

Optic and spectroscopic investigations of ZnO nanosized particles in aqueous solution with cetylpyridinium chloride

M.M.Omelchenko, M.V.Ziobro, V.B.Kapustianyk

Scientific-Technical and Educational Center of Low Temperature Studies,
I.Franko National University of Lviv, 50 Dragomanova Str.,
79005 Lviv, Ukraine

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The results on time dependence of optic absorption spectra of H_2O+ZnO and $H_2O+ZnO+CPCL$ suspensions were reported. The two steps mechanism of coagulation of ZnO nanosized particles has been offered: 1) the passivation of ZnO particles nanosize surface by $ZnOOH^-$ resulting from interaction with OH^- groups existing in water. As a second result of this interaction ZnO nanosized particles obtain the negative charge which prevents the coagulation; 2) the next compensation of charges with H^+ in water. As a result the neutral compounds form that does not prevent from their coagulation and ZnO precipitation from aqueous solution. The adding of cetylpyridinium chloride surfactant into suspension increase the compensation of the charge of ZnO nanosized particles that causes the process of its coagulation and tends rodlike systems forming.

Приведены результаты исследований оптического поглощения наноразмерных частиц ZnO в суспензиях H_2O+ZnO и $H_2O+ZnO+CPCL$. Предложен двухступенчатый механизм временных изменений в обеих суспензиях: 1) пассивация поверхности наноразмерных частиц ZnO соединением $ZnOOH^-$ с участием находящихся в воде групп OH^- , в результате чего наноразмерные частицы ZnO получают отрицательный заряд, который препятствует коагуляции; 2) следующая стадия – это компенсация зарядов ионами H^+ , в результате чего формируются нейтральные образования, которым ничто не препятствует коагулироваться с последующим частичным оседанием ZnO из раствора. Добавка лиотропного суфронематика цетилпиридинийхлорида в суспензию увеличивает компенсацию зарядов, чем ускоряет процесс коагуляции наноразмерных частиц ZnO и стимулирует формирование стержнеподобных систем.

1. Introduction

Investigations of different compounds influence on properties of nanosized particles in liquid crystal media became urgent recently. The perceptible changes of optical characteristics of liquid crystals with low concentration of nanosized particles, less than 1 wt. %, were detected in a number of experiments [1–5]. However the main problem is the formation and provision of homogenic distribution of nanoparticles in the liquid crystal medium. For example, such problem has been successfully solved for the

carbon nanotubes in thermotropic liquid crystals [5].

The ZnO is very promising and convenient material for getting different types of nanostructural systems. As a confirmation of this statement can be the huge amount of publications related to these nanoparticles investigations, for example [6–8]. This attention to ZnO nanoparticles in the different form and media is conditioned by their practical application in various fields of electronics: solar elements [9], microresonators [10], UV detectors [11], and gas sensors [12]. Therefore, an investigation of the

optical characteristics of systems containing liquid crystals and ZnO nanoparticles is very important and applicable problem.

But the absence of method of forming homogeneous and uniform distribution of ZnO nanoparticles in liquid crystals at present time does not allow us to do such investigations. Whereas water is the basis of lyotropic liquid crystal cetylpyridinium chloride/hexanol/brine [13] it is very important to investigate at first the behavior of ZnO nanosized particles in aqueous solution of cetylpyridinium chloride (CPCL).

An influence of water on luminescence properties of ZnO nanoparticles in alcohol medium was studied in the works [14, 15]. It was revealed that increasing water concentration in the solution resulted in decreasing the intensity of luminescence. Burakov, Nevar and Nedelko [16] reported about successful formation of ZnO nanoparticles by an electrical discharge in distilled water. After sedimentation of those nanoparticles at silicon plate and evaporation of suspension at the temperature 90°C the authors of the paper [16] had fixed the intensive luminescence of sediment. That is why the problem of interaction of ZnO nanoparticles with water is not solved yet.

We report in the present work on the results of optic and spectroscopic investigations of aqueous suspension with ZnO nanosized particles and the influence of cetylpyridinium chloride surfactant.

2. Experimental methods

ZnO nanopowder with the grain dimension <100 nm of the Sigma production (the maximum of ZnO nanosized particles distribution by size is near the 60 nm) has been used for the investigations in this work. Two variants of suspension were prepared and investigated: the first one is H₂O+0.015 %ZnO and the second one — H₂O+0.015 %ZnO+0.015 % CPCL wt. %. The suspensions were different from each other with the obtaining method. A preparation order of the suspensions is following: after weighting the ZnO nanopowder was placed in the glass bottle with water and after mixing it, the suspension was homogenized in Ultrasound bath at 24°C during 30 min. The difference for H₂O–ZnO–CPCL system was that before mechanical mixing the mixture was heated up to 26°C for homogeneous aqueous dilution of the surfactant.

The spectra of optical absorption were investigated in spectral region 300–420 nm

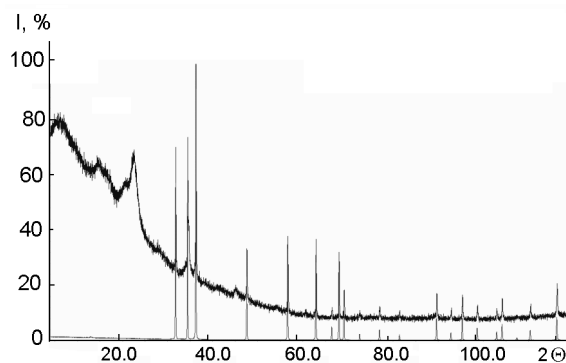


Fig. 1. X-ray diffractogram of the precipitate of the suspension ZnO+H₂O drying at 290 K. The lines — calculated profiles ZnO compound.

with using monochromator of the ZMR-3 type. The suspension was placed in quartz cuvette with the thickness 1.05 mm of the investigated layer. The surface electron microscope REMMA-102-02 was used for observation of the ZnO nanosized particles. For probing in microscope the suspension was placed on the conductive ITO-type surface-pad than it was dried.

3. Results and discussion

Hydration of ZnO nanoparticles (in other words a formation of Zn(OH)₂) was considered by authors [14] as a reason of water influence on luminescent properties of the ZnO particles. To estimate the characteristics of the hydration process the direct X-ray phase analysis of the H₂O+ZnO sediment was performed after over a long period of time (>150 h.) of the ZnO nanosized particles sojourn in water. The sediment drying we carried out at room temperature for preventing of possible decomposition of Zn(OH)₂ if it was formed (Zn(OH)₂ decomposes at a temperature little larger than 100°C). As it is shown at diffraction graph (Fig. 1) the X-ray phase analysis with accuracy ≤1 % (the accuracy of X-ray analysis for Zn) points at an absence of Zn(OH)₂ in the system. All diffraction maxima belong to ZnO. That is mean that the presence of Zn(OH)₂ compound at the ZnO surface at aqueous solution is available only as surface passivation process. The authors R.Sreeja et al. mentioned in their recent work [17] about thin passivation layer of Zn(OH)₂ on the surface of ZnO nanosized particles in PMMA matrix.

In Fig. 2 the time changes of optical density spectra of the H₂O+0.015%ZnO (Fig. 2a) and H₂O+0.015%ZnO+1 %CPCL (Fig. 2b)

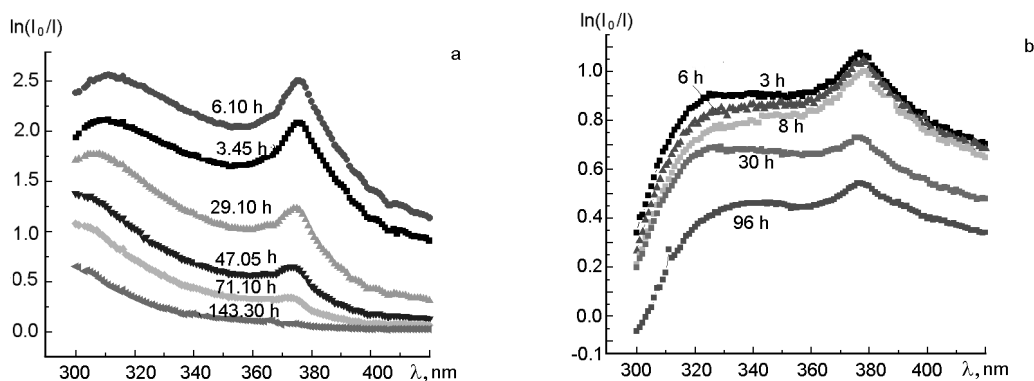


Fig. 2. Optical density spectra of the suspension a) 0.015 % ZnO+H₂O; b) 0.015 % ZnO + H₂O+1 % CPCL.

systems. As we can see in the Fig. 2a on the spectra for the H₂O+0.015 % ZnO system two bands (near 376 nm and 310 nm) are well-observed. The bands intensities change identically in time with respect to the first recording spectrum (Fig. 3). It is apparent from the Fig. 2, that the both peak maxima are little shifted sideways of the short wave-lengths. In particular the peak at 376 nm is shifted to 373 nm during 4000 min (nearly 66 h). At the decrease of percent of the ZnO in H₂O+ZnO system the intensity, the positioning and the character of time changes of the dominate peak (376 nm) are practically similar to these parameters of the systems with higher contents of ZnO. However the band 310 nm is fully levelled and the spectrum become similar to the spectrum for the H₂O+0.015 % ZnO+1% CPCL suspension (Fig. 2b). The spectrum return practically to the starting curve after the 143 h processing of the H₂O+ZnO system in the Ultrasound bath (lowest curve on Fig. 2a).

It should be mentioned that the spectra on Fig. 2 are in a good agreement with the spectra obtained in the work [16] for ZnO nanosized particles in alcohol suspensions and the absorption peak at 376 nm correlates with absorption excitonic peak (at 373 nm) for ZnO nanostructured films [18]. This confirms that we have nanoparticles of ZnO in the aqueous suspense and hydrates are absent. The shift of the peak at 310 nm to the shortwave region testifies that this maximum is conditioned by light scattering on ZnO nanosized particles. With the laps of time the amount of coagulants of big size decreases in the aqueous solution. It is also confirmed by the Fig. 2b on which we can see that adding of CPCL to the H₂O+0.015 % ZnO solution increases the sedimentation of ZnO big coagulated complexes. As a result of this process only di-

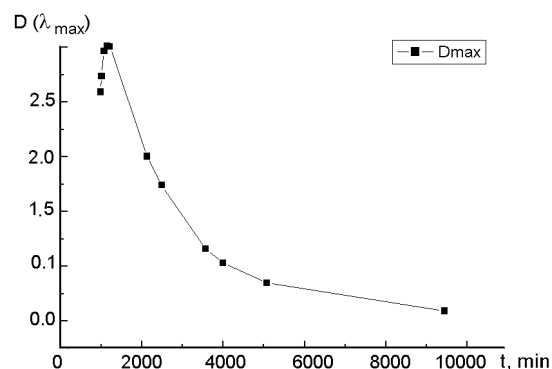


Fig. 3. Time evolution of the 0.015 % ZnO + H₂O suspension spectra at the peak 376 nm.

minutive nanoparticles of ZnO left in the solution. There are changes at the short-wave region — the peak at 310 nm fades away, and maximum at 376 nm is present at every curve.

Blooming of H₂O+0.015 % ZnO and H₂O+0.015 % ZnO+1% CPCL suspensions up to total disappearing of the absorption maxima (Fig. 2) is undoubtedly connected with the decrease of the ZnO nanosized particles concentration in suspension that is with their precipitation. Simple evaluation by a Stokes formula shows that the time of precipitation in water for the ZnO nanoparticles with dimension of the grain 100 nm is several degrees more than time observed in our experiment. It means that in our suspensions the coagulation process of ZnO nanosized particles to submicron complexes take place and these complexes precipitate quit rapidly. In case of H₂O+0.015% ZnO suspensions precipitated ZnO nanosized particles coagulate in the formless conglomerate, while in H₂O+0.015 % ZnO+1 % CPCL suspensions these particles form rod-like structures (Fig. 4).

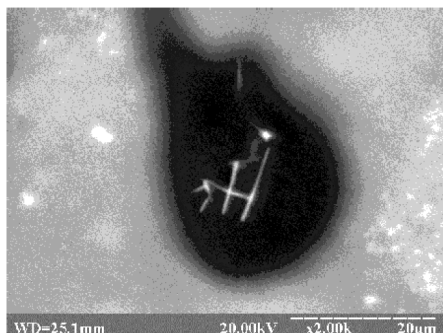


Fig. 4. The image of the ZnO rod-like structures (white) surrounded by CPCL (dark) after drying the suspension 0.015 % ZnO + H₂O + 1 % CPCL, obtained with electron microscopy REMMA-102-02.

As shown in Figs. 2, 3 the time changes of optical density of suspension 0.015 % ZnO+H₂O have 2 regions with the different signs of time changes (the sign change is realized in the limit 6–7 h). These circumstances testify about two different mechanisms of interaction of ZnO nanoparticles with water which are dominated in the different stages. At the first stage after dispersion of the starting ZnO nanopowder by homogenization in US-bath it is activated the individual ZnO nanosized particles interaction with aqueous molecules i.e. with the hydroxyl group OH⁻, which even in light concentrations, as H⁺ ions, ever present in water. As a result the ZnO nanosized particles surface are passivated by ZnOOH⁻ groups that causes obtaining a negative charge of ZnO nanosized particles. As it is well known from colloid chemistry this charge is hindered of the coagulation. An increase of optical density during first 6–7 h after ceasing of US-action can testify about the accumulation of charges and assist to the further dispersibility of the ZnO i. e. the concentration of optical active centres of ZnO slightly increased. But with time passing the ZnO nanosized particles surface (which contain ZnOOH⁻ groups) are surrounded by H⁺ ions, which compensate the charge. Under such conditions charges do not prevent the coagulation and it becomes the dominated mechanism in dynamics of ZnO particles in suspension after 7 h. This process stimulates the rising of nanosized particles size and their following precipitation. In the spectra (Fig. 3) this process is visualized as the exponential decrease of absorption after 400 min.

According to coagulation mechanism assumption it is easy to explain some acceleration of lightning of suspension of

H₂O+0.1 % ZnO under CPCL adding (i.e. in H₂O+0.015 % ZnO+1 % CPCL suspension). The molecules of surfactant are polarized. That is why they rotate in such way to compensate the charge of ZnO nanosized particles surface passivated with ZnOOH⁻. Therefore it is necessary to find out the reversible process of coagulation of ZnO nanosized particles under the forming liquid crystal phase with cetylpyridinium chloride.

4. Summary

The results on time dependence of optic absorption spectra of H₂O+ZnO and H₂O+ZnO+CPCL suspensions allow us to offer the two steps mechanism of coagulation of ZnO nanosized particles: 1) the passivation of ZnO nanosized particles surface by ZnOOH⁻ resulting from interaction with OH⁻ groups existing in water. As a second result of this interaction ZnO nanosized particles obtain the negative charge which prevents the coagulation; 2) the next compensation of charges with H⁺ in water. As a result the neutral compounds form that does not prevent from their coagulation and ZnO precipitation from aqueous solution. The adding of cetylpyridinium chloride surfactant into suspension increase the compensation of the charge of ZnO nanosized particles that causes the process of its coagulation and tends rodlike systems forming.

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Оптико-спектральні дослідження нанорозмірних частинок ZnO у водному розчині з цетилпіридиніум- хлоридом

М.М.Омельченко, М.В.Зьобро, В.Б.Капустяник

Приведено результати досліджень оптичного поглинання нанорозмірних частинок ZnO у суспензіях H_2O+ZnO та $H_2O+ZnO+CPCL$. Запропоновано двостадійний механізм часових змін спектрів поглинання обох суспензій: 1) пасивація поверхні нанорозмірних частинок ZnO сполукою $ZnOON^-$ за участю наявних у воді груп OH^- , в результаті чого нанорозмірні частинки ZnO отримують від'ємний заряд, який перешкоджає коагуляції; 2) наступна компенсація зарядів завдяки H^+ , в результаті чого формуються нейтральні утворення, котрим ніщо вже не перешкоджає коагулюватися з наступним частковим осіданням ZnO з розчину. Додаток ліотропного суфронематика cetylpyridinium chloride у суспензію збільшує компенсацію зарядів, чим пришвидшує процес коагуляції нанорозмірних частинок ZnO і сприяє формуванню стержнеподібних систем.