Synthesis of a hybrid material from CdS nanoparticles and carbon nanotubes

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A method for synthesis of a hybrid material from CdS nanoparticles and carbon nanotubes (CNT) by the precipitation of CdS nanoparticles on the CNT surface from an aqueous solution containing the Cd^{II} salt, thiourea, and ammonia was developed. The dependences of the size of particles formed on the CNT on the temperature of the solution and the duration of precipitation were observed. The degree of imperfection of the CNT surface exerts a substantial effect on the density of the precipitated CdS particles.

Key words: carbon nanotubes, cadmium(II) sulfide, nanoparticles, hybrid materials.

The development and use of nanoparticles of semiconductors is of interest for the preparation of photoabsorbing and photoemitting cells. The range of absorption and luminescence frequencies depends on the nanoparticle size. Hybrid nanosystems combining the properties of one-dimensional carbon nanotubes (CNT) and quantum dots of semiconducting materials are being actively developed presently. It is expected that the interaction of semiconducting nanoparticles with light would result in the electron photocurrent through the nanotube and localization of the hole on the nanoparticle. This would allow one to desigh new types of photogalvanic devices.[1] Recently it was repeatedly reported the precipitation of various types of nanoparticles of metal sulfides and selenides, such as CdSe (see Ref. 2), Cu_2S (see Ref. 3), and CdS (see Refs 4—6) on the CNT. In particular, modified CdS nanoparticles were pre-prepared and then precipitated from solution on the CNT surface, which made it possible to use such systems as biosensors.[7] During the electrochemical precipitation of CdS nanoparticles ~15 nm in diameter on bamboo-like nanotubes 100 nm in diameter, the CNT were pre-oxidized with nitric acid for better precipitation.[8] The photoconductivity of the hybrid CdS/CNT materials was enhanced. The precipitation of CdSe nanoparticles on bundles of double-wall CNT was described.[9] The CNT were pre-fluorinated to provide a more uniform distribution of nanoparticles on the surface. A more complicated multistep approach to the formation of CdS nanoparticles on the nanotube surface is known.[6] By oxidizing the CNT surface with a mixture of acids the surface was firstly functionalized with carboxyl groups and then Cd^{2+} ions were "cross-linked" to these groups. As a result of the interaction with Na_2S, CdS nanoparticles ~8 nm in size were formed on the CNT surface.

Hydrogen sulfide is often used for the synthesis of CdS. Hydrogen sulfide should be replaced by less toxic organic sulfur-containing compounds capable of acting as a supplier of sulfur atoms. One of the most available sulfur-containing reagents of this type is thiourea $(NH_2)_2CS$ (Thio). For example, CdS films were obtained[10,11] from aqueous solutions containing Thio, Cd^{II} salts, ammonia, and NaOH. A possibility to prepare CdS nanoparticles by this reaction was described.[12]

The purpose of the present work is to study the formation of CdS nanoparticles on the surface of an array of multiwalled CNT aligned perpendicularly to the silicon support using the thiourea method of CdS synthesis from solution. Preliminary experiments were carried out on pure silicon supports. It was desirable to determine the influence of the temperature and reaction time on the size and shape of nanoparticles formed and on the density of nanoparticles on the support.

Experimental

Arrays of CNT were obtained under an inert atmosphere at ~800 °C on silicon single-crystal supports with the orientation [100] having a size of 10×10 mm^2 by the method of catalytic decomposition of hydrocarbon vapor (CVD method).[13] The synthesis was carried out in a tubular reactor equipped with a mobile manipulator, a gas-leaking equipment, and a device to feed reaction mixture at the synthesis zone. Vapor of the reaction mixture consisting of a 2% solution of ferrocene in toluene or aceto-

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nitrile was transferred with an argon flow to the synthesis zone. As a result, films of multiwalled carbon and nitrogen-containing CNT oriented predominantly perpendicular to the support surface were obtained. The external diameter of the nanotubes was ~20 nm, and the length was ~100 μm.

The modified method proposed earlier[11] for the preparation of CdS films was used to precipitate CdS particles from an aqueous solution containing $CdCl_2$, Thio, and NH_3. The following reagents were used in the work: $CdCl_2 \cdot 2.5H_2O$, Thio, an aqueous solution of NH_3 (analytical purity grade). The procedure of formation of CdS nanoparticles was approved on silicon supports (KEF-0.4-01 trade mark) oriented in the [100] direction, and then the CdS nanoparticles were precipitated on the arrays of aligned multiwalled CNT formed on the silicon support due to CVD synthesis.

A solution of Thio (0.3 mol L^{-1}) in 100 mL of an aqueous solution of NH_3 (70.3 g L^{-1}) was prepared in a glass beaker. Holders with pure silicon supports or with supports covered a layer of oriented CNT were placed in the beaker in such a way that the supports would be above the level of the solution and the side of the support deposited with CdS would be turned to the bottom of the beaker. A solution of $CdCl_2 \cdot 2.5H_2O$ (0.03 mol L^{-1}) in 100 mL of an aqueous solution of NH_3 was prepared in the second beaker. The both solutions were heated in a thermostat to 40 °C (silicon supports) or to 30—60 °C (supports with CNT), and then a solution of $CdCl_2$ was rapidly added to a solution of Thio. As a result, the supports were in the reaction solution. The reaction mixture was rapidly stirred with a glass stick, after which time reading was started. The initial concentrations of $CdCl_2$, Thio, and NH_3 in the reaction mixture were 0.015, 0.15 mol L^{-1} and 70.3 g L^{-1}, respectively. The silicon supports were taken from the reaction mixture after 1, 2, 4, 5, and 10 min. The supports with the layer of oriented CNT were taken out after 1, 2 min (temperature of the mixture 30 and 40 °C) and after 5, 10 min (60 °C). The supports were washed with distilled water and dried in air.

Electron microscopic studies of the samples obtained were carried out by scanning electron microscopy (SEM) on a Jeol JSM-6700F instrument.

Rusults and Discussion

Preliminary experiments showed that the conditions of experiments used earlier[11] for the preparation of CdS films are unsuitable for precipitation of CdS nanoparticles. Therefore, in this work we decreased the temperature of the reaction mixture and shortened the duration of the synthesis. In addition, the order used to heat solutions and prepare the reaction mixture was changed. The procedure developed made it possible to precipitate CdS nanoparticles on the silicon supports and CNT. According to the concepts[14] on the mechanism of CdS formation in aqueous solutions containing $CdCl_2$, Thio, and NH_3, the reaction affords Cd^{II} ammonia—thiourea complexes followed by basic hydrolysis of coordinated Thio. The Cd—S bond is retained during this process

$$[Cd(NH_3)_{m-i}(Thio)_i]^{2+} \longrightarrow CdS + (m - i)NH_3 + (i - 1)Thio + \text{decomposition products.}$$

The SEM images of the surface of the silicon supports stored for different times in the reaction mixture at 40 °C are shown in Fig. 1. A small amount of individual nanoparticles was precipitated on the silicon surface at the first

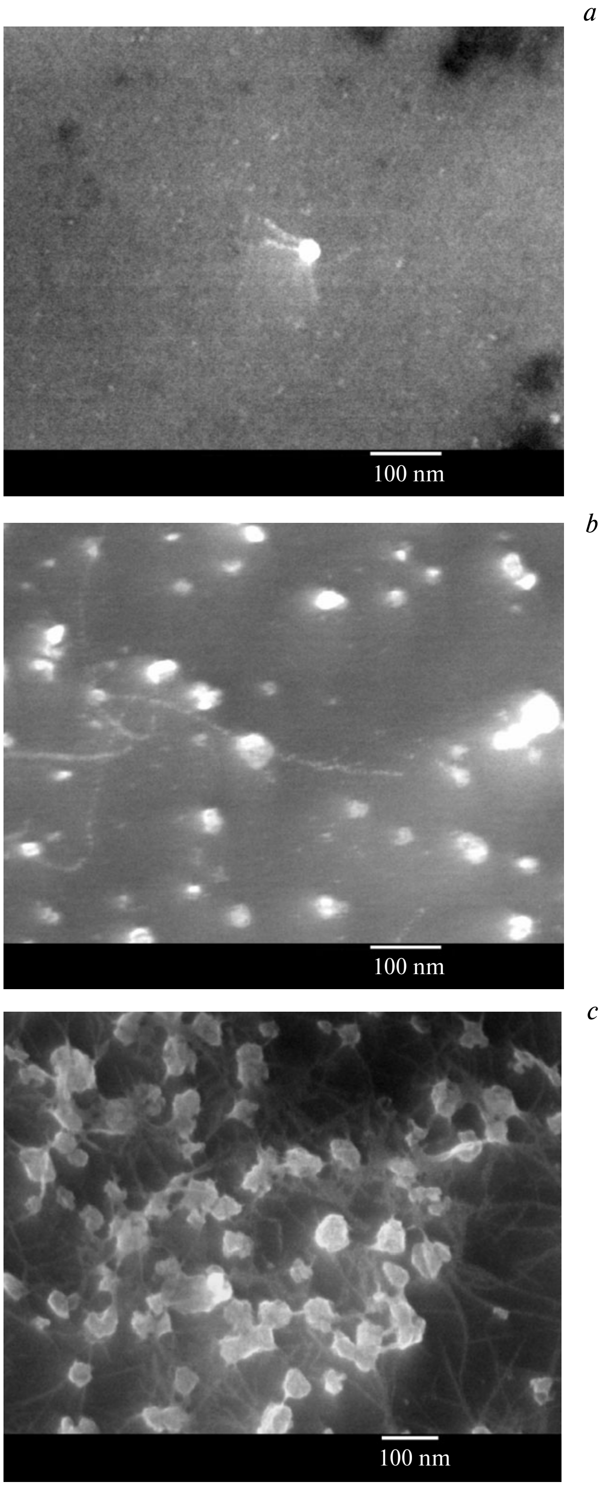

Fig. 1. SEM images of CdS nanoparticles formed on the silicon support surface at 40 °C for 1 (*a*), 5 (*b*), and 10 min (*c*).

step of formation of the CdS nanoparticles (1 min) (see Fig. 1, *a*). The image shows a small number of large particles ~30 nm in size (typically separated by a distance of ~1 μm) and numerous number of fine particles ~5 nm in size (usually separated by a distance less than 50 nm). Short nanowires not longer than 100 nm begin to form from the small CdS particles in the immediate vicinity from the surface of large particles. The wires so formed have a nonuniform structure, indicating that they are built of bound nanoparticles. The average size of the connected particles that form a nanowire does not exceed 5 nm. An increase in the duration of precipitation of CdS particles on the silicon support to 5 min increases the size of the large nanoparticles to 50 nm (see Fig. 1, *b*). The wires, whose length reaches several microns, continue to grow. The density and size of fine particles on the silicon surface remain almost unchanged.

An increase in the precipitation duration to 10 min results in the formation of a network of particles bound by nanowires on the silicon support (see Fig. 1, *c*). Compared to the morphology of the particles obtained by precipitation for 5 min, the number of large particles increases insignificantly. However, their size increases to 80 nm, and the particle attain the shape differed from spherical. Some particles stick together to form larger agglomerates. Large particles form additional bonds at the expanse of wires, and the direction of this growth is uncontrolled. It can be monitored that the growth of nanowires begins from the vertices of the large CdS particles having a polyhedral shape. An increase in the synthesis duration also thickens the wires.

In addition to the precipitation of the CdS particles from solution on the silicon plate surface, some particles further grow with time due to agglomeration with fine particles.

The SEM studies of samples of the CNT arrays showed that the precipitation process of the CdS nanoparticles on the nanotube surface differs from that of nanoparticle precipitation on the pure silicon support. The differences are that in these processes the nanoparticles and their agglomerates produced attain different morphology (Fig. 2). If the CNT array is stored in the reaction mixture for 2 min at 30 °C, many CdS nanoparticles ~20 nm in size are formed on the nanotube surface (see Fig. 2, *a*). On some nanotubes the CdS particles are uniformly distributed with a characteristic distance between them of ~100 nm, whereas almost no nanoparticles are observed on other nanotubes. These differences in the surface properties of the CNT can be related to different degrees of imperfection. The nucleation of the CdS particles on the nanotube surface begins in the defect points, where the electron density and charge are distributed nonuniformly. This is especially important for the nanotubes obtained by the CVD method, because they are highly faulted.

A comparison of Figs 1 and 2 shows that, under the same synthesis conditions, the weight fraction of the CdS particles formed on the CNT surface is much higher than that on the silicon surface. The CNT samples studied ex-

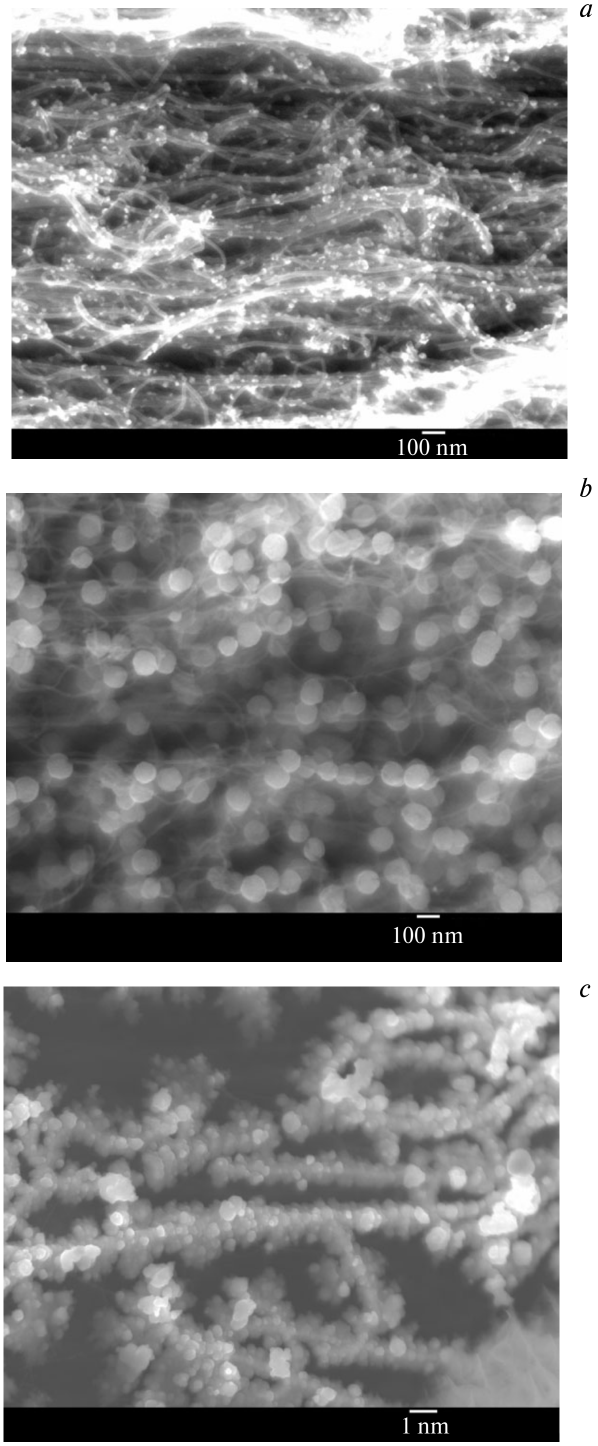

Fig. 2. SEM images of CdS nanoparticles formed on the multi-walled CNT surface at 30 °C for 2 min (*a*), at 60 °C for 5 (*b*) and 10 min (*c*).

hibit no formation of nanowire structures from fine CdS particles similar to those observed on the silicon surface. It is possible that in the absence of fine particles, differences in topology of planar supports and bent CNT surfaces play a certain role. A more plausible explanation is that the chains are built from fine CdS particles formed in the solution. A certain degree of oversaturation of the solution should be achieved for these particles to form in the solution and then precipitate on the support. The large specific surface of the nanotubes favors a decrease in the concentration of the Cd^{2+} and S^{2-} ions, which are consumed by growing particles earlier born on the surface of nanotubes of the particles. The specific surface of the initial silicon plates is small and since the number of nuclei on the support is also small, oversaturation is achieved in solution in experiments with these plates. This results in the situation that fine CdS particles are formed directly in the solution and precipitate on the support as nanowires.

As assumed, the precipitation of nanoparticles from solution at 60 °C should ensure an increase in the rate of nanoparticle growth and in their number. Indeed, the precipitation from solution for 5 min resulted in the formation of large spherical structures (see Fig. 2, *b*). The particles ~100 nm in size consist of many agglomerated and grown into spheres nanoparticles. The formation of microspherical CdS particles in solutions has been observed previously[15] under the hydrothermal synthesis conditions, and the microspheres obtained consisted of many hexagonal crystals ~20 nm in size.

An increase in the precipitation duration to 10 min resulted in the formation of a dense layer of nanoparticles 100—200 nm in diameter on the CNT surface, and the particles completely covered the CNT surface (see Fig. 2, *c*). It is possible that the increase in the nanoparticle density on the nanotube surface is due to an increase in imperfection on their surface, because the nitrogen-containing CNT with more defect structures were used in this experiment.[16]

The procedure developed for CdS precipitation makes it possible to synthesize nanoparticles on the silicon plate surface and on the CNT surface. The size of the CdS nanoparticles is controlled by the duration and temperature of precipitation. The experiments performed showed that agglomerates of nanoparticles on the silicon support and on the nanotube surface are formed by different ways under the same conditions of CdS precipitation. It is most likely that the degree of imperfection of the nanotube surface affects the mechanism of formation of CdS nanoparticles on the CNT surface. Particles of smaller sizes and of another shape precipitate on the surface of the silicon supports, which can be due to the preliminary formation of particles in solution and their subsequent precipitation on the support.

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