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INFLUENCE OF TECHNOLOGICAL CONDITIONS OF SYNTHESIS ON THE FORMATION OF PHOTOLUMINESCENCE SPECTRA OF CdS QDs

Here are presented the results of influence of two parameters of synthesis process of quantum dots sulfide cadmium (CdS QD) on the spectrum luminescence, namely, the acid-base balance of the growth solution and the correlation of reaction components (cadmium and sulfur salts). Carried out the syntheses in which the pH solution was changed in the interval of values from 2 to 10. There were also synthesized CdS QD with different ratios of the initial components. The results obtained by evidence of the fact that the technological process has a significant impact on the formation of bands luminescence CdS QDs.

Introduction

Quantum dots (QDs) are nanocrystals 2 to 10 nm in diameter synthesized from semiconductor materials.

Semiconductor CdS QDs have attracted considerable interest due to their unique properties, which are absent in bulk materials due to the effect of quantum confinement of charge carriers. For a number of areas of science and technology, colloidal quantum dots are a promising material. They are of particular interest as a basis for creating biomedical markers and sensors[1].

A necessary condition for the practical implementation of CdS QDs is the development of a technology for obtaining them with controlled properties. One of the simplest and technological methods of QDs synthesis is the colloidal chemical method. The colloidal method of synthesizing quantum dots attracts a lot of attention, as it provides an opportunity to precisely control the size and surface properties of the resulting nanoparticles. The properties of QDs obtained by this method depend on such parameters as the concentration of the starting materials, the pH of the growth solution, etc.

The greatest interest, from the point of view of application of quantum dots (QDs) of A_2B_6 compounds, is caused by their luminescent properties. A large number of works have been devoted to the study of the luminescence of CdS QDs, but the question of the nature of the centers that determine the luminescence and form the luminescence spectrum still remains relevant. Currently, the question of the nature of the luminescence centers and which luminescence bands are created by intrinsic and impurity lattice defects [2] remains relevant. Modern literary sources only mention the possibility of defects, but do not pay attention to the disclosure and description of their nature and the conditions of their creation in the process of synthesis [3]. This issue also includes the development of controlled synthesis, during which QD luminescence spectra can be predicted.

The colloidal-chemical synthesis of CdS QDs is influenced by a large number of factors related to the conditions of the synthesis (duration, rate of introduction of reaction components, synthesis temperature). The formation of luminescence centers in CdS QDs depends on many technological factors, including the concentration of cadmium and sulfur ions and their ratio, as well as the acid-alkaline balance in the aqueous growth solution of CdS QDs. The results of the influence of these factors are presented in this study.

1. Object and Research Methods

The studied nanocrystals of cadmium sulfide were obtained by a chemical method from solutions of cadmium and sulfur salts in a colloidal solution of gelatin. The formation of

CdS particles occurs as a result of the exchange reaction: $Cd(NO_3)_2+Na_2S \Rightarrow CdS+_2NaNO_3$.

To obtain a colloidal solution, 5% gelatin and equimolar concentrations of cadmium and sulfur salts were used. The volumes introduced into the colloidal solution of the components were the same. The pH values of the solutions were changed by adding a solution of alkali or hydrochloric acid to an aqueous solution of gelatin with cadmium nitrate to obtain the required pH values (2 ÷ 10).

Samples were also created in which the concentration of cadmium and sulfur ions and their ratio changed. The pH value during the synthesis process was constant and equal to 7. During the study, four combinations of solutions with different ratios of the initial components of cadmium and sulfur were created. The molar concentration ratio of the initial components $Cd(NO_3)_2/Na_2S$ was equal to: 1/4, 1/2, 1/1, 2/1. In each of these combinations, seven samples were obtained: with a constant volume of $CdNO_3$, namely 5 ml, but in each of them the volume of introduced Na_2S changed: 0.25; 0.5; 1; 2; 3; 4 and 5 ml.

The luminescence was excited by a pulse laser LCS-DTL-374QT with a light wavelength of 355 nm. Laser power - 35 mW.

2. Analysis of Results

2.1. The effect of the acid-base balance in an aqueous solution with QDs of CdS.

It is known that salts are hydrolyzed in aqueous solutions. In our case – hydrolysis of nitrate and sodium sulfate. The molar concentration of cadmium ions is calculated according to formulas (1-2) and graphically presented in Figure 1.

$$C_0 = [Cd^{2+}] + Cd(OH)^+ + Cd(OH)_2^0, \qquad (1)$$

$$\alpha_1 = \frac{|Cd^{2+}|}{C_{Cd(NO_3)_2}} = \frac{1}{1+\frac{k_1}{[H^+]}+\frac{k_1k_2}{[H^+]^2}}; \quad \alpha_2 = \frac{k_1\alpha_1}{[H^+]};$$

$$\alpha_3 = \frac{k_1k_2\alpha_1}{[H^+]^2}. \qquad (2)$$

where α – molar concentration of components; k is the ionization coefficient (taken from the table [4]).

It can be seen that at pH values <8, the concentration of cadmium ions in the solution is dominant, and up to pH = 6, it remains unchanged. At pH > 6, the concentration of cadmium ions decreases and $Cd(OH)^+$ is formed. At pH values greater than 9, cadmium hydroxide $Cd(OH)_2$ is formed.

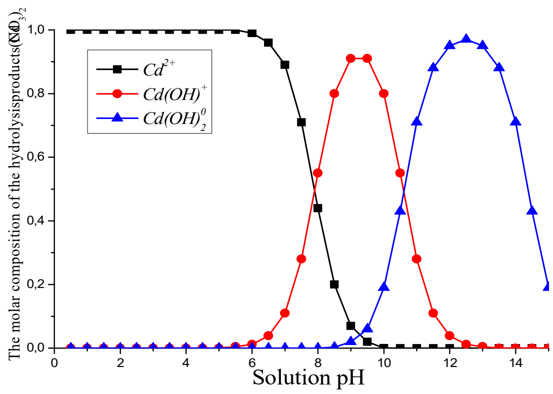

Fig. 1 – Dependence of the concentration of ions on the pH of the solution

Cadmium sulfide nanocrystals were synthesized at the following pH values of the solution: 2, 4, 7, 10.

Regarding the hydrolysis of sulfur sulfide, it is known that the hydrolysis of sulfur salts occurs at pH values>6. At lower pH values, the source of sulfur is impurity sulfur, which is present in gelatin.

In fig. 2 shows the normalized luminescence spectra of CdS QDs synthesized at different pH values. It can be seen that the luminescence spectra of samples obtained at low pH (2 and 4) and at pH (7 and 10) differ sharply. from. At low pH values, a short-wave luminescence band with a wavelength of λ_{max} = (480 – 490) nm dominates, and at higher values, a long-wave band localized at λ_{max} = (700 – 720) nm.

It was interesting to study the sensitivity of the luminescence spectrum of already grown CdS QDs to the acid-base composition of the colloidal solutions in which they are located, to determine whether the defect formation process is reversible as a result of a change in the pH of the solution, and how the pH value affects the change in QD size.

CdS QDs obtained at a neutral pH = 6 (initial sample) with an equimolar ratio of cadmium and sulfur ions with a wide luminescence band in the region (λmax = 667 nm) were chosen as the objects of the study. To the colloidal solution containing these QDs, solutions of alkali or hydrochloric acid were added to obtain pH (2, 4, 6, 8).

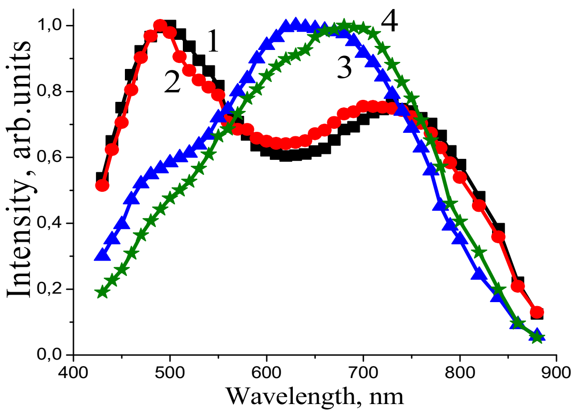

Fig. 2 – Normalized luminescence spectra of CdS QDs grown at different pH values of the solution: 2(1), 4(2), 7(3), 10(4)

As a result, colloidal solutions of CdS QDs were obtained, the color of which changed from yellow to orange (Fig. 3). It can be seen that the color of the solutions corresponding to pH = 2 and 4 is practically the same, which is confirmed by the data of the absorption spectra presented in Fig. 4.

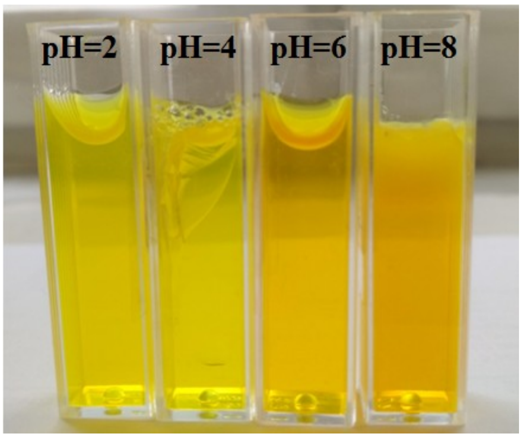

Fig. 3 – Samples of CdS QDs obtained at different pH values

Extrapolation of the absorption curves to the energy axis gives the value of the effective band gap of nanocrystals at different pH, and, accordingly, the size of the particles can be determined: 2 and 4 (2.9 nm), 6 (3.5 nm), 8 (4 nm).

The average particle radius was estimated from optical absorption spectra.

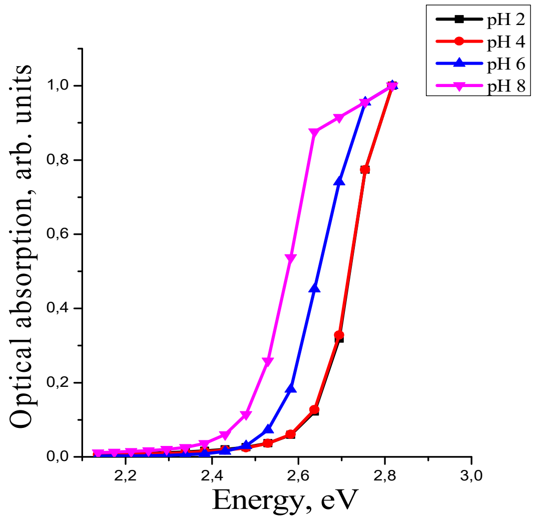

Fig. 4. Normalized absorption spectra of CdS QDs grown at different pH values of the solution: 2(1), 4(2), 6(3), 8(4)

According to the theory of interband absorption, the effective band gap of nanocrystals Eg* (the transition energy between the upper hole and lower electronic levels) increases with decreasing particle radius according to the law:

$$\hbar\omega = E_g^* + E_{l,n}^{e,h} \qquad (3)$$

where E_g^* - optical band gap width of bulk crystal; $E_{l,n}^{e,h}$ – dimensional quantization energy, which is inversely proportional to the square of the nanoparticle radius; l and n – orbital and principal quantum number. The dimensional quantization energy is defined as the difference between the effective band gap of a nanocrystal and a single crystal. It can be calculated using the formula (3):

$$E_{l,n}^{e,h} = h^2\, \varphi_{l,n}^2/2\, m_{e,h}\, r^2 \qquad (4)$$

where $m_{e,h}$ – effective masses of an electron and a hole; r – average radius of the nanoparticle; $\varphi_{l,n}$ – the root of the Bessel function (for quantum numbers $l = 0$ and $n = 1$, $\varphi_{0l} = 3{,}142$).[5]

The observed results can be explained by the following phenomena. A decrease in the size of QDs upon addition of hydrochloric acid (pH=2.4) may occur as a result of their dissolution, the size of QDs decreases from 3.5 nm to 2.9 nm. The reason for the increase in QDs size when alkali is added can be their coagulation, or the formation of a cadmium hydroxide shell.

Normalized luminescence spectra of samples measured after acid-alkaline treatment of already grown CdS QDs are shown in Fig. 5.

The obtained spectra repeat the results of the experiment on the influence of pH of the solution during the synthesis of nanocrystals [6].

In the spectra of nanocrystals with low pH (2 and 4), a short-wave luminescence band (570 nm) is detected. At high pH (6, 8), a long-wavelength band localized at a wavelength of λmax =690 nm dominates, the nature of which is associated with intrinsic defects in nanocrystals.

It was found that both in an acidic environment (pH=2.4) and in an alkaline environment (pH=8) the luminescence spectrum consists of two bands. The short-wave band (λmax = 580 nm) dominates in an acidic environment, and the long-wave band dominates in an alkaline environment (λmax = 683 nm).

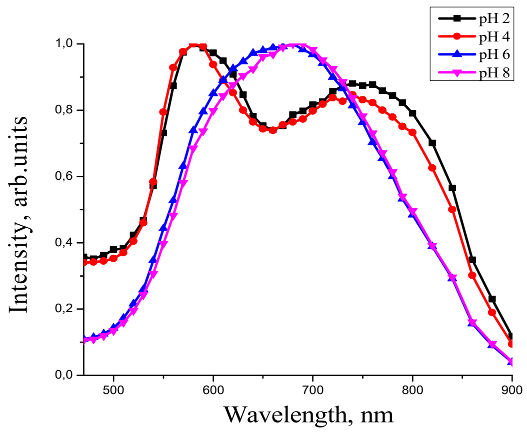

Fig. 5 – Normalized luminescence spectra of CdS QDs grown at different pH values of the solution: 2(1), 4(2), 6(3), 8(4).

In studies carried out earlier [6], when the acid-alkaline balance of the solution changed during the synthesis, a change in the spectrum was observed with the help of a change in the nature of surface defects. In this publication, the acid-base balance of a previously prepared solution with QDs was changed. In this case, it was noted that the change in the position of the luminescence spectrum correlates with the change in the size of the CdS QDs.

Thus, despite the different conditions of conducting the experiment regarding the effect of pH on the luminescence spectrum of CdS QDs, both obtained at different pH values during the synthesis and processed after synthesis, a qualitative correspondence between their luminescence spectra is observed.

2.2. The influence of the relative concentration of the starting components on the PL of CdS QDs

The graphs presented in Figure 6 correspond to the relative concentrations of $Cd(NO_3)_2/Na_2S$ components: 1/4, 1/2, 1/1, 2/1 (Figure 6 a, b, c, d, respectively). It can be seen that with an increase in the concentration of cadmium, the short-wavelength (λ_{max} = 490 nm) band becomes dominant, and in Fig. 6 (a), where the concentration of cadmium is quite low, this band is hardly noticeable.

This also confirms the nature of the evolution of the spectra of Figs. 6 (a, b, c, d) in which Na_2S:0.25 was added to the initial solution; 0.5; 1, 2; 3, 4 and 5 ml, (curves 1-7), respectively. Indeed, it can be seen that the addition of sulfur contributes to the increase in the intensity of the long-wave band. In the experiments, the samples containing the short-wave luminescence band (λ = 462 ÷ 493 nm) have an excess of cadmium, and the long-wave band (λ = 660 ÷ 711 nm) has an excess of sulfur.

Thus, the curves of the luminescence spectra in both experiments are composite, that is, they consist of several elementary bands. In this regard, the luminescence spectra were approximated by Gaussian curves, as a result of which three luminescence bands were detected in CdS QDs. Table 1 shows the schedule results.

Note that in the photoluminescence spectra of nanocrystals, a band is recorded in the region λ = 555 ÷ 598 nm. This band develops in nanocrystals, the synthesis of which was carried out at the same concentration of cadmium and sulfur ions.

Thus, the given results indicate that the luminescence of CdS QDs obtained by the method of colloidal chemistry is due to their own defects and it is related to the influence of the stoichiometric composition of cadmium and sulfur. Some discrepancy in the localization of the luminescence maxima of individual bands can be explained by the spread of QD size.

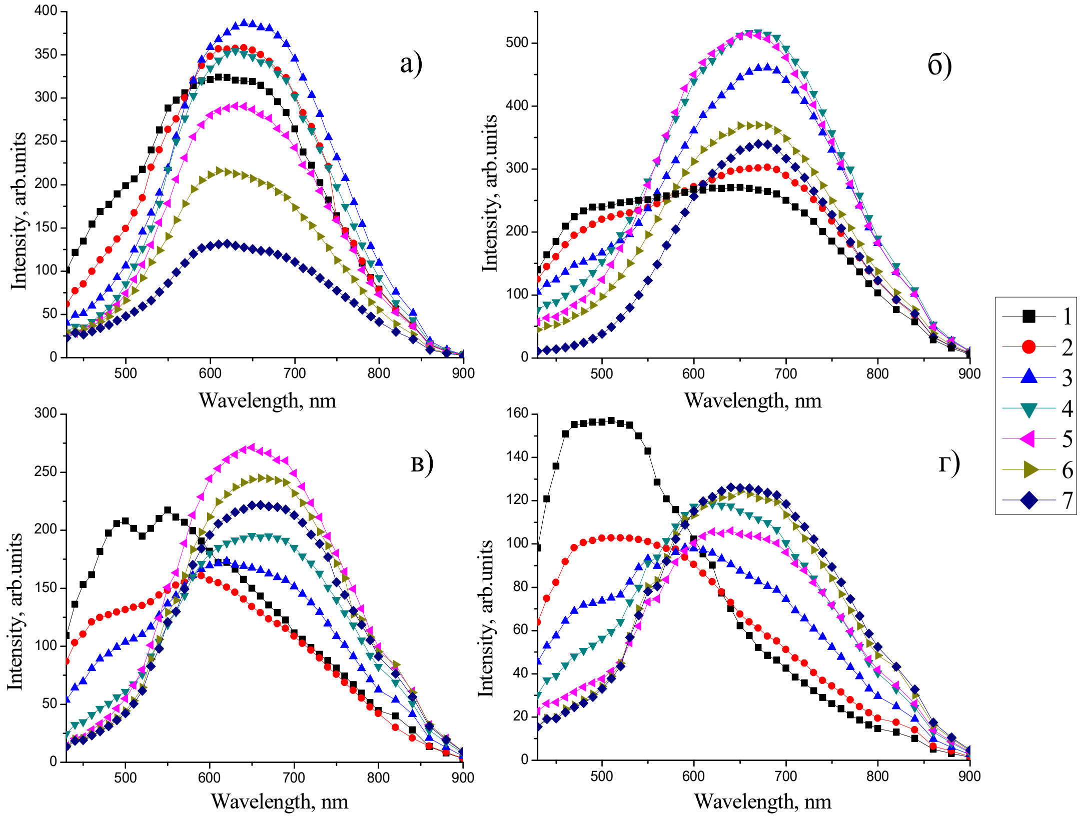

Fig. 6 – Luminescence spectra of CdS QDs obtained at the molar ratio of the initial components CdNO3 /Na2S: 1/4 (a); 1/2 (b); 1/1 (c); 2/1 (g).

Table 1. Dependence of the position of the maxima of the QD luminescence bands, obtained as a result of spectrum decomposition, on the pH value of the solution and at different ratios of the initial components.

The influence of the acid-base balance in an aqueous solution with CdS QDs (Fig. 2)				*The influence of the relative concentration of the initial components on the PL of CdS QDs (Fig. 6)*			
pH	λ_1, nm	λ_2, nm	λ_3, nm	*$CdNO_3$ /Na_2S*	λ_1, nm	λ_2, nm	λ_3, nm
2	490	-	716	*2/1 (curve 1)*	462	555	660
4	493	-	708	*1/1 (curve 3)*	462	573	690
7	483	592	694	*1/2 (curve 5)*	464	598	703
10	481	578	703	*1/4 (curve 7)*	-	593	711

Conclusions

The results of the research showed that the luminescence spectrum of CdS QDs depends on the acid-alkaline composition of the medium. At low pH values, the bands localized in the 500-580 nm region dominate, and at high values - in the 640÷680 nm region. It is shown that the luminescence spectrum can be changed both by changing the synthesis conditions and by changing the acid-base composition of colloidal nanocrystals.

The work also investigated the effect of two parameters of the QD synthesis process on their luminescence spectrum, namely: the acid-alkaline balance of the growth solution and the ratio of reaction components (cadmium and sulfur salts). Syntheses were carried out in which the pH of the solution varied in the range from 2 to 10. CdS QDs with different ratios of starting components were also synthesized. The obtained results indicate that the technological process has a significant effect on the formation of cadmium sulfide QD radiation bands. In both cases, the radiation spectrum contained three bands localized in the wavelength range λ_1 = 462 ÷ 493 nm, λ_2 = 555 ÷ 598 nm, λ_3 = 660 ÷ 711 nm.

The observed features of the influence of the mentioned technological factors on the luminescence spectrum of CdS QDs are explained by the fact that the concentration of cadmium and sulfur ions is a determining parameter in the synthesis. In the first, the concentration of ions is regulated by the starting pH of the solution, and in the second, by the initial concentration of $Cd(NO_3)_2$ and Na_2S.

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INFLUENCE OF TECHNOLOGICAL CONDITIONS OF SYNTHESIS ON THE FORMATION OF PHOTOLUMINESCENCE SPECTRA OF CdS QDs

Summary

The purpose of the work is to study the influence of technological conditions of synthesis on the formation of photoluminescence spectra of CdS QDs. This article presents the results of the effect of pH on the luminescence of colloidal CdS QDs. A qualitative agreement was shown between the luminescence spectra of CdS QDs, both obtained at different pH values during synthesis, and CdS QDs subjected to treatment after synthesis. It was shown that the luminescence spectrum can be changed both by changing the synthesis conditions and by changing the acidity of colloidal CdS QDs. It are presented the results influence of two parameters of synthesis process of quantum dots sulfide cadmium (CdS QD) on the spectrum luminescence, namely, the acid-base balance of the growth solution and the correlation of reaction components (cadmium and sulfur salts). Carried out the syntheses in which the pH solution was changed in the interval of values from 2 to 10. There were also synthesized CdS QD with different ratios of the initial components. The results obtained by evidence of the fact that the technological process has a significant impact on the formation of bands luminescence CdS QDs . In both cases, the luminescence spectrum had three bands that are localized at λ_1 = 462 ÷ 493 nm, λ_2 = 555 ÷ 598 nm, λ_3 = 660 ÷ 711 nm. The observed features of the effect of these technological factors on the spectrum luminescence of CdS QDs are explained by the fact that, in the synthesis, the concentration of cadmium and sulfur ions is a determining parameter. In the first case, the ion concen-

tration is controlled by the pH value of the solution, and in the second, by the initial concentration of Cd $(NO_3)_2$ and Na_2S.
Keywords. cadmium sulfide quantum dots, absorption, photoluminescence, nanomaterials.

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ВПЛИВ ТЕХНОЛОГІЧНИХ УМОВ СИНТЕЗУ НА ФОРМУВАННЯ СПЕКТРІВ ФОТОЛЮМІНЕСЦЕНЦІЇ КТ CdS

Реферат
Мета роботи полягає в дослідженні впливу технологічних умов синтезу на формування спектрів фотолюмінесценції КТ CdS. У роботі наведено результати впливу pH на люмінесценцію колоїдних КТ CdS. Показано якісну відповідність між спектрами люмінесценції КТ CdS, отриманих при різних значеннях pH під час синтезу, і КТ CdS, підданих обробці після синтезу. Також показано, що спектр люмінесценції можна змінювати як зміною умов синтезу, так і зміною кислотності колоїдних КТ CdS. Представлені результати впливу двох параметрів процесу синтезу квантових точок сульфіду кадмію (КТ CdS) на спектр люмінесценції, а саме, кислотно-лужного балансу ростового розчину і співвідношення компонентів реакції (солей кадмію і сірки). Здійснено низку експериментів з синтезом, в якому pH розчину змінювалася в інтервалі величин від 2 до 10. Також були синтезовані КТ CdS з різним співвідношенням вихідних компонентів. Отримані результати свідчать про те, що технологічний процес має суттєвий вплив на формування смуг випромінювання КТ CdS. В обох випадках спектр випромінювання містив три смуги, які локалізовані у $\lambda_1 = 462 \div 493$ нм, $\lambda_2 = 555 \div 598$ нм, $\lambda_3 = 660 \div 711$ нм. Спостережувані особливості впливу зазначених технологічних факторів на спектр люмінесценції КТ CdS пояснюються тим, що в синтезі визначальним параметром є концентрація іонів кадмію та сірки.У першому – концентрація іонів регулюється значенням pH розчину, а у другому – вихідною концентрацією $Cd(NO_3)_2$ та Na_2S.
Ключові слова. квантові точки сульфіду кадмію, поглинання, фотолюмінесценція, наноматеріали.

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