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PHYSICAL PROPERTIES OF NANOPARTICLE SILICA GEL DOPED WITH CdS PREPARED BY SOL-GEL TECHNIQUE

I. K. BATTISHA

Solid State Physics Department, National Research Center, Cairo, Egypt

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CdS/silica xerogel glasses were prepared via silica gels containing mixture solution of 0.2 M ($CdCl_2$ and thiourea) with molar ratio 1:1. Doping the gels with this mixture solution and its heat treatment gave transparent yellow silica-gel glasses doped with CdS crystals. X-ray diffraction and transmission electron microscope make it possible to evaluate the nanoparticle size of the prepared samples. The nanoparticle size was dependent on the concentration of the dopant materials and the heating temperature. In the optical transmission spectra, the absorption edge exhibited a blue shift compared to that of the bulk CdS, and its energy shift was reciprocally proportional to the square of the radius. Thus the quantum-size effect could be found for the silica gel containing CdS prepared by the sol-gel process. The energy band gap shifted to higher energy for smaller nanoparticle size.

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1. *Introduction*

Recently, there has been a significant increase of interest in small-size semiconductor particles, in which electron and hole wave functions are quantum-confined by a deep potential well. Since Jain and Lind first reported efficient non-linear optical properties of CdS_xSe_{1-x} doped glasses, many studies of these glasses have been carried out [1,2,3]. CdS_xSe_{1-x} doped glasses that are commercially available as cut-off filters have low concentration of crystalline phase and a large variation in crystal size, which may limit their practical applications. Therefore, it is desired to develop glasses with semiconducting crystals of well-controlled size, size distribution and content, which would extend the application of these glasses to the new optical function devices such as optical switches. [4,5].

Previous workers [6,7] suggested that the microcrystals produced from the glass state offers an excellent material for studying the structural and spectroscopic properties of semiconductors. These materials have new applications as non-linear optical materials. The glasses doped with semiconductor microcrystals are interesting for both the fundamental study of quantum confinement of electron excitations in semiconductor microcrystals in glass matrices and for applied optics. The latter is due to the very fast optical non-linearity of the glasses and their potential applicability as active media of novel solid state lasers, optical harmonic generators, optical memories, etc... The optical characteristics of the materials are determined by the microcrystals embedded in the glass matrix. Thus, the proper choice of semiconductor dopants, their concentration and the average size distribution of the microcrystals can govern the linear and non-linear properties and electro-optical sensitivity of the material.

In comparison with the other techniques, sol-gel method is more suitable to prepare optical materials as it permits molecular-level mixing and progressing of the raw materials and precursor at relatively lower temperature and produces nanostructured bulk, powders and thin films [8,9,10]. Therefore, it allows the production of silica matrices with a higher semiconductor concentration at temperatures significantly lower than those required by the classic melting methods [11].

In the present work, silica-gel glasses doped with three different concentrations of 10, 20 and 30% of aqueous solution of cadmium chloride and thiourea of 0.2 M ($CdCl_2$:thiourea) with molar ratio 1:1, prepared by a simple sol-gel process to produce nanoparticle materials as was confirmed by transmission electron microscope (TEM) [4]. The novelty of our method lies in using simple aqueous solution containing cadmium and sulfur to dope the silica gel. Their crystal sizes were determined using X-ray diffraction (XRD). The energy gap E_g of the prepared samples was investigated. A structural and thermal characterization was carried out using Fourier transform infrared (FTIR) spectroscopy, thermal gravemetric analysis (TGA) and differential thermal analysis (DTA).

2. *Experimental*

2.1. *Preparation of silica gel (solution I)*

Silica gel used in the present experiments was prepared using the acid catalyst procedure, via the hydrolysis and condensation of tetraethoxysilane, $(CH_3CH_2O)_4Si$ (TEOS), ethanol and distilled water, in the presence of hydrochloric acid, with molar ratios 0.028: 0.174: 0.28: 0.0823 for TEOS: CH_3CH_2O: H_2O: HCl. These solutions were then filtered, followed by stirring for one hour at room temperature.

2.2. *Preparation of* ($CdCl_2$*: thiourea) solution (solution II)*

The starting solution which gives CdS was prepared from a mixture of an aqueous solution of 0.2 M of ($CdCl_2$:thiourea) dissolved in distilled water with the molar ratio 1:1.

2.3. Preparation of silica gel doped with CdS

Solution (II) with different concentrations of 10, 20 and 30% was added to the solution (I) (by volume), to give silica gel doped with CdS crystals. These solutions were then filtered, followed by stirring for an hour at room temperature. The resultant homogeneous solutions of bulk materials were poured into molds and placed in a drying oven at 60 °C for 21 days until the shrinkage stopped. The final products were monoliths of 15 mm × 15 mm × 3 mm. The samples were clear, transparent, yellow in colour, uniform and without cracks. While drying, the reaction between Cd and S took place. But the concentration of CdS crystallites were small due to a drastic reduction of efficiency of the reaction. At that stage, residual water and organic material, which decrease the density of the prepared samples, are still present.

Densification of the gel was obtained by annealing in air for two hours at temperatures ranging from 500 °C up to 1150 °C in a muffle furnace. The heating rate of the muffle furnace was 1.5 °C/min. Nanoparticle silica gels doped with CdS with different sizes of crystallites were obtained by controlling both the amount of CdS precipitates in the gel, and the heat treatment temperature which causes hydrolysis and polycondensation of silano group and then the hydroxyl groups. The heat treatment temperatures at 500 °C up to 1150 °C allows one to produce small nanoparticles with a narrow size distributions [12,13]. The prepared samples were (a) pure silica gel heated at 1000 °C, (b) silica gel doped with 10% of the mixture solution (II), heat treated at 500 °C and (c) silica gel doped with 20% of the same dopant materials, dried at 60 °C for 21 days, (d) heat treated at 500 °C, (e) 800 °C, (f) 1000 °C and (g) 1150 °C, and (h) silica gel doped with 30% of the same dopant materials heated at 1150 °C. The list of the samples is shown in Table 1.

TABLE 1. List of the prepared pure silica gel sample and samples doped with dopant material ($CdCl_2$:thiourea) with different concentrations.

T(°C)	Pure samples	Doped samples		
		10%	20%	30%
60			c	
500		b	d	
800			e	
1000	a		f	
1150			g	h

2.4. Characterization

The thermal decomposition behaviour of the prepared samples was characterized by differential thermal analysis (DTA), while the weight loss was measured by thermal gravimetric analysis (TGA), from room temperature up to 1000 °C in inert

N_2 gas and the heating rate of 10 °C/min. The X-ray diffraction (XRD) patterns of the prepared samples were recorded with a Philips X-ray diffractometer PW/1710, with monochromatised CuKα radiation of wavelength 0.15418 nm (1.5418 Å) at 40 kV and 30 mA. The peak profile, recorded with corrected full-width at half-maximum (FWHM) and good resolution of 0.125 deg/min, was performed and the accurate crystallite sizes were determined from the X-ray diffraction data using the Scherrer formula ($G = \lambda / D \cos\theta$), where G is the grain size, λ is the wavelength of the X-rays (1.5418 Å), D is the width of the peak at half maximum and θ is the angle of incidence of X-ray beam. In order to obtain the values of the instrumental parameters, scans have been carried out for strain-free crystallite quartz samples of sizes ranging between 5 and 10 μm, under exactly the same conditions as conducted with the investigated samples. Silica-gel microstructures were studied with transmission electron microscope (TEM). Optical transmission (T) spectra of the prepared samples were measured using Jasco V-570 spectrophotometer, in the wavelength range 0.2 to 2.5 μm. FTIR spectra were measured with a Perkin Elmer 1600 spectrophotometer in the 4000 – 100 cm^{-1} region.

3. Results and discussion

Pure silica-gel glasses are colourless and transparent, while the present samples obtained by doping with ($CdCl_2$:thiourea) are still transparent but the colour changed to yellow. The colouration was dependent on both the concentration of the dopant and the temperature. A less intense colour and higher transparency at lower concentrations of dopant material characterize the prepared samples. This behaviour indicates the formation of CdS crystals embedded in the host gel glasses and their growth. Figure 1 shows DTA and TGA curves of silica gel samples doped

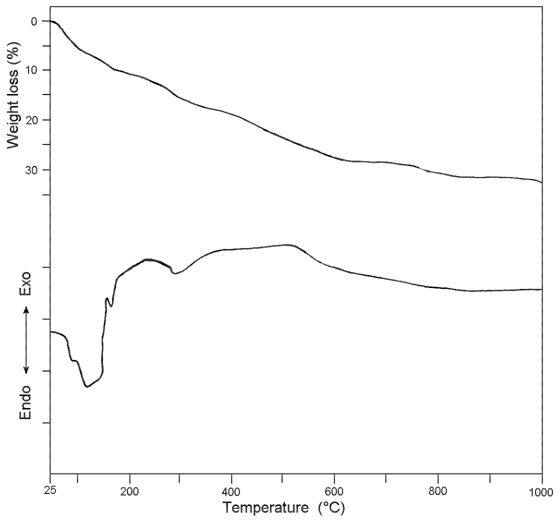

Fig. 1. DTA and TGA curves of silica gel doped with 20% dopant materials after heat treatment at 60 °C for 21 days.

with 20% CdS. The gel shows an endothermic behaviour at temperatures between 50 °C and 200 °C, accompanied by a large weight loss of 11%, primarily due to the removal of water and alcohol trapped in micropores. The exothermic peaks accompanying the weight loss of about 2.8% at temperature between 300 °C and 400 °C are probably due to the combustion of the residual organic in the gel and the oxidation of incompletely hydrolyzed alkoxide. On further heating, smaller weight loss continued at higher temperatures as a result of the slow removal of residual water and organic groups by a condensation reaction.

Figure 2 shows the effect of heat treatment on the XRD patterns of the samples a, b, c, d, e, f, g and h, listed in Table 1. Samples show the typical amorphous pattern of pure silica gel, Figs. 2a and b, indicating that in the material doped with small concentration 10% (even at one of the high temperatures of 500 °C) the crystalline phase did not appear. By fixing the concentration at 20% and increasing the temperature from 60 °C up to 1150 °C, we obtained amorphous phase at the lower temperature of 60 °C (Fig. 2c). When increasing the temperature up to 500 °C, the XRD pattern of the sample (Fig. 2d) showed several broad peaks with low intensity at around $2\theta \simeq 24°, 25.3°$ and $26.6°$, which can be indexed as the (100), (002) and (101) diffraction principle lines of CdS, respectively, indicating the beginning of the appearance of the CdS crystalline phase. As the temperature was

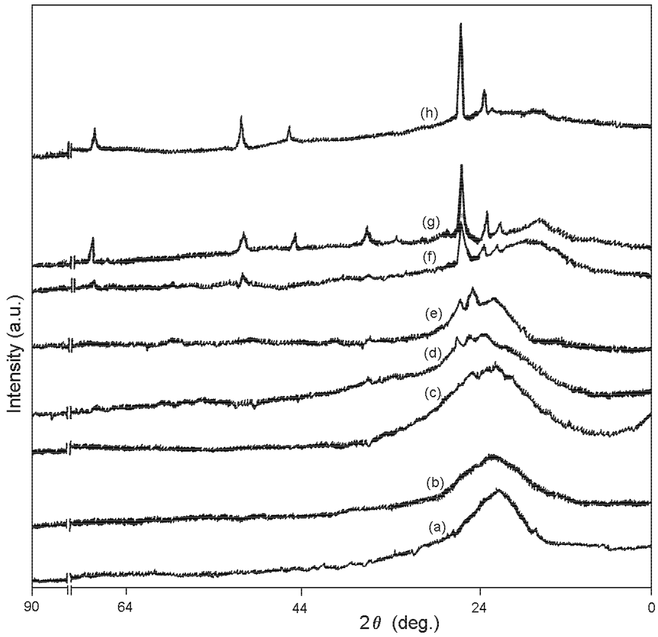

Fig. 2. XRD patterns of pure silica gel heated at (1000 °C) (a), silica gel doped with 10% of dopants heated at (500 °C) (b), and silica gel doped with 20% of dopants heated at 60 °C for 21 days (c), heated at (500 °C) (d), heated at (800 °C) (e), heated at (1000 °C) (f), heated at (1150 °C) (g), and silica gel doped with 30% of dopants heated at (1150 °C) (h).

increased up to 1000 °C and 1150 °C (Figs. 2f and g), the intensity of the three peaks increased and the peaks seem to shift to a lower diffraction angle. Also, new peaks appeared at around $\theta = 36°, 44°, 51.9°$ and $67.5°$, corresponding to (102), (110), (112) and (331) diffraction lines, respectively, indicating a good crystallinity of CdS crystals embedded in the silica gel. These results may be due to the drying at temperature 60 °C for 21 days what caused that majority of water evaporated, although the density was still low. The remaining residual water and hydroxyl groups prevent the complete reaction between Cd and S, and the complete growth of CdS crystals in the host gel glasses. At intermediate heat treatment temperature, polycondensation water, due to the combination of hydroxyl groups, is eliminated between about 100 °C and 400 °C. The gel looses 11% in weight between 50 °C and 200 °C and 2.8% between 300 °C and 400 °C, as shown in Fig. 1. After that it is expected that the density will increase. At this stage, the texture of the material appears to be without open pores. Then the beginning of crystallization occurs due to the continuous growth of CdS crystals. When heated between 500 °C and 1150 °C, this structure collapses: the pores close and fuse together, and smooth material is obtained. By increasing the temperature up to 1150 °C, the fusion of pores is expected to increase, and a complete reaction between Cd and S arises causing an increase in the density. At this stage, the growth of CdS crystals increases causing an enhancement in the crystallinity of the samples as shown in Figs. 2f and g [14]. When increasing the concentration up to 30%, the sample crystallinity enhances (Fig. 2h), and the intensity of the peak at around $2\theta = 26.5°$ indexed as (101) increases as a result of the nucleation and growth mechanism. All XRD peaks of the heated samples with dopant concentrations of 20% and 30% can be indexed by the same hexagonal wurtzite structure as that of polycrystalline CdS thin films [15], confirming that the hexagonal wurtzite CdS crystals have formed. This may be due to the complete evaporation of water and the residual organic which increase the the reaction rate between Cd and S and allow the aggregation of CdS which results in a network of gel glasses containing CdS crystals.

The line broadening, defined as the full-width at half-maximum (FWHM) intensity of the Debye-Sherrer line, was determined. Table 1 shows the values of the crystallite sizes calculated from Bragg's law giving the following average values of the crystallite size: 8.5, 10.4, 15, 22.3 and 38 nm for samples d, e, f, g and h, respectively. It was found that the crystallite size increases by increasing both the heat-treatment temperature and the percentage of CdS ranging from 10% up to 30%, as a result of the aggregation of CdS crystals due to the complete evaporation of residual organic and water at higher temperature, and may be due to the increasing amount of CdS precipitated in the gel by increasing its growth rate in the host glass.

TEM was used to confirm the results obtained by XRD analysis. Figure 3 shows the representative TEM micrograph for samples d and h of silica gel which reacted with 20 and 30% of ($CdCl_2$:thiourea) at 500 °C and 1150 °C, respectively. The obtained patterns are typical of nano-crystalline SiO_2/CdS for samples d and h in which smaller-sized granular structure and radii lower than 10 nm (about 5 nm) were observed. These results coincide with the results of the calculated crystallite size from XRD shown in Table 1.

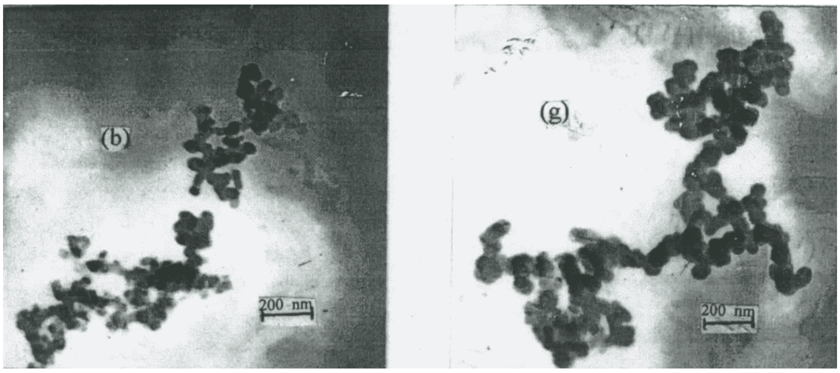

Fig. 3. TEM mycrographs of silica gel containing (b) 20% of dopants materials heated at 500 °C and (g) 30% of dopants materials heat treated at 1150 °C.

The energy gaps of CdS embedded in silica-gel glasses are calculated as follows:

$$E_g = \frac{hc}{\lambda_{\rm cf}}\,, \tag{1}$$

where h is the Plank's constant, c is the velocity of light and $\lambda_{\rm cf}$ is the threshold (cutoff) wavelength of the transmission spectrum of the investigated samples as shown in Fig. 4. We obtained the following values: 2.9 eV (438 nm), 2.7 eV (460 nm) and 2.4 eV (500 nm) for samples d, e and f, shown in Table 1. It is apparent that the absorption edges of samples doped with CdS crystals are blue shifted compared with the bulk CdS crystals. These blue shifts are attributed to the quantum-size effect of the carrier confinement. These results are in agreement with the those reported by Iwami [4]. The shifts exhibit a dependence on the crystal size moving

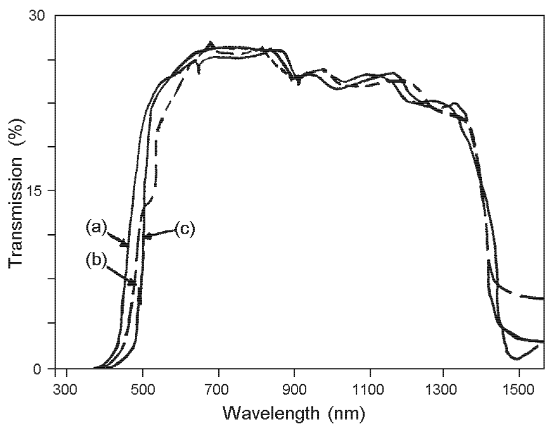

Fig. 4. Optical transmission spectra of silica gel doped with 2 different concentrations of dopant materials, (1) 20% at heating temperature (a) 500 °C (b) 800 °C, (c) 1000 °C.

upward in energy as the crystallite size decreases by decreasing the percentage of dopants to 20% at 1150 °C. This is also observed when decreasing the heat-treatment temperature to 500 °C for the same concentration of dopants (20%).

The gap energy, E_g, is inversely proportional to the square of the particle radius, R [16],

$$E_g = E + \frac{\hbar^2 \pi^2}{2\,\mu R^2}\,, \tag{2}$$

where E is the bulk band gap of CdS, $\hbar = h/2\pi$, h the Plank's constant and μ is the effective mass of electron and hole (about 0.08 m_{electron}). Figure 5 shows the absorption-edge energy as a function of inverse-square average particle radius. A linear relationship confirms the quantum-size effect in SiO_2/CdS prepared by this method. The corresponding bulk band-gap energy ($E = 2.39$ eV) is obtained by interpolating the straight line to $1/R^2 = 0$. The results for the crystallite sizes and energy gaps are shown in Table 2.

TABLE 2. Values of crystallite size and energy band gap of silica gel doped with CdS.

Sample name	T °C	Dopant (%)	XRD cryst. sizes (nm)	Threshold cutoff (nm)	E_g (eV)
d	500	20	8.5	438	2.9
e	800	20	10.4	460	2.7
f	1000	20	15	500	2.4
g	1150	20	22.3		
h	1150	30	38		

TABLE 3. Transmission FTIR bands of silica gel doped with 20% of CdS.

60 °C	1150 °C	Band assignments
445 cm^{-1}	475 cm^{-1}	Si-O-Si, bending mode
802 cm^{-1}	800 cm^{-1}	Si-O-Si, symmetric stretching mode
780 cm^{-1}		shoulder becomes intense peak
1091 cm^{-1}	1097 cm^{-1}	Si-O-Si, asymmetric stretching mode
1384 cm^{-1}		ethyl group, vibrations mode
1636 cm^{-1}		H_2O molecules, bending mode
3420 cm^{-1}		hydroxyl group, stretching mode

Table 3 shows the FTIR bands associated with network vibrational modes, observed at different wave numbers for two samples of silica gel doped with 20% of dopant materials, aged at 60 °C for three weeks and heat treated at 1150 °C. The

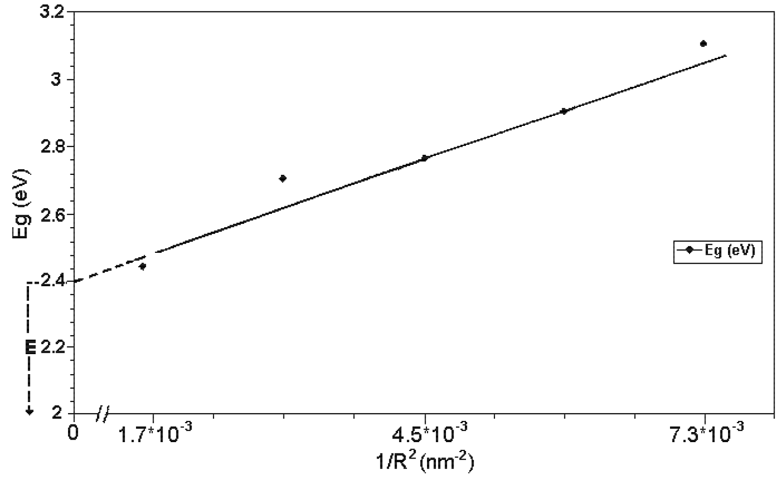

Fig. 5. The energy gap as a function of the particle inverse-square radius.

475 cm^{-1} band, which is assigned to the Si-O-Si bending modes, shifted to 445 cm^{-1} at 1150 °C. The 802 cm^{-1} band is associated with the symmetric Si-O-Si stretching or vibrational modes of rings structures, which become more intense with a small shoulder at 780 cm^{-1} at heating temperatures up to 1150 °C. The peak at 1091 cm^{-1}, which shifted towards higher wave numbers (to 1097 cm^{-1}) by increasing the temperature, is assigned to Si-O-Si asymmetric stretching mode. At lower temperature, a shoulder at 960 cm^{-1} is superimposed on this broad band, which becomes an intense sharp peak at 1097 cm^{-1}. The peak located at 1384 cm^{-1}, which is assigned to vibrations of tetraethoxysilane (TEOS) ethoxy group, disappears at 1150 °C. Both peaks centered at 1636 and 3420 cm^{-1}, corresponding to the bending mode of water molecules and to the fundamental stretching vibrations of different hydroxyl groups, respectively, disappear by heat treatment to 1150 °C. This may be attributed to the evaporation of residual water and hydroxyl group at higher temperature [17].

4. Conclusion

Silica-gel glasses doped with the mixture solution of 0.2 M of ($CdCl_2$:thiourea) with different concentrations and for different heat treatment temperatures were prepared. Small size nanoparticle, bulk, yellow and transparent silica gel glasses doped with nanocrystalline CdS were successfully produced. Microcrystallite size was controllable by the amounts of dopant and heat treatment temperature. The optical absorption edge, which shifts upward in energy as the crystallite size of the prepared samples decreases, indicated a blue shift due to the quantum size effect. A linear relationship of the energy band gap as a function of the inverse square particle radius is apparent, which satisfies the theoretical relationship that gap energy is reciprocally proportional to the square of the particle radius. Thus it is concluded that our CdS doped silica-gel glass exhibits the quantum size effect.

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FIZIČKA SVOJSTVA NANOČESTIČNOG KREMENOG GELA PUNJENOG S CdS I PRIPREMLJENOG METODOM OTOPINA-GEL

Pripremili smo kserogel stakla CdS/kremen od kremenih gelova otopine 0.2M $CdCl_2$ i tiouree s molarnim omjerom 1:1. Punjenje gelova tom otopinom i njihova toplinska obrada dali su prozirna žuta stakla s CdS kristalićima. Veličinu nanočestica u pripremljenim uzorcima odredili smo rendgenskom difrakcijom i prolaznom elektronskom mikroskopijom. Veličina nanočestica ovisi o koncentraciji punila i temperaturi pri toplinskoj obradi. Apsorpcijski rub optičkih prolaznih spektara pokazuje pomak prema plavom u odnosu na uzorke CdS, a energijski pomak je obrnuto proporcionalan kvadratu polumjera čestica. Tako se utvrdio kvantni učinak u kremenom gelu punjenom s CdS i pripremljenom metodom otopina-gel. Energijski se procjep povećava za manje veličine nanočestica.