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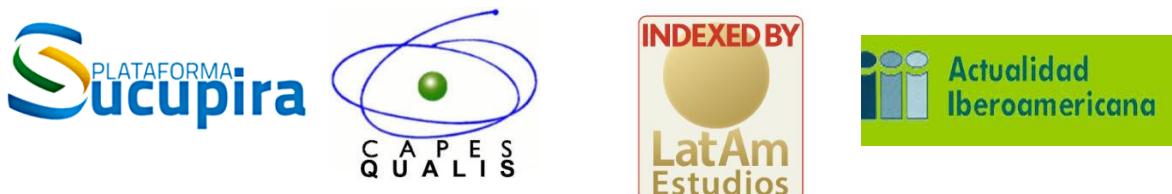
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LIGHT SCATTERING STUDIES OF CUPRUM OXIDE WATER SUSPENSIONS

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Abstract

In this work, stimulated low-frequency Raman scattering (SLFRS), caused by laser pulses interaction with nanoparticles acoustic vibrations was registered in water suspension of Cu oxide nanoparticles. SLFRS conversion efficiency and threshold are measured. It was found that frequency shifts of the scattered light from the exciting light are located in gigahertz range.

Keywords

Nanoparticles – Cupric oxide – Light scattering

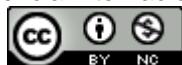
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Introduction

Nanoparticles play very important role as in scientific investigations, so in different industrial applications. They are used for practical tasks and also are often prove to be result of industrial processes¹. Thus, it is very important to study different nanoparticles systems and develop methods of their characterization². Among large number of methods for nanoparticles investigations low frequency Raman scattering (LFRS) is a powerful tool which can give the information about the size distribution and morphological properties of the nanoparticles. Any nanoparticle has a number of acoustic frequencies which is determined by its shape, size and acoustic properties³.

Not all but some acoustic modes may obey Raman selection rules and can manifest in the LFRS spectra. Frequency shifts of Stokes and anti-Stokes LFRS components are in terahertz or gigahertz range and are determined by the nanoparticles and environment properties⁴. The line width of LFRS is defined mainly by the homogeneous broadening due to acoustic vibration damping and the inhomogeneous broadening due to particle size distribution⁵.

Analysis of LFRS spectral characteristics can give important information about the morphological properties of the nanoparticles and their surrounding environment properties⁶. Was shown⁷ that in different systems consisting of nanoparticles of different nature stimulated analogue of LFRS can be excited. SLFRS was observed in different materials: highly ordered samples such as opal matrices and nanocomposites on their base, nanostructured thin films and disordered materials such as suspensions of different nanoparticles (metal, semiconductor and dielectric)⁸.

¹ A. S. Averyushkin; A. N. Baranov; N. A. Bulychev; M. A. Kazaryan; A. D. Kudryavtseva; M. A. Strokov; N. V. Tcherniega y K. I. Zemskov, "Stimulated low-frequency Raman scattering in aqueous suspension of nanoparticles", Optics Communications, Vol: 389 (2018): 51-53.

² A. S. Averyushkin; N. A. Bulychev; V. F. Efimkov; A. I. Erokhin; M. A. Kazaryan; S. I. Mikhailov; I. N. Saraeva y I.G. Zubarev, "Stimulated Scattering in Ag nanoparticles colloids". Russian Laser Journal, Vol: 27 num 5 (2017): article number 055041.

³ A. E. Erokhin; I. V. Smetanin; S. M. Mikhailov y N. A. Bulychev, "Spectral shifts of stimulated Rayleigh – Mie scattering in Ag nanoparticle colloids". Optics Letters, Vol: 43 num 7 (2018): 1570-1573.

⁴ Yu. O. Kirilina; I. V. Bakeeva; N. A. Bulychev y V. P. Zubov, "Organic-inorganic hybrid hydrogels based on linear poly(N-vinylpyrrolidone) and products of hydrolytic polycondensation of tetramethoxysilane", Polymer Science Series B, Vol: 51 num 3-4 (2009): 135.

⁵ N. A. Bulychev; E. L. Kuznetsova; V. V. Bodryshev y L. N. Rabinskiy, "Nanotechnological Aspects of Temperature-Dependent Decomposition of Polymer Solutions", Nanoscience and Technology: An International Journal, Vol: 9 num 2 (2018): 91-97.

⁶ A. V. Rudnev; N. G. Vanifatova; T. G. Dzherayan; E. V. Lazareva y N. A. Bulychev, "Study of stability and dispersion composition of calcium hydroxyapatite in aqueous suspensions by capillary zone electrophoresis", Russian Journal of Analytical Chemistry, Vol: 68 num 8 (2013): 700.

⁷ I. S. Burkhanov; L. L. Chaikov; N. A. Bulychev; M. A. Kazaryan y V. I. Krasovskii, "Nanoscale metal oxide particles produced in the plasma discharge in the liquid phase upon exposure to ultrasonic cavitation. 2. Sizes and stability. Dynamic light scattering study", Bulletin of the Lebedev Physical Institute, Vol:41 num 10 (2014): 297-304.

⁸ Yu. P. Aleksandrova; N. S. Budanova; A. A. Farmakovskaya; N. S. Okorokova; G. N. Ustyuzhaninova; N. P. Zharova y V. Kohlert, "Ultrasonic treatment impact on the stability of aqueous dispersions of inorganic and organic pigments in the presence of surfactants", Revista Inclusiones, Vol: 7, num Especial (2020): 387-397.

High efficiency of SLFRS conversion is exact evidence of intense coherent nanoparticle oscillations at terahertz or gigahertz frequencies⁹. The precise frequency is determined by the nanoparticles and environment characteristics¹⁰. The coherent phonons excitation at THz or GHz frequencies can lead to many practical applications and from this point of view the experimental SLFRS observation in different systems is of great practical importance.

The purpose of this article is experimental demonstration SLFRS in CuO nanoparticles water suspension, definition the threshold and frequency shift of the scattered wave¹¹.

Preparation and characterization of nanoparticles

In previous studies it was found that combined excitation of electric arc discharge and acoustic cavitation in water and organic liquids was the effective method to create various kinds of solid nanoparticles¹². Chemical compositions, dimensions, morphologies, optical and other properties of these nanoparticles can be easily regulated by the plasma discharge parameters, materials of electrodes and liquids¹³. In other works, it was demonstrated that ultrasonic cavitation itself is a promising way for modification of properties of solid nano- and microparticles¹⁴.

In this work, the capability of plasma combined with ultrasonic cavitation for synthesis of novel nanoparticles was used. For this purpose, electric discharge in aqueous medium was initiated using electrodes made from copper at the voltage range 30-50 V and fixed direct current of 6 A¹⁵. For the detailed description of nanoparticles synthesis in acoustoplasma discharge, it is referred to the works¹⁶.

⁹ Yu. P. Aleksandrova; N. S. Budanova; A. A. Farmakovskaya; N. S. Okorokova; G. N. Ustyuzhaninova; N. P. Zharova y V. Kohlert, "The effect of surface mechanical activation of inorganic pigments on the stability of their aqueous dispersions in the presence of ethyl hydroxyethyl cellulose". Revista Inclusiones, Vol: 7 num 4 (2020).

¹⁰ Yu. P. Aleksandrova; N. S. Budanova; A. A. Farmakovskaya; N. S. Okorokova; G. N. Ustyuzhaninova; N. P. Zharova y V. Kohlert, "Organic pigments surface modification by isobutyl vinyl ether copolymers under the action of ultrasonic", Revista Inclusiones, Vol: 7, num Especial (2020): 11-21.

¹¹ Yu. P. Aleksandrova; N. S. Budanova; A. A. Farmakovskaya; N. S. Okorokova; G. N. Ustyuzhaninova; N. P. Zharova y V. Kohlert, "New approaches to stabilize aqueous soot suspensions in the field of ultrasound". Revista Inclusiones, Vol: 7 num 4 (2020).

¹² Yu. V. Ioni; S. V. Tkachev; N. A. Bulychev y S. P. Gubin, "Preparation of Finely Dispersed Nanographite", Inorganic Materials, Vol: 47 num 6, (2011): 597-602.

¹³ N. A. Bulychev; M. A. Kazaryan; E. S. Gridneva; E. N. Murav'ev; V. F. Solinov; K. K. Koshelev; O. K. Kosheleva; V. I. Sachkov y S. G. Chen, "Plasma discharge with bulk glow in the liquid phase exposed to ultrasound", Bulletin of the Lebedev Physical Institute, Vol: 39 num 7 (2012): 214-220.

¹⁴ A. V. Ivanov; V. N. Nikiforov; S. V. Shevchenko; V. Yu. Timoshenko; V. V. Pryadun; N. A. Bulychev; A. B. Bychenko y M. A. Kazaryan, "Properties of Metal Oxide Nanoparticles Prepared by Plasma Discharge in Water with Ultrasonic Cavitation", International Journal of Nanotechnology, Vol: 14 num 7/8 (2017): 618-626.

¹⁵ N. A. Bulychev; M. A. Kazaryan; A. Ethiraj y L. L. Chaikov, "Plasma Discharge in Liquid Phase Media under Ultrasonic Cavitation as a Technique for Synthesizing Gaseous Hydrogen", Bulletin of the Lebedev Physical Institute, Vol: 45 num 9 (2018): 263-266.

¹⁶ K. V. Pushkin; S. D. Sevruk; N. S. Okorokova y A. A. Farmakovskaya, "The most efficient corrosion inhibitors for aluminum anode of electrochemical cell used as a controlled hydrogen generator", Periodico Tche Quimica, Vol: 15 num 1 (2018): 414-425.

Cupric oxide nanoparticles were characterized by particle size measurements and their absorption in suspension was studied¹⁷. The results are presented in Figures 1 and 2.

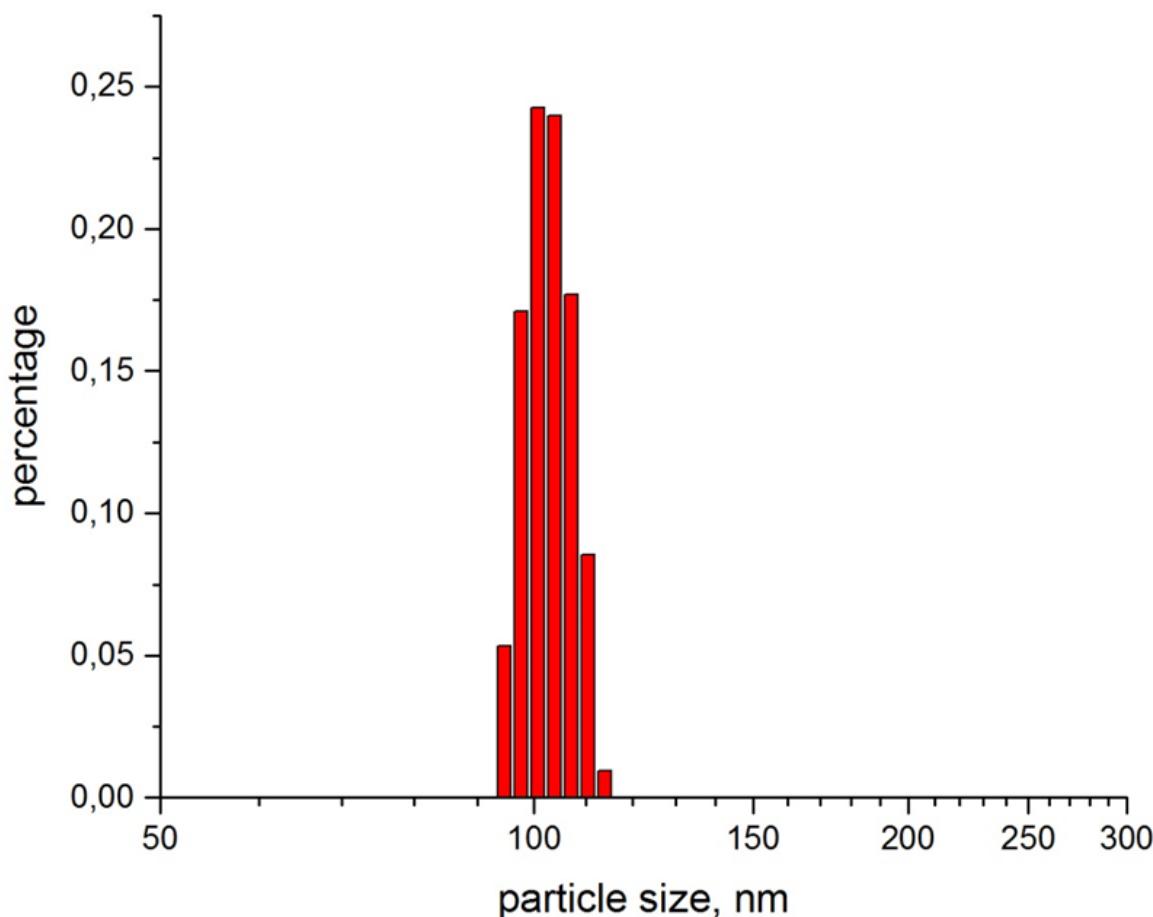


Figure 1
Size distribution of Cu oxide nanoparticles

¹⁷ Yu. P. Aleksandrova; N. S. Budanova; A. A. Farmakovskaya; N. S. Okorokova; G. N. Ustyuzhaninova; N. P. Zharova y V. Kohlert, "Modification of the surface of carbon black with vinyl ether copolymers under ultrasonic treatment". Revista Inclusiones, Vol: 7 num 4 (2020).

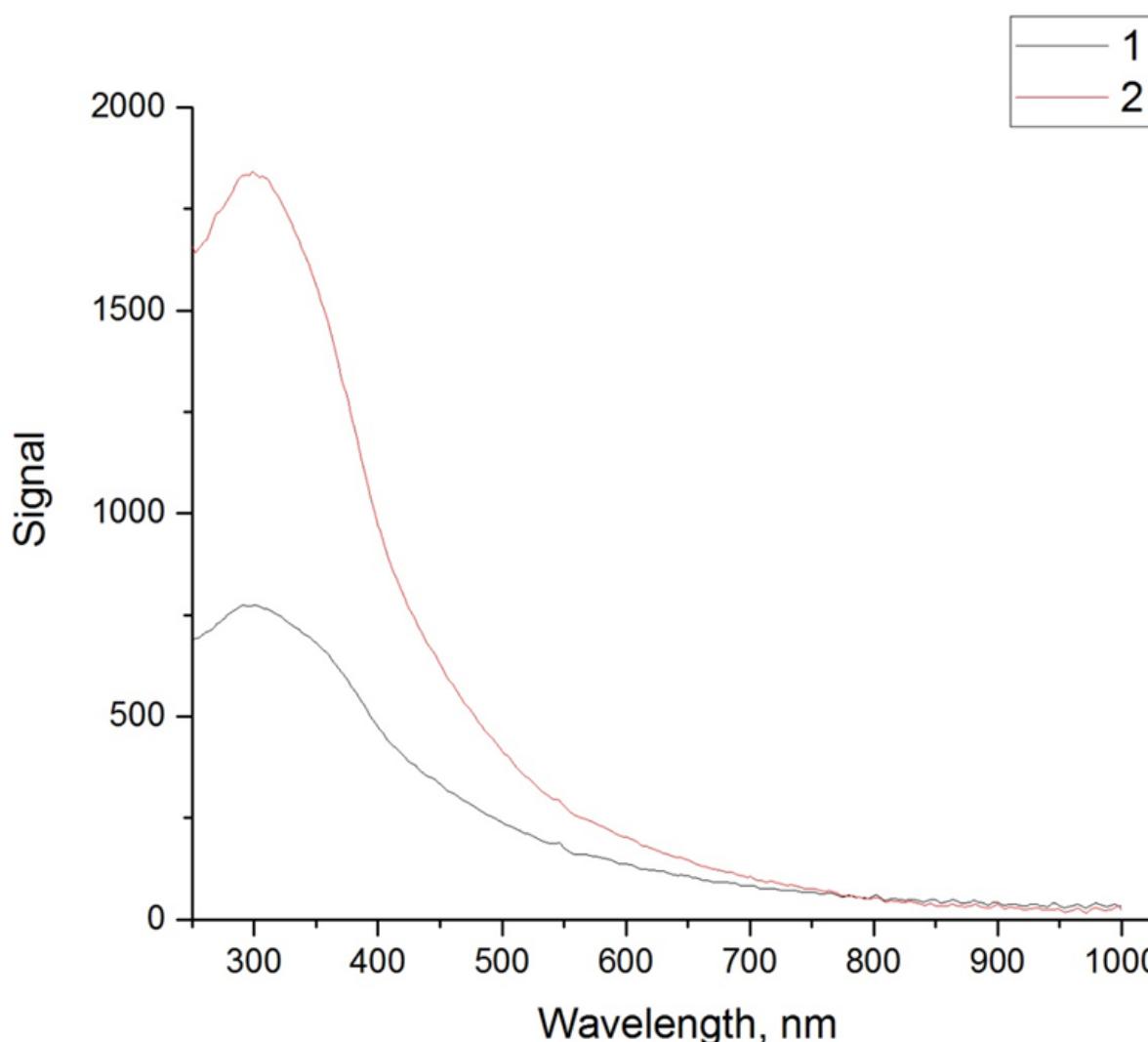


Figure 2
Absorption of Cu oxide nanoparticles suspension

At input laser pulse intensity exceeding a certain threshold SLFRS propagating in forward and backward directions was registered¹⁸. Scattering has been observed both in backward and forward direction approximately at the same threshold. Line width and divergence of SLFRS were near to the corresponding values of the exciting laser light¹⁹. Fig. 3 shows the spectrum of light which passed the cell with Cu oxide suspension. Figure corresponds to the laser intensity 0.02 GW/cm² (above the threshold).

¹⁸ N. Bulychev; W. Van Camp; B. Dervaux; Y. Kirilina; K. Dirnberger; T. Schauer; V. Zubov; F. E. Du Prez y C. D. Eisenbach, “Comparative Study of the Solid-Liquid Interface Behaviour of Amphiphilic Block and Block-like Copolymers”, Macromolecular Chemistry and Physics, Vol: 210 (2009): 287-298.

¹⁹ Yu. P. Aleksandrova; N. S. Budanova; A. A. Farmakovskaya; N. S. Okorokova; G. N. Ustyuzhaninova; N. P. Zharova y V. Kohlert, “Theoretical and experimental studies of the spectral characteristics of doped semiconductors using zinc oxide and sulfide”, Revista Inclusiones, Vol: 7, num 3 (2020): 453-463.



Figure 3

Fabry-Perot spectrum of laser light passing through the cell with Cu oxide nanoparticles suspension (dispersion range 0.714 cm^{-1}).

The SLFRS threshold was estimated to be 0.01 GW/cm^2 and was nearly the same for scattering propagating in forward and backward directions. Maximum efficiency conversion laser light into the scattered wave was about 10 %.

The physical mechanism of SLFRS excitation and amplification is exactly the same as for stimulated Raman scattering in transparent bulk solids and liquids and can be briefly described in the next way. The electromagnetic laser field induces the polarization of the nanoparticles which are vibrating with their own frequency²⁰. This polarization is the source of the inelastically scattered wave. When the laser intensity exceeds the threshold value, the initially spontaneously scattered light can enhance further scattering of the incident wave, and lead to an effective growth of the total scattered light. There is one more force defined by the interaction of the induced dipole moments of neighboring nanoparticles. High SLFRS conversion efficiency is exact evidence of effective coherent excitation of nanoparticles vibrations. The maximum intensity value which can be transformed into acoustic nanoparticles excitation is defined by the nanoparticle own frequency and laser wave's frequency ratio and is about 10^{-4} of the laser intensity.

Conclusions

SLFRS excitation of cupric nanoparticles was initiated and measured. Frequency shift between these waves depends on the nanoparticles dimension and material properties, so, its exact value can easily be controlled. It gives possibility to create a source of biharmonic pumping, which may be used in basic research and for many applications in nonlinear spectroscopy particularly for investigation of the systems with frequencies in giga- and terahertz range. Biharmonic pumping may be used for spectroscopy of different systems with eigenfrequencies in nano and gigahertz range. Due

²⁰ V. N. Nikiforov; N. A. Bulychev y V. V. Rzhevskii, “Elastic properties of HTSC ceramics”, Bulletin of the Lebedev Physical Institute, Vol: 43 num 2 (2016): 74-79.

to short pulse duration, lying in nanosecond range, SLFRS can be applied for determination of nanoparticles size in real time, for instance, in aerosols.

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