



Control over the distribution of luminescent impurities inside opal photonic crystals



Sergey Klimonsky*, Alexander Knotko, Nikolay Borodinov, Andrey Eliseev

Department of Materials Science, M.V. Lomonosov Moscow State University, Lenin Hills, 119991 Moscow, Russia

ARTICLE INFO

Article history:

Received 24 April 2015
 Received in revised form 28 May 2015
 Accepted 17 June 2015
 Available online 17 June 2015

Keywords:

Photonic crystal
 Opal
 Luminescence
 Europium
 Quantum dots

ABSTRACT

The work is focused on the problem of control over the distribution of emitting centers inside photonic crystals. Two ways of luminescent impurity incorporation into synthetic silica opals are considered. First is based on the infiltration of the opal with a water solution of organic complexes (HEuEDTA) and leads to a formation of a uniform luminescent layer on the surface of silica microspheres. The other involves the infiltration of the structure with a heptane solution of CdSe quantum dots leading to the localization of the luminescent component around contact points between microspheres. Thus two different types of strongly ordered distribution of luminescent component inside opal can be obtained. Corresponding samples were prepared and their optical properties are discussed.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Luminescent photonic crystals (PhCs) are novel materials for high efficient light emitting devices, low threshold lasers, opalescent coverings, etc. One of the simplest and cheapest ways for their production involves incorporation of luminescent compounds into an opal matrix. However first samples of opals infilled with rare-earth elements [1] or quantum dots (QDs) [2–5] had random or nonuniform distribution of luminescent species inside crystal voids leading to a disturbance of the photonic properties. On the other hand, authors [6] focused their efforts on preparation of inverse PhCs from QDs and, correspondingly, tried to get high filling of the volume of the opal matrix voids. In this case different QDs occupy different positions in the unit cell of the PhC also. However it was shown [5,7,8], that emission characteristics are ruled out by local density of optical states, which depends on exact location of a light source (such as an excited atom, molecule or QD) inside the periodic structure. To date, it is a very relevant problem to drive the positions of emitting centers in PhC lattice, whereas only few experimental works [9,10] were aimed to solve it and to get uniform distribution of luminescent species on the surface of opaline host voids. Here we consider two possible ways of luminescent component incorporation into SiO₂ synthetic opals leading to different types of controllable distribution of emitting centers. One is connected with an infiltration of the opal with a water solution of europium (III) organic complex forming thin uniform luminescent layer on the surface of SiO₂ microspheres. The other involves the infiltration of the structure with a heptane solution of CdSe QDs leading to the localization of the luminescent component around contact points between microspheres.

* Corresponding author.

E-mail address: klim@inorg.chem.msu.ru (S. Klimonsky).

2. Experimental

2.1. Opal-HEuEDTA

Eu^{3+} metal–organic complex was synthesized by the reaction of europium (III) oxide with ethylenediaminetetraacetic acid. Eu_2O_3 (99.9%) and H_4EDTA (Riedel-de Haen, AG) were mixed in the molar ratio 1:2 and dispersed in distilled water. The suspension was boiled for several hours until the formation of transparent solution. The latter was evaporated resulting in the crystallization of $\text{HEuEDTA}\cdot\text{H}_2\text{O}$.

For the preparation of bulk PCs we used monodisperse silica microspheres synthesized by hydrolysis of freshly distilled tetraethyl orthosilicate $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS, 99%, Sigma–Aldrich) in a water–ethanol mixture in the presence of ammonium hydroxide as a catalyst [11]. After the synthesis, the suspension of spherical particles was diluted with distilled water and left undisturbed for a few months. The resulting sediment was dried in air, slowly heated up to 600 °C and annealed for several hours. After the shrinkage the average size of the microspheres was about 280 nm. Finally, opals were infiltrated with a water solution of HEuEDTA and then dried in air.

The microstructure of PCs was studied by scanning electron microscopy (SEM) using a LEO Supra VP 35 instrument. No conductive coating was applied to the samples prior to imaging. Since the samples were dielectric, we used a variable pressure mode, injecting a small amount of nitrogen into the SEM chamber in order to neutralize the surface charge.

2.2. Opal-CdSe quantum dots

CdSe nanoclusters were prepared from supersaturated solution in diphenylether using cadmium oleate and trioctylphosphine selenide as starting precursors and oleic acid as a stabilized agent [12,13]. Particle growth was carried out for 5 min at 250 °C and the reaction mixture was quickly cooled down to the room temperature. Then CdSe colloid was precipitated by equal volume of acetone, repeatedly washed and redispersed in heptane. For narrowing particle size distribution the colloidal solution was subjected to size selective precipitation using acetone/heptane solvent pair. According to a well-known CdSe exciton absorption sizing curves an average diameter of the resulting particles was 2.7 nm [14].

Thin opal films grown from SiO_2 colloid solution were used as a matrix for introduction of CdSe nanoparticles. Silica microspheres were prepared by seeded growth approach described elsewhere [15–18]. Nanosized SiO_2 nuclei with an average diameter of 30–36 nm and a standard deviation of 2–3 nm were synthesized by the Stöber method [11] at 60 °C from a reaction mixture containing 100 mL of 95% ethanol, 5 mL of 25% aqueous ammonia, and 0.5 mL of tetraethyl orthosilicate. Then a mixture composed of 20 mL of the seed suspension prepared in the first step, 80 mL of ethanol, and 6 mL of an ammonia solution was prepared (the SiO_2 nucleus concentration in the mixture was 0.243 g/L). Subsequent multistep growth was carried out at room temperature by adding small TEOS portions in 10 min intervals; the amount of introduced TEOS doubled every hour. Opal films were grown from colloid solutions by the vertical deposition method [19]. Then the films were infiltrated with the heptane solution of QDs by dripping it onto the slanted surface of opal film, followed by drying in air. Finally, an excess of QDs was removed from the film surface by short washing in heptane. The structure of the surface was studied by a Carl Zeiss NVision 40 scanning electron microscope. Micro sized fragments scratched out of opal-QDs films were placed on a copper grid and then studied by transmission electron microscopy (TEM) using a Libra 200 instrument (Carl Zeiss, 200 kV acceleration voltage). Lambda-950 UV–VIS spectrometer with the light spot square of $20 \times 5 \text{ mm}^2$ and LS 55 luminescent spectrometer with the excitation spot square of $10 \times 5 \text{ mm}^2$ (both from Perkin Elmer company) were used for recording of optical transmittance spectra and luminescence spectra correspondingly. All luminescence spectra were recorded under 390 nm excitation and normalized in amplitude.

3. Results and discussion

It is well known, that some organic complexes can attach to various materials surface forming thin covering layer. For example, thin (5–8 nm) uniform polyelectrolyte/nanocrystal layer can be formed on the surface of polystyrene microspheres [20]. Here we study such possibility for HEuEDTA metal–organic complex on SiO_2 microsphere surface inside opals. SEM images of free-standing microspheres on a cleaved surface of opal- HEuEDTA composite is shown in Fig. 1. It is clearly seeing that spheres are covered with a uniform HEuEDTA layer. For the sample studied the thickness of HEuEDTA layer was about 20 ± 5 nm. Obviously, this thickness should depend on the concentration of organic complex in the solution used for the infiltration of PhC. We also believe that many other luminescent organic compounds can cover microsphere surface inside opals by the similar manner, however this possibility was not considered in great detail so far. An alternative approach is connected with precoating microspheres with a luminescent layer prior to their self-assembly [9,20].

Luminescent properties of opal- HEuEDTA composites were published by us previously [21]. Strong spatial variation of Eu^{3+} emission lines intensity was observed. In particular, a drop of the intensity of 614 nm line by a factor of 3 was recorded with the change of the emission output angle from 5° to 10° to the normal. However, an interpretation was difficult due to a polydomain structure of the samples.

Our further work with QDs was done on thin opal films having well controlled orientation of the structure. The problem of polycrystalline structure of opaline samples is discussed in [19,22–24]. The orientation of vertically deposited films is

Download English Version:

<https://daneshyari.com/en/article/1553044>

Download Persian Version:

<https://daneshyari.com/article/1553044>

[Daneshyari.com](https://daneshyari.com)