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Supercontinuum generation and filamentation of ultrashort laser pulses in hybrid silicate nanocomposite materials on the basis of polysaccharides and hyperbranched polyglycidols

Yu.N. Kul'chin, S.S. Golik, D.Yu. Proschenko, A.A. Chekhlenok, I.V. Postnova, A.Yu. Mayor, Yu.A. Shchipunov

Abstract. **The possibility of using hybrid silicate nanocomposite materials on the basis of polysaccharides and hyperbranched polyglycidols for efficient conversion of pulsed radiation of a femtosecond Ti:sapphire laser at the wavelength 800 nm into supercontinuum in the range from 400 to 1000 nm is experimentally demonstrated. It is established that the addition of a small concentration of Au and CdS nanoparticles to the studied materials essentially affects the efficiency of conversion of the laser radiation energy into the supercontinuum spectrum.**

Keywords: *femtosecond laser, filamentation, supercontinuum, sol-gel process, organo-inorganic nanocomposites, Au nanoparticles, CdS nanoparticles.*

1. Introduction

When high-intensity femtosecond laser pulses propagate through transparent dielectric media, one can observe essential variation of spatial and temporal characteristics of the electromagnetic radiation, which is a consequence of joint manifestation of various nonlinear processes. As a result, the observed spatiotemporal localisation of energy of radiation under the conditions of filamentation is accompanied, in particular, by significant broadening of the initial laser pulse spectrum, referred as supercontinuum generation [1–4]. The resulting radiation possesses a number of unique properties. The frequency spectrum of the supercontinuum is continuous, has no pronounced spectral lines, and is broad enough to overlap one or two octaves in the visible or IR region [2–4]. In some cases the spectral broadening can exceed three octaves [5]. The spectral components of the radiation are characterised by a high degree of spatial and temporal coherence [6], being at the same time phase-coherent with respect to the initial laser pulse [7]. These properties caused wide application of the supercontinuum generation effect in numerous fields, in particular, optical metrology [8, 9], nonlinear spectroscopy [10], optical coherence tomography [11, 12], and super-multiplex data transmission systems [13].

At present the supercontinuum generators are implemented presumably on the basis of optical fibres. However, such generators are unable to offer the possibility of controlling the spatial parameters of the generated radiation, which is necessary for a variety of applications, first of all, in scientific research [14]. Particularly, in the case of photonic crystal fibres, the spatial profile of the supercontinuum is determined by the fibre modal structure, whereas in the case of supercontinuum generation in a solid uniform medium, where the mode selection is absent, the spatial structure of the obtained supercontinuum can be determined by the spatial mode of the initial laser pulse [15]. This fact allows the use of uniform transparent media for generating supercontinuum with complex spatial configuration [16]. Thus, the authors of [15] demonstrated the possibility of using CaF_2 samples under the action of femtosecond laser radiation to generate supercontinuum with helical rotation of the wave front. The resulting screw dislocations having different frequencies may be of particular interest in such fields as interferometry [17], image formation [18], as well as microscopy and lithography [19].

All mentioned above, in turn, stimulates the invention of new materials for supercontinuum generation, which should meet a number of specific requirements. The latter include high nonlinear-optical susceptibilities and fast nonlinear response to the external electromagnetic field, optical stability with respect to propagating high-intensity laser pulses, small optical losses. Beside the physical characteristics, not the least of the factors are fabrication cost of such materials, simplicity of fabrication, reliability in operation, and easy integration in various optical devices. A promising line of development is the production of optical media on the basis of organic or hybrid organo-inorganic polymers [20–22] using the sol-gel technology of synthesis [23], which is somewhat similar to the natural synthesis of such silica-containing biological object, as the sea glass sponge spicules, possessing high nonlinear optical susceptibilities [24].

In the present paper the generation of supercontinuum is experimentally studied for the first time in novel transparent solid nanocomposite materials based on the silica matrix [tetrakis (2-hydroxyethyl) orthosilicate] with addition of sodium

Yu.N. Kul'chin, A.Yu. Mayor Institute of Automation and Control Processes, Far Eastern Branch, Russian Academy of Sciences, ul. Radio 5, 690041 Vladivostok, Russia; e-mail: kulchin@iacp.dvo.ru, mayor@iacp.dvo.ru;
S.S. Golik Institute of Automation and Control Processes, Far Eastern Branch, Russian Academy of Sciences, ul. Radio 5, 690041 Vladivostok, Russia; Far Eastern Federal University, ul. Sukhanova 8, 690091 Vladivostok, Russia; e-mail: golik_s@mail.ru;
D.Yu. Proschenko, A.A. Chekhlenok Institute of Automation and Control Processes, Far Eastern Branch, Russian Academy of Sciences, ul. Radio 5, 690041 Vladivostok, Russia; G.I. Nevelskoy Maritime State University, Verkhneportovaya ul. 50a, 690059 Vladivostok, Russia; e-mail: dima.prsk@mail.ru, alexeyche88@gmail.com;
I.V. Postnova, Yu.A. Shchipunov Institute of Chemistry, Far Eastern Branch, Russian Academy of Sciences, prosp. 100-letiya Vladivostoka 159, 690022 Vladivostok, Russia;
e-mail: ipost@chem.dvgu.ru, YAS@ich.dvo.ru

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hyaluronate polysaccharide and macromolecules of hyperbranched polyglycidols, with inclusion of Au and CdS nanoparticles, pumped with a femtosecond Ti : sapphire laser.

2. Samples

We studied solid nanocomposite materials, produced on the basis of the precursor, completely soluble in water, tetrakis (2-hydroxyethyl) orthosilicate (THEOS) [25], with addition of sodium hyaluronate polysaccharide or macromolecules of hyperbranched polyglycidols (HBP) [26], as well as the same materials with inclusion of Au and CdS nanoparticles. The synthesis of the studied materials was carried out in the aqueous solution, the basic features of the synthesis procedure are described in [21, 27]. To stabilise the obtained nanoparticles of CdS in the aqueous solution and to serve as a catalyser of the hydrolysis reaction in the synthesis of the materials, we used mercaptosuccinic acid ($C_4H_6O_4S$). The study of selected CdS quantum dots by means of electron microscopy has shown that they have spherical shape with the dimensions 1 – 3 nm. To prepare the materials with gold nanoparticles the tetrachlorogold acid was used in the process of synthesis. The electron microscopy has shown that the size of the reduced Au nanoparticles amounts to ~5 nm [21].

Table 1 presents the samples (base substance + additions) used in the synthesis of new nanocomposite materials, differing in the molecular composition and concentration of additions. The base substance and its concentration were kept the same in all samples: H_2O + THEOS (50 mass %). Figure 1 shows the transmission spectra of the samples, obtained using the Varian Cary 5000 spectrophotometer.

Table 1. The samples under study.

Addition	Addition concentration
HBP	1 wt %
Sodium hyaluronate + $HAuCl_4$	1 wt % + 0.0008 or 0.0015 wt %
HBP + $HAuCl_4$	1wt % + 2×10^{-5} or 3.8×10^{-5} M
$C_4H_6O_4S$ + CdS nanoparticles	0.3 wt %

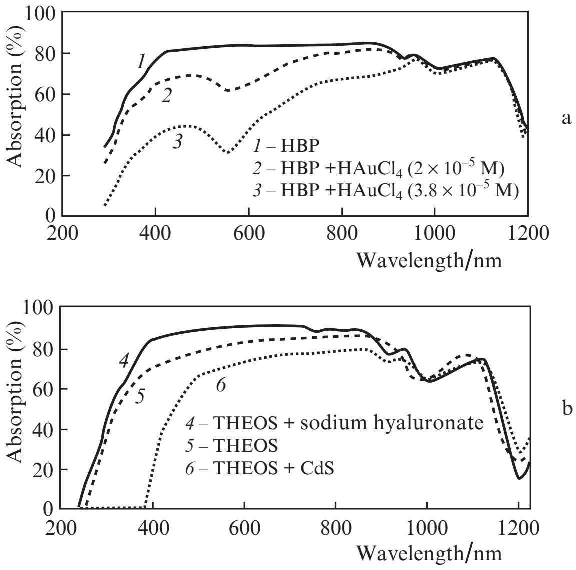

Figure 1. Spectra of transmission of the samples based on THEOS (50 wt %) and HBP macromolecules (1 wt %) with Au nanoparticles (a) and sodium hyaluronate with CdS nanoparticles (b).

The experimental studies have shown that the optical properties of the investigated samples depend on the THEOS concentration and the type of additions. The samples, synthesised basing on HBP and THEOS (10 wt %), demonstrated insignificant opalescence; with the growth of THEOS concentration the transparency of the material increased. This effect is caused by the structure of mineralised macromolecules. Nanocomposite materials based on THEOS (10 wt %) are inhomogeneous. They contain micron- and submicron-size clusters, the presence of which may be the cause of the above-mentioned opalescence [20]. The samples, containing THEOS with the concentration of 50 mass %, are more homogeneous, because they consist of clusters with the size of ~300 nm and smaller [20]. For this reason all the materials, studied in the present paper, were synthesised with the optimal content of THEOS (50 wt %).

3. Experimental technique

The study of supercontinuum generation in new solid nanocomposite materials was carried out using the experimental setup shown in Fig. 2. The laser system, consisting of the Tsunami femtosecond oscillator (*1*) (Spectra Physics) and the Spitfire PRO 40F regenerative amplifier (*2*) (Spectra Physics), generated pulses having the duration ~42 fs with the centre wavelength 800 nm and the half-width of the spectrum 35 nm. The maximal energy in a single pulse was 1 mJ, the repetition rate of the pulses was 100 Hz, and the beam diameter was 7 mm.

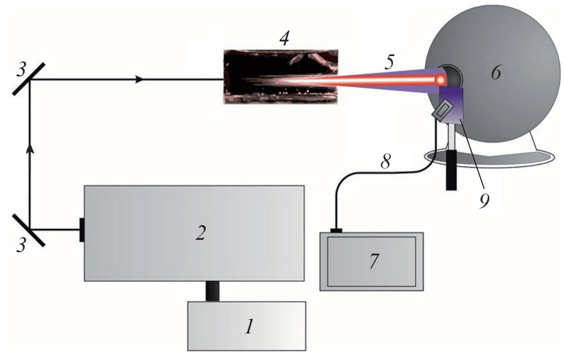

Figure 2. Schematic diagram of the experimental complex.

The input pulse duration was monitored using the autocorrelation method with second harmonic generation. By means of the optical system, consisting of multilayer dielectric mirrors (*3*), the laser radiation was sent into the studied sample (*4*), and the supercontinuum radiation was collected with the integrating sphere (*6*). The supercontinuum spectra were recorded using the Maya 2000Pro spectrometer (Ocean Optics) (*7*); the blue-green light filters (*9*) were installed in front of the entrance objective of the optical waveguide (*8*). Finally, the spectra were processed using computer programmes with the instrument function of the recording system taken into account.

4. Results and discussion

The spectral characteristics of the resulting conical supercontinuum radiation in 15-mm-long samples, based on THEOS (50 wt %) and containing the HBP macromolecules with various molecular masses, as well as the HBP macromolecules with various concentrations of gold nanoparticles, are presented in Fig. 3. The initial spectrum of the laser pulse is also shown.

In accordance with Fig. 3, the gold nanoparticles, which are the dopant of these materials, exert essential influence on the process of frequency conversion of femtosecond pulses. The integral intensity of the transmitted radiation in the range of wavelengths 420–720 nm for samples with addition of gold nanoparticles exceeded by more than an order of magnitude the corresponding values for the samples based on the HBP macromolecules. The increase in the molecular mass of hyperbranched polyglycidols from 3000 to 6000000 amu caused the reduction of the supercontinuum intensity in the entire wavelength range. The effect of tetrachlorogold acid on the resulting transmission coefficient of the materials was caused by the presence of the reduced Au nanoparticles, which significantly increase the absorption of the supercontinuum spectrum in the optical range of wavelengths (see Fig. 1). The absorption is due to the localised surface plasmon of gold nanoparticles. In the sample, for which the spectrum is shown by curve (*3*) in Fig. 1, the plasmon resonance corresponds to the wavelength 528 nm.

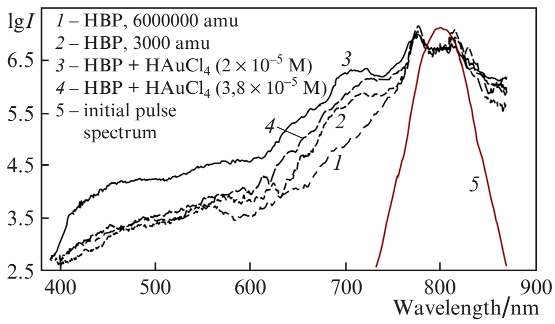

Figure 3. Supercontinuum spectra generated in the samples based on THEOS (50 wt %) and HBP macromolecules (1 wt %) with different molecular mass and concentration of gold nanoparticles. The initial spectrum of the laser pulse is also shown.

In the 15-mm-long samples based on THEOS (50 wt %) with sodium hyaluronate, the presence of gold nanoparticles in small concentrations led to less efficient conversion of the initial pulse energy into the resulting spectra of supercontinuum, as compared to the analogous samples without Au nanoparticles (Fig. 4). Increasing the concentration of tetrachlorogold acid $HAuCl_4$ in the process of the material synthesis gave rise to additional absorption of the supercontinuum radiation in the sample.

The supercontinuum generation spectrum in the sample based on THEOS (50 wt %) with the addition of $C_4H_6O_4S$ and CdS nanoparticles is presented in Fig. 5 [curve(*1*)]. In the same figure the spectra of laser pulses, passed through the THEOS sample without additions [curve (*2*)] and through the thin-wall silica cuvette filled with distilled water [curve (*3*)] are shown for comparison. The registration of supercontinuum spectra was implemented using the FSQ-BG39 optical filter (Newport, USA). From the comparison of curves (*1*) and (*2*) it follows that the presence of CdS nanoparticles in the samples based on THEOS leads to nearly fourfold increase in the supercontinuum generation intensity in the wavelength range 550–600 nm.

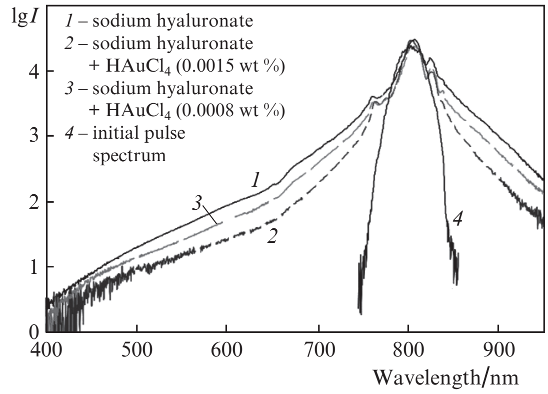

Figure 4. Supercontinuum spectra generated in the samples based on THEOS (50 wt %) and sodium hyaluronate (1 wt %) with different concentrations of $HAuCl_4$. The initial laser pulse spectrum is also shown.

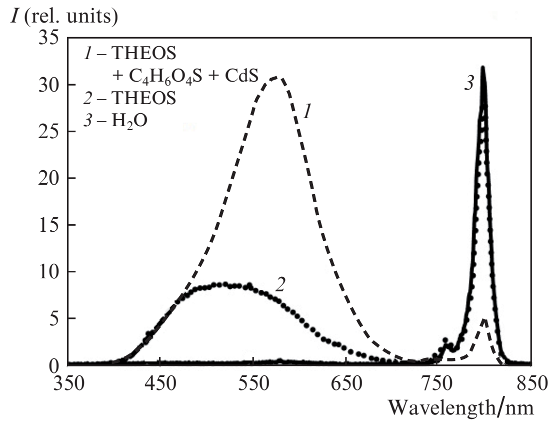

Figure 5. Supercontinuum spectra generated in the process of propagation of femtosecond pulses through samples based on THEOS (50 wt %) + CdS + $C_4H_6O_4S$ (0.3 wt %), THEOS (50 wt %) without additions, and through the cuvette with distilled water. The thickness of samples and cuvette with water was 10 mm.

Figure 6 presents the photograph of the sample based on THEOS (50 wt %) with addition of sodium hyaluronate (0.25 wt %), in which one can observe multiple filamentation of the ultrashort pulses. The coordinate axes correspond to the geometrical dimensions of the sample; the laser radiation propagates from left to right. In accordance with Fig. 6, the minimal distance, at which a filament begins to form in the sample, amounts to ~3 mm. This allows estimation of the nonlinear refractive index of the material, using the semiempirical formulae [28] for the critical value $P_c = 3.72\lambda^2(8\pi n_2 n_0)^{-1}$ of the input power of the ultrashort pulse and the self-focusing length

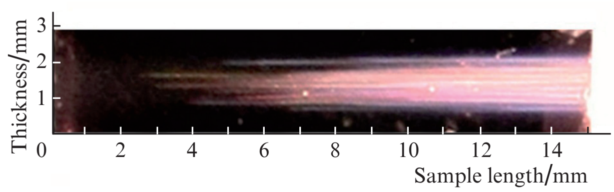

Figure 6. Photograph of multiple filamentation of laser radiation in the sample, based on THEOS with sodium hyaluronate.

$$z_c = \frac{0.367kn_0r_0^2}{[(\sqrt{P/P_c} - 0.852)^2 - 0.0219]^{1/2}}.$$

Here k is the wavenumber; r_0 is the initial radius of laser beam; and n_0 is the linear refractive index of the material. The corresponding values of these parameters in our experiment were $n_0 = 1.54$, $r_0 = 3.5$ mm, $\lambda = 800$ nm, $P = 2.38 \times 10^{10}$ W, $z_c = 3$ mm. Hence, the approximate estimation of the nonlinear refractive index of the sample based on THEOS (50 wt %) with addition of sodium hyaluronate (0.25 wt %) yields $n_2 \sim 85 \times 10^{-13}$ cm^2 W^{-1}.

5. Conclusions

Novel solid nanocomposite materials based on completely water soluble precursor, tetrakis (2-hydroxiethyl) orthosilicate, with addition of polysaccharide sodium hyaluronate and macromolecules of hyperbranched polyglycidols with inclusion of Au and CdS nanoparticles allow the generation of supercontinuum under the pumping with the radiation of the femtosecond Ti : sapphire laser with the pulse energy up to 1 mJ at the interaction length from 3 mm. The variation of the addition type, its concentration and the number of nanoparticles in the process of the material synthesis affect the resulting spectral characteristics of the generated supercontinuum. Thus, in the samples, based on macromolecules THEOS (50 wt %) + HBP (1 wt %) + $HAuCl_4$ (2×10^{-5} M), small concentrations of gold nanoparticles give rise to an essential increase in the integral intensity of the transmitted radiation in comparison with the analogous samples, containing no nanoparticles. Further growth of the concentration of the reduced gold nanoparticles in this material increases the linear absorption coefficient and reduces the efficiency of the spectral transformation of the initial laser pulse into the supercontinuum. The presence of small concentrations of CdS nanoparticles in the samples based on THEOS (50 wt %) (CdS + $C_4H_6O_4S$, 0.3 wt %) increases the intensity of supercontinuum generation in the range 550–600 nm by four times.

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