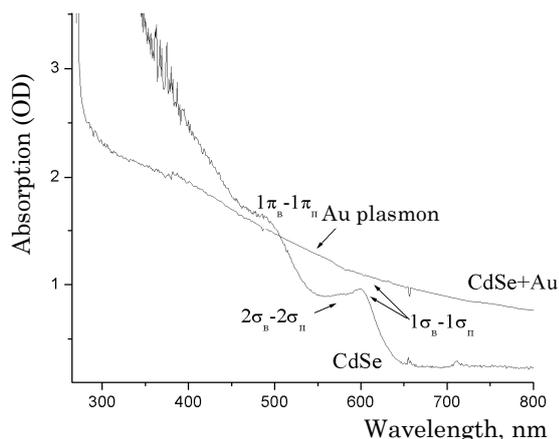


Fig. 1 – Absorption spectra of the synthesized CdSe nanobars and hybrid CdSe-Au nanoparticles

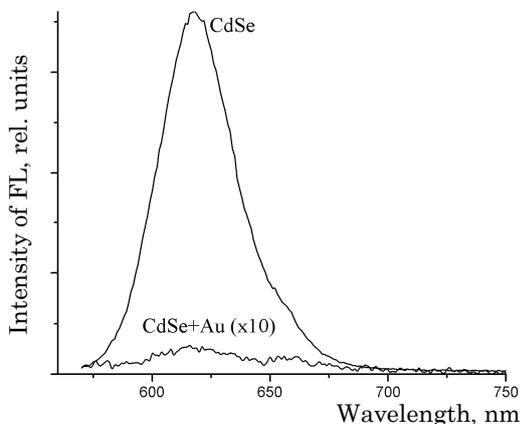


Fig. 2 – FL spectra of the synthesized CdSe nanobars and hybrid CdSe-Au nanoparticles (FL was excited at 550 nm)

Spectrum of nanoparticles after interaction with colloidal gold is much less informative. Except very diffuse maximum near 535 nm (it corresponds to the plasmon resonance in spheres of colloidal gold of the diameter of about 40 nm) there are traces of the transitions in CdSe nanobars. Mean optical density of the solution (≥ 1) indicates the formation of aggregates of sufficiently large sizes and weight contribution of the Rayleigh component.

Elements of plasmon spectrum of colloidal nanogold as well as the exciton characteristics of CdSe are found to be only the traces in monotonous spectrum which is complex and is not obtained by simple summing of the spectra of metal and semiconductor nanoparticles: the system has more complicated electron structure of mixed electron states of metal and semiconductor. Such behavior is also typical for the FL spectra (Fig. 2). Spectrum of cadmium selenide nanobars contains intensive (samples had 14% quantum yield) band at 618 nm connected with radiative recombination of the above described exciton levels.

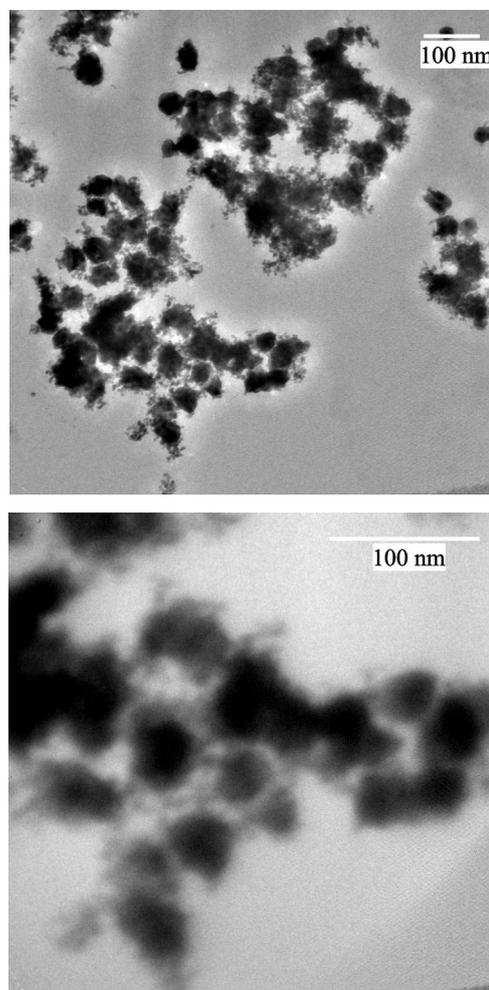


Fig. 3 – TEM images of hybrid CdSe-Au nanoparticles

Considerable quenching of luminescence (more than two orders) is connected directly with the interaction of nanobars with parts of colloidal gold. This is explained by the formation of channels of radiationless recombination through electron states of the parts. The value of such process indicates almost total connectivity of nano-

bars with gold nanoparticles. Moreover, the band near 660 nm is present in the spectrum. This band is explained by some amount of radiation transitions near the interface. More electronegative atoms of gold in the immediate vicinity of semiconductor lattice act as the electron traps. Recombination of such trapped electrons is mainly radiationless. Its small radiation component should be characterized by the low-energy shift due to the above described processes.

TEM (Fig. 3) finally clarifies the nature and growth mechanisms of hybrid nanostructures. One can immediately see a sufficient amount of cadmium selenide nanobars of the length of about 15 nm which are attached by one end to nanospheres of colloidal gold of the diameter of 30-35 nm. Free (unconnected) nanobars are not observed as well as nanospheres of gold (except one) in the region of scale ruler.

Rapid injection of gold precursor can provide high speed of the growth process and domination of the lat-

ter over the initiation processes. As well as in the case of nanodumbbells, weak interaction of the type of acid-the Lewis basis is sufficient for aggregation of different types of nanoparticles into hybrid objects; large spheres of gold can interact with numerous nanobars whose diameter is one order less. Absence of free nanoparticles explains the optical characteristics which are non-typical for both metallic and semiconductor materials and implies the formation of principally new hybrid nanoensemble. Interaction between particles of one type is excluded by the volume properties of ligands (TDPA-TOPO for cadmium selenide and DDAB-DDA for gold).

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