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Influence of Surface Modification of $BaTiO_3$ Nanoparticles by Sodium Oleate and Chitosan on their Optical Properties and Agglomeration in Aqueous Solutions

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Abstract. Spherical titanium barium nanoparticles with an average size about 100 nm in the tetragonal crystal phase were obtained by peroxide synthesis. To prevent their agglomeration and reduce the toxic effect, the surface of nanoparticles was chemically modified with sodium oleate and chitosan. Influence of surface modification by these compounds on agglomeration of nanoparticles in aqueous solutions, their spectral features, as well as generation of the second optical harmonic were investigated.

1. Introduction

Nowadays, significant interest in the application of ferroelectric $BaTiO_3$ nanoparticles in nanomedicine as imagine probes for different methods of microscopy, cell proliferation agents and nanotransducers for cell stimulation are observed [1, 2]. Introduction into biological systems requires stabilizing nanoparticles in biocompatible systems, usually aqueous solutions. At the same time, due to the tendency to agglomeration, as well as the leaching of metal ions, their surface is modified using different coatings [3]. Various types of coatings make it possible to obtain particles with different thickness of modifying layer, surface charge value, strength of coating adhesion. All these factors have a significant influence on the interaction of nanoparticles with cells.

Experimental results indicate that surface modification has a significant impact on the optical properties of $BaTiO_3$ nanoparticles. It is shown, that modification of the surface of $BaTiO_3$ nanoparticles by a layer of polymethylmethacrylate (PMMA) leads to an increase in the intensity of photoluminescence, which can be associated with passivation of surface defects [4]. Modification of the surface of nanoparticles of barium nanoparticles by a polystyrene layer leads to remarkable changes in phase transitions. In contrast to the volumetric samples, for these nanoparticles the orthorhombic crystal phase exists in the temperature range of 10-388 K, coexisting with the rhombohedral phase at lower temperatures and the tetragonal phase at higher temperatures. This fact has an impact on the nonlinearity of optical and dielectric properties [5]. In [6] significant influence of surfactant used in hydrothermal synthesis of $BaTiO_3$ nanoparticles was demonstrated.

Sodium oleate is widely used to stabilize inorganic nanoparticle suspensions in aqueous solutions and different organic solvents, which changes the chemical composition of the surface from hydrophilic to oleophilic [7]. Chitosan compounds are also actively used for increasing of the cytocompatibility of $BaTiO_3$ nanoparticles in cancer therapy [8]. Thus, the purpose of the work is an experimental study of the influence of the modifying layer on the optical properties, including the generation of the second harmonic in $BaTiO_3$ nanoparticles, as well as their aggregation in aqueous solutions.

2. Materials and methods

$BaTiO_3$ nanoparticles were synthesized using the peroxide method [9]. An aqueous solutions of $BaC1_2{\cdot}2H_2O$ (Merck) and $TiC1_3$ (Sigma-Aldrich) were mixed at 10 ℃ and then aqueous solution of H_2O_2 (J.T. Baker) was added. Then drop by drop of the NH_3 water solution was added to reach pH=9. The resulting light-yellow precipitate $BaTiO_2(O_2){\cdot}3H_2O$ was filtered, washed and dried. To obtain barium titanate, the obtained peroxide precursor was annealed for 6.5 hours at the temperature 900 ℃.
Modification of the surface of the obtained nanoparticles with sodium oleate was performed according to [7]. Further, 1 g of $BaTiO_3$ nanoparticles was refluxed in a 400 mL 30% aqueous solution of H_2O_2 (J.T. Baker) to enrich the surface by hydroxyl groups. Then the particles were filtered and added with solid loading of 2 wt% to a 100 mL of 0.5 wt% aqueous sodium oleate solution. Aqueous solution of SOA was prepared by mixing oleic acid (Sigma-Aldrich) and NaOH with a molar ratio of 1:1. Then mixture was heated at 90 ℃ for 3 h. The obtained nanoparticles were washed, filtered and dried at 90 ℃ during a day.
For the modification of the nanoparticle surface by chitosan, the following method was used. Chitosan (low molecular weight, Sigma-Aldrich) 0.125 g was added and diluted in 50 mL of acetic acid (CH_3COOH) and mixed up for 24 hours at 40 ℃. The pH of the solution was regulated to 4.7 used 10% aqueous solution NaOH and then the solution was filtered through a membrane of 0.45 µm. Then 0.1 g of $BaTiO_3$ treated with H_2O_2 was added and mixed 4 hours at a temperature of 40 ℃. As in the previous case, obtained nanoparticles were washed, filtered and dried at 90 ℃ during a day.
Obtained samples of nanoparticles with modified (sodium oleate or chitosan) surface were dispersed in aqua by ultrasonic treatment (60 W, 5 min.).
Structure of the synthesized nanoparticles was studied by SEM (TESCAN VEGA 3 LM) with EDX (Bruker X-Flash 6I10) and XRD (Bruker D8 ADVANCE ECO) with using Co Kα radiation line (0.17903 nm). The surface chemistry of treated nanoparticles was characterized by FTIR (Thermo Fisher Nicolet iS-50). Generation of the second harmonic by samples was researched with Nd:YAG laser 1064 nm (pulse duration 10 ns, 2.1 mJ). Dynamic light scattering analysis (Nicomp Nano Z3000) was used to evaluate the dispersibility of 1 wt.% BaTiO3 nanoparticles in aqueous solutions and for the measurement of the zeta potentials of the obtained solutions. Absorption spectra of solutions in the ultraviolet range were measured by UV/Vis spectrometer SPECORD 250 PLUS (Analytik Jena).

3. Results and discussion

SEM images of the synthesized samples demonstrate the formation of spherical nanoparticles with an average size approximately 100 nm (Figure 1).

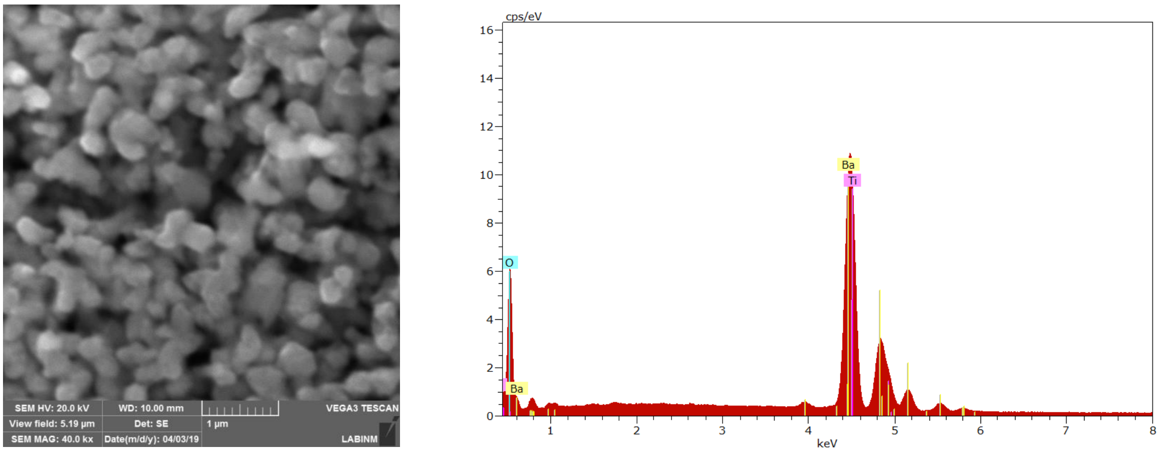


Figure 1. SEM image and EDX spectrum of $BaTiO_3$ nanoparticles obtained by peroxide synthesis.

Diffraction pattern also demonstrates the formation of nanoparticles with perovskite structure (Figure 2). Estimation of average nanoparticle size made from the widening of the peak (101) according to the Sherer equation:

$$D=0.9\lambda/\beta \cos \theta \qquad (1)$$

where D is the grain diameter, β is the half intensity width of the relevant diffraction peak, λ is the X-ray wavelength, and θ is the diffraction angle. The average particle size is estimated at 94 nm, which is close to the size estimated from the SEM images. Splitting of reflexes (001/100) and(002/200) clearly indicates the formation of the ferroelectric tetragonal crystalline phase of $BaTiO_3$.

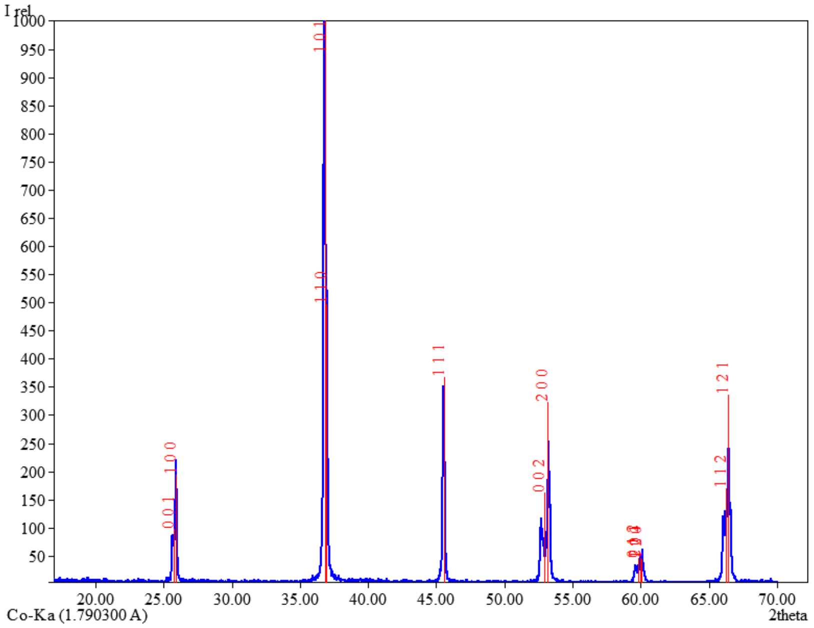


Figure 2. Diffraction pattern of $BaTiO_3$ nanopaticles obtained by peroxide synthesis.

FTIR spectrum of unmodified $BaTiO_3$ nanoparticles (Figure 3) demonstrates the presence of bands 520 cm^{-1}, caused by stretching vibrations of the Ti-O bond and 1455 cm^{-1} which is due to the stretching vibration of $–CO_3^{2-}$ associated with residual barium carbonate in $BaTiO_3$.

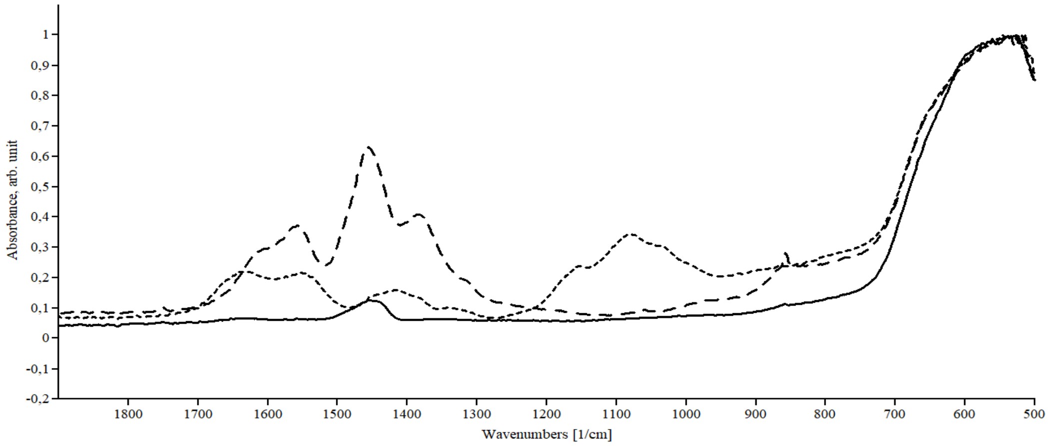


Figure 3. FTIR spectra of as-received $BaTiO_3$ nanoparticles (solid line), modified by sodium oleate (dashed line) and modified by chitosan (dotted line).

In addition, the sample of nanoparticles with modified sodium oleate surface is characterized by bands of 1384, 1557 and 1733 cm^{-1}, that indicate formation of bidentate-type bond between the surface of nanoparticles and sodium oleate molecules [7]. The spectrum of nanoparticles modified by chitosan (Figure 3) is characterized by the presence of bands 1077, 1552 and 1632 cm^{-1}. Peak 1077 cm^{-1} corresponding to C–O–C stretching in the glucosamine. The band at 1552 cm-1corresponds to the NH_2 group and the band at 1632 cm-1 to the N–H bending vibration [10].

Both synthesized samples with unmodified surface and samples with modified surface according to the specified methods demonstrate the generation of the second harmonic with wavelength 532nm during irradiation by 1064 nm Nd:YAG laser pulses (10 ns, 2.1 mJ) (Figure 4). It should be noted that the signal intensity for samples with modified sodium oleate and chitosan surface is much lower, which can be due to the absorption of the modifying coating. In addition, modification of the surface by sodium oleate reduces the intensity of generation of the second harmonic more significantly than modification by chitosan.

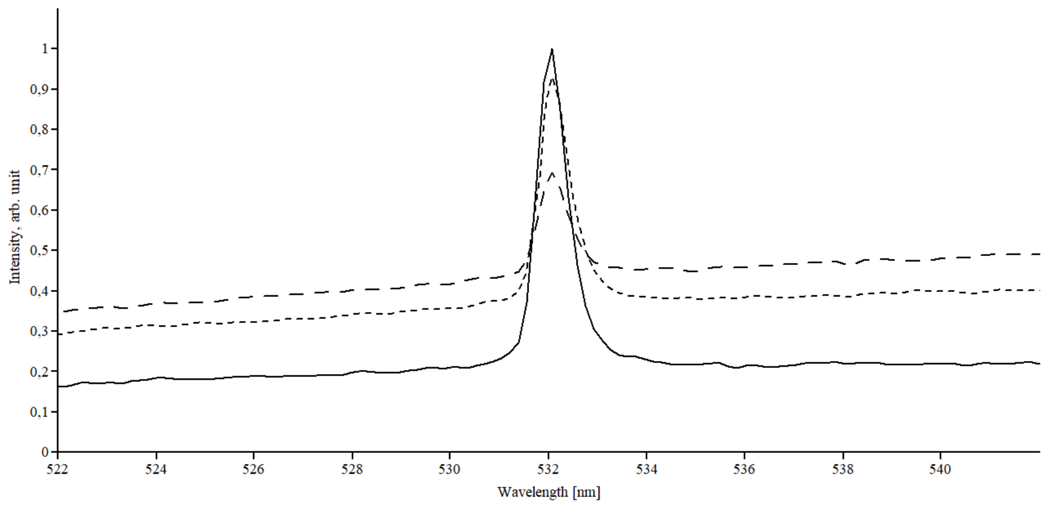
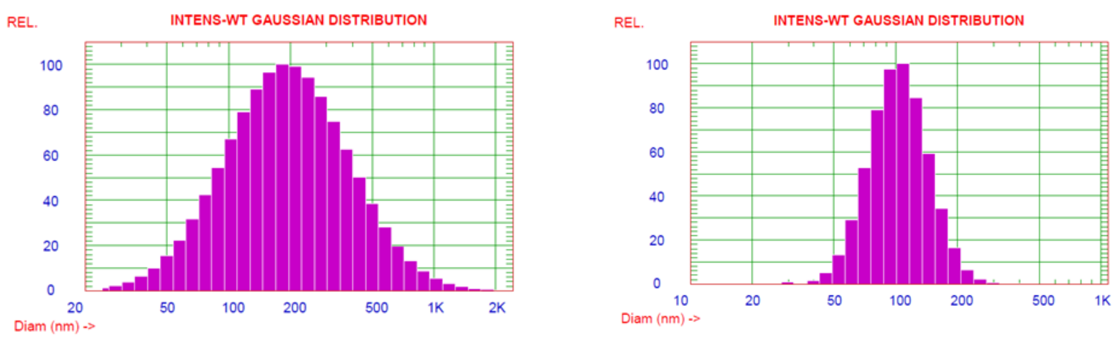
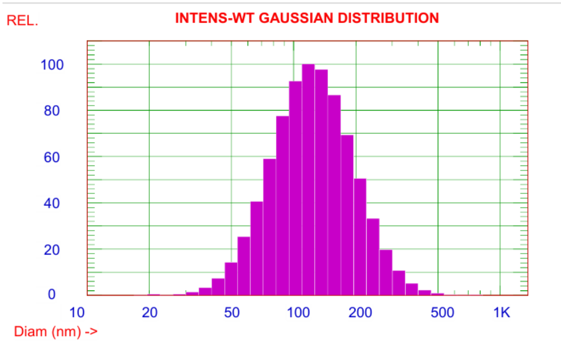


Figure 4. Second harmonic generation intensity of as-received $BaTiO_3$ nanoparticles (solid line), modified by sodium oleate (dashed line) and modified by chitosan (dotted line).

Dynamic light scattering data obtained for the dispersions of unmodified and modified nanoparticles indicates a reduction in average size for particles with modified surfaces from 216 nm for unmodified to 107 nm for sodium oleat modified and 135 nm for chitosan modified nanoparticles $BaTiO_3$ (Figure 5). It should also be noted that there is a decrease in the polydispersity of nanoparticles with modified surfaces, especially for sodium oleate modified types. It was found that for the dispersions under study, the modification of the surface with sodium oleate leads to changes in the zeta potential from 24 mV, which is close to the values obtained in [11], to -53 mV (pH=7).



a) b)



c)

Figure 5. Dynamic light scattering particle size distribution for as-received (a), modified by sodium oleate (b) and modified by chitosan (c) 1 wt.% $BaTiO_3$ nanoparticles in aqueous solutions**.**

At the same time, for nanoparticles modified by chitosan, the zeta potential practically does not change (26 mV).

Offset of the edge of UV absorption to shorter wavelengths for the dispersions of $BaTiO_3$ with modified surface (Figure 6) could be caused by a decrease of their polydispersity and average particle size. Thus, in these systems, the dimensional effect associated with the increase in the bandgap energy of nanostructured semiconductors is more evident [12]. Moreover, for the dispersions of modified nanoparticles another wide absorption peak around 240 nm is observed, which can be associated with different types of surface defects, including oxygen vacancies [13]. The intensity of this peak for the dispersion of sodium oleate modified nanoparticles is significantly higher than for nanoparticles with a chitosan modified surface.

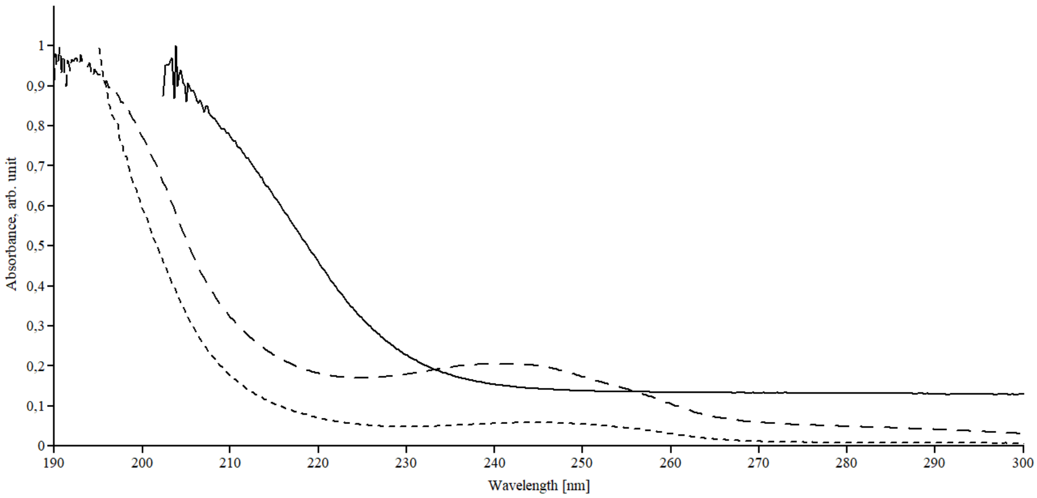


Figure 6. UV absorption spectra of 1% wt dispersions of as-received (solid line), modified by sodium oleate (dashed line) and modified by chitosan (dotted line).

4. Summary

Surface of ferroelectric $BaTiO_3$ nanoparticles with average size of 100 nm was modified by sodium oleate and chitosan. It was established that surface modification leads to a decrease in the agglomeration of nanoparticle dispersions in aqueous solutions. In this case, modification of sodium oleate, unlike chitosan, leads to a significant change in the zeta potential (from 24 to -53 mV). It is shown that the modification of the surface by these compounds also leads to a decrease in the intensity of the second harmonic generation. It is established that the modification of sodium oleate leads to a more significant reduction in the intensity of the second harmonic signal. Surface modification also leads to appearance of the broad UV absorption peak (240 nm) which can be associated with surface defects. This peak also has a significantly higher intensity for nanoparticles modified with sodium oleate than for nanoparticles modified with chitosan.

5. References

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