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Wet chemical synthesis and characterization of luminescent colloidal nanoparticles: $ReVO_4:Eu^{3+}$ (Re = La, Gd, Y) with rod-like and spindle-like shape

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A simple method for the synthesis of aqueous solutions of $ReVO_4:Eu^{3+}$ (Re = La, Gd, Y) nanoluminophores with rod-like and spindle-like shape has been proposed. $LaVO_4:Eu^{3+}$ nanoparticles have rod-like shape of 57×4.4 nm^2 average size while $ReVO_4:Eu^{3+}$ (Re = Gd or Y) ones have spindle-like shape with an average size of 22×6.3 nm^2. Transparent colorless aqueous solutions of nanocrystalline luminophores possess a bright luminescence and remain stable for more than 6 months.

Предложен простой способ синтеза водных растворов нанолюминофоров $ReVO_4:Eu^{3+}$ (Re = La, Gd, Y) стержнеобразной и веретенообразной формы. Наночастицы $LaVO_4:Eu^{3+}$ имеют стержнеобразную форму со средним размером 57×4,4 $нм^2$, а наночастицы $ReVO_4:Eu^{3+}$ (Re = Gd или Y) — веретенообразную форму со средним размером 22×6,3 $нм^2$. Прозрачные бесцветные водные растворы нанокристаллических люминофоров обладают яркой люминесценцией и остаются стабильными более 6 месяцев.

1. Introduction

Luminescent nanomaterials are becoming increasingly important in engineering, electronics, biology and medicine [1–2]. It has been shown using numerous physical, chemical, and biological objects as examples that the transition from macro-objects to particles of 1–10 nm size results in qualitative changes of physicochemical properties of certain compounds and systems obtained using these compounds. The properties of nanosized crystals depend essentially on quantity of atoms on the surface, localized electronic state and may provide new features compared to bulk phase [3–5].

Investigation of nanosized effects plays a significant part in manufacturing of new materials with unique properties. It is known that physical, chemical and biological properties of a nanomaterial depend to a large extent on its size, shape, and surface surrounding of nanoparticles. Nowadays, the most actual issue is the influence of inorganic nanoparticles on biological objects, the cytotoxicity thereof, and possibility of targeted delivery to certain biological structures. The luminescent probes based on orthovanadates doped by Rare-Earth elements are among the most prospective materials for investigation of inorganic nanomaterial interaction with biological objects. Numerous research works are dedicated to synthesis methods and studying of properties of rare-earth doped vanadates of Y, Gd, and La nanomaterials [6–12].

There are quite many synthesis methods for such compounds, for example, solid-phase [6], wet ultrasonic [7], sol-gel [8] and wet chemical methods in different synthesis conditions [9–11]. Using the different methods, it is possible to obtain a great variety

of nanoparticle structural and geometric parameters. In many occasions, aqueous solutions contain particles in the aggregate form. Toxic impurities and surfactants may be present in solutions.

Before, we have reported a synthesis method and properties of rare-earth elements orthovanadates aqueous colloidal solutions [12, 13]. The synthesis method spherical particles of different size and colloidal properties thereof were described in these works. In this work, we report the synthesis method for aqueous colloidal solutions containing spindle-like and rod-like shaped nanocrystals. Transparent aqueous solutions of $ReVO_4:Eu^{3+}$ (Re = La, Gd, Y) nanoluminophores possess bright luminescence and do not contain impurities which could cause side effects in biological experiments.

2. Experimental

Lanthanide chlorides 99.9 %, sodium ethylenediaminetetraacetate (EDTA·2Na) 99.8 %, and anhydrous sodium metavanadate 96 % were purchased from the "Acros organics" Company and were all used without further purification. Na_3VO_4 solution with pH value of 13 was obtained by adding solution NaOH (1 mol/L) to $NaVO_3$ aqueous solution.

Solutions of spindle- and rod-like nanocrystals were obtained as follows:

To 11 mL of rare-earth element chlorides aqueous solutions (0.01 mol/L) 8.25 mL EDTA·2Na solution (0.01 mol/L) was added. To obtained solution, 8.25 mL Na_3VO_4 (0.01 mol/L) was added dropwise. The mixture was intensively stirred using a magnetic stirrer. The yellowish solution obtained after stirring for 10 min had a pH value of about 10.3–10.8. After stirring, the solution was placed into a round-bottom flask and refluxed for 24 h. As a result, transparent colorless solutions with a pH value of about 8.0–9.0 were obtained; under side illumination Tyndall cone was observed. Formula of nanoparticles is $Re_{0.9}Eu_{0.1}VO_4$, where Re = Y and Gd for spindle-like particles and La for nanorods.

Finally, the solution was dialyzed against water to remove the excess ions. A dialysis membrane tubing with a molecular weight cutoff of 12 000 Da (pore size of about 2.5 nm) was used, and the water was renewed each 4 h (the water/colloid volume ratio is 40). Control of dialyzed solution purification from electrolytes impurities was carried out by determining the dialyzate electroconductivity. The solution after dialysis for 24 h had a pH value of about 7.4–7.8. Optimal synthesis conditions were found experimentally.

Nanocrystalline powders were obtained by removing the water from the colloidal solution with a rotary evaporator (bath temperature 60°C) and drying of solid phase at 140°C for 10 h.

UV-vis absorption spectra of the colloidal solutions were measured with a SPECORD 200 spectrometer ("Analytik Jena"). Photoluminescence spectra of samples in solutions and dried precipitates were recorded using an MDR-23 monochromator with control and information- gathering system in CAMAC standard at room temperature under excitation by helium-cadmium laser, λ = 325 nm.

Transmission electron micrographs of the particles were taken using TEM-125K ("SELMI") electron microscope. Samples for microscopy were applied on substrates with carbon film via dipping and drying of dilute solution.

3. Results and discussion

The variation of synthesis conditions — temperature, synthesis duration, pH value, EDTA/Re ratio, presence of detergents — effect considerably the shape and size цшер colloidal particles [14–16]. In this work, the synthesis method for the nanocrystals of different shape under identical synthesis conditions is discussed. Fig. 1 shows some of the TEM images and respective particle size histograms. These histograms were built using aspect ratios values of solid phase in aqueous solutions of spindle-like and rod-like shaped particles.

The spindle-like nanocrystals (Fig. 1a) are formed at the synthesis of $YVO_4:Eu^{3+}$ or $GdVO_4:Eu^{3+}$ and have an average size of 22×6.3 nm (aspect ratios of 14 nm; standard deviation is 1.7 nm). The rod-like nanocrystals (Fig. 1b) with an average size of 57×4.4 nm (aspect ratios of 30.5 nm; standard deviation is 2.4 nm) are formed at the synthesis of $LaVO_4:Eu^{3+}$. Obviously, such a difference in the nanocrystal shape is associated with various type of crystal lattices. The morphology and shape of nanocrystals can be defined by structure characteristics of the crystal [14–17]. The orthovanadate crystallizes in two types, namely, tetragonal zircon type and monoclinic monazite type [18–20]. According to the literary data [20], Y and Gd orthovanadates reveal tetragonal crystal structures with similar lattice parameters,

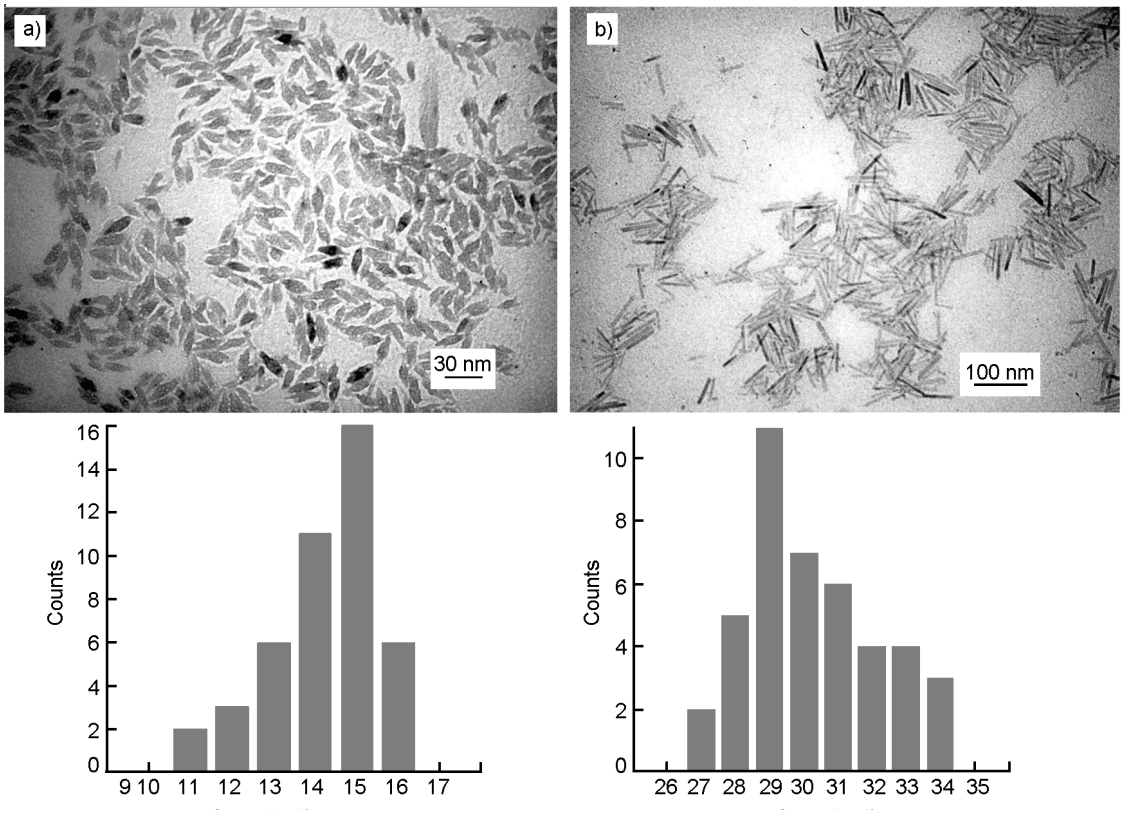

Fig. 1. TEM images of $GdVO_4:Eu^{3+}$ (a) and $LaVO_4:Eu^{3+}$ (b) nanocrystals and respective particles aspect ratios histograms.

whereas $LaVO_4$ reveals monoclinic structure. The crystal structures and lattice parameters can determine the way of crystalline structure formation, which, in turn, affects the nanocrystal shape. In our case, under the same synthesis parameters, $YVO_4:Eu^{3+}$ and $GdVO_4:Eu^{3+}$ nanocrystals are characterized by the same spindle-like shape, while $LaVO_4:Eu^{3+}$ reveals another, rod-like shape. It is to note that the variation of some synthesis parameters or using combined presence of Y and Gd in a host lattice can cause changing of nanoparticles size, however, the form factor value (particle length- to-width ratio) remains unchangeable, namely 3.5±0.2 for spindle-like and 13±0.5 for rod-like one. Nanoparticles of wide and uncontrolled shape range and disperse composition are formed under combined presence of Y and La or Gd and La in a host lattice.

Fig. 2 shows the UV-vis absorption spectra of the initial Na_3VO_4 and as-prepared $ReVO_4:Eu^{3+}$ colloid solutions. The broad band peaked at 276 nm for spindle-like and 280 nm for rod-like nanoparticles is attributed to a charge transfer from the oxygen ligands to the central vanadium atom inside

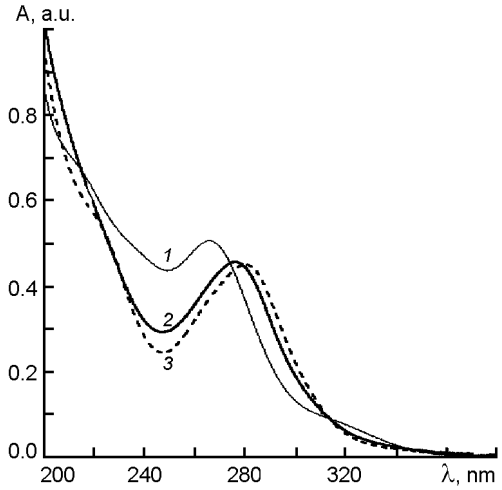

Fig. 2. UV-vis absorption spectra of Na_3VO_4 (thin line), spindle-like $ReVO_4:Eu^{3+}$ (Re = Gd or Y) nanoparticles (solid line) and rod-like $LaVO_4:Eu^{3+}$ nanoparticles (dotted line).

the VO_4^{3-} ion. This band is almost identical to that observed in free VO_4^{3-} solutions for which the absorption maximum is 266 nm. Fig. 2 shows that the absorption peak shifts to a lower energy with growth of nanoparticles linear sizes, that is in accordance with the described data for similar systems [7, 14].

Figs. 3a, c show the photoluminescence (PL) spectra of samples in solutions, Figs. 3b, d — of precipitates dried at 140°C. The most intense luminescence bands are associated with the transitions from the excited $^5D_0$ level to $^7F_2$ located in the range of 610–620 nm corresponding to the red emission, in good accordance with the Judd-Ofelt theory [21] and with results obtained by different authors for similar systems [6–17, 20]. It should be noted that excited $^5D_0$ level to $^7F_2$ are split into two peaks — 615.6 and 619.6 nm for spindle-like nanoparticles (Fig. 3a, b) and 614.4 and 618.8 nm for rod-like (Fig. 3c, d). It is seen from the emission spectra (Fig. 3) that the peak intensity in the range near 615 nm is higher than at 619 nm for aqueous solutions. After drying of solid phase, the intensity relation of split peaks changes. Obviously that it is connected with the decrease of defects number in nanocrystal and formation of its regular structures.

The aqueous solutions of rod-like and spindle-like nanocrystalline luminophores can be stored for more than 6 months under normal conditions without losing an aggregate stability. Colloidal properties, namely, particle charge and solution aggregate stability, are similar to those described before for spherical particles [13]. The role of EDTA is double in this synthesis. Firstly, it limits the growth of the nanoparticles via interactions with lanthanide ions. Secondly, it ensures the stability of the colloidal solutions via electrostatic repulsions with nanoparticle surface and formation of double electrical layer.

Similarly to the spherical particles, the rod-like and spindle-like ones are negatively charged and stabilized by EDTA. The aqueous solutions appear as a hydrophobic colloidal system. In the presence of inorganic electrolytes, cationic surfactants, and dyes, coagulation of solid phase is not observed. The concentration of solid phase in solutions is 1 g/L. The solutions can be concentrated to 20 g/L via evaporation under mild conditions with a rotary evaporator (bath temperature 50–60°C) without changing the properties. At higher concentrations, storage stability of solutions reduces and coagulation of solid phase may be observed.

4. Conclusions

Proposed a simple synthesis method for aqueous solutions of nanoluminophores based on orthovanadates Y, Gd, La, doped by Eu, that provides obtaining of colloidal solutions with rod-like and spindle-like shaped particles without using autoclave, adding any polymers or templates application. The conditions being the same, the host lattice is the shape-forming factor for nanoparticles. Nanocrystalline phase of solution possesses bright luminescence. Aqueous solutions of nanoluminophores can be used to solve applied problems, including the application as biological markers.

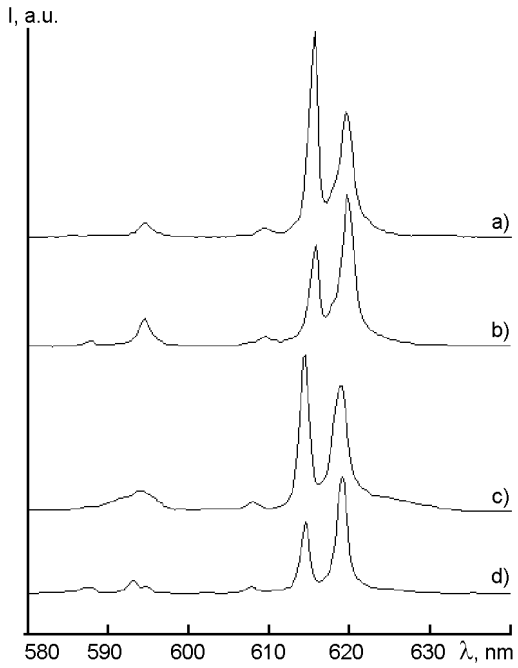

Fig. 3. Emission spectra: a) colloid solution and b) dried precipitate of spindle-like $ReVO_4:Eu^{3+}$ (Re = Gd or Y) nanoparticles, c) colloid solution and d) dried precipitate of rod-like $LaVO_4:Eu^{3+}$ nanoparticles.

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Рідкий хімічний синтез та визначення характеристик люмінесцентних колоїдних наночасток $ReVO_4:Eu^{3+}$ (Re=La, Gd, Y) стрижне– та веретеноподібної форм

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Запропоновано простий спосіб синтезу водних розчинів нанолюмінофорів $ReVO_4:Eu^{3+}$ (Re = La, Gd, Y) стрижнє– та веретеноподібної форм. Наночастинки $LaVO_4:Eu^{3+}$ мають стрижнеподібну форму з середнім розміром 57×4,4 нм^2, а наночастинки $ReVO_4:Eu^{3+}$ (Re = Gd или Y) — веретеноподібну форму з середнім розміром 22×6,3 нм^2. Прозорі безбарвні водні розчини нанокристалічних люмінофорів мають яскраву люмінесценцію та лишаються стабільними понад 6 місяців.