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Observation of surface plasmon resonance of gold nanoparticles in energy-related material: pentaerythritol tetranitrate

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Abstract. **The surface plasmon resonance of gold nanoparticles in a polycrystalline energy-related material – pentaerythritol tetranitrate (PETN) – has been observed for the first time. The extinction spectra of this material are recorded, and its absorption characteristics are determined by the photoacoustic method using pulsed laser irradiation. Using the data obtained, it is concluded that gold nanoparticles are promising inclusions in explosive materials when designing an optical detonator.**

Keywords: *gold nanoparticles, surface plasmon resonance, energy-related materials, PETN, laser, optical spectroscopy, photoacoustic method.*

1. Introduction

To increase safety when carrying out blasting, it has been proposed to use new energy-related materials that are selectively sensitive to pulsed laser irradiation and have a relatively low sensitivity to heating, impact, friction, etc. [1–6]. These materials include composites based on high explosives and light-absorbing additives. The ignition criteria for octogen $C_4H_8N_8O_8$ and triaminotrinitrobenzene $C_6H_6N_6O_6$ (TATB) under CO_2 laser irradiation were determined in [4]. It was found in [5] that the introduction of soot reduces the critical energy density for initiation of diaminodinitroethylene $C_2H_4N_4O_4$ (FOX-7) and octogen. As was shown in [2, 3], the critical laser pulse energy density, initiating the explosive decomposition of PETN–metal nanoparticle composites, depends on the radiation wavelength, material of nanoparticles, and their mass fraction in the composite. At the same time, the optimisation of the composite components is far from being complete. An approach to analysing the initiation that is based on determination of the critical conditions (combined with direct measurements of the optical spectra of the materials under study) and their relationship with the excitation wavelength and sample composition is being developed [7]. It was suggested in [8] that a chemical reaction is initiated in the optical breakdown channel, and it was shown in [9] (within the microzone model of thermal explosion) that laser heating of nanoparticles leads to the formation of exothermic reaction zones. To explain the probabilistic character of explosion, a fluctuation initiation model was proposed in [10, 11].

We propose to use gold nanoparticles as additives to explosives. A specific feature of the application of gold nanoparticles of certain size as fine additives is that the maximum of their surface plasmon resonance band lies in the spectral region close to the neodymium laser second harmonic (λ = 532 nm). Therefore, the study of the absorptive ability of mixed compositions based on high explosives and inclusions of gold nanoparticles at a wavelength of 532 nm is an urgent problem. Gold nanoparticles, being added to explosives, can selectively initiate explosion only at certain optical radiation parameters (wavelength and energy density).

The purpose of this study was to determine the fundamental possibility of designing an energy-related material that can selectively absorb radiation of certain wavelength. To this end, we developed a technique of imbedding gold nanoparticles into explosives by an example of PETN and investigated the composite obtained by optical spectroscopy and the photoacoustic method.

2. Fabrication technique and extinction spectra of the composite

Colloidal solutions of gold nanoparticles were obtained by the Frens method [12, 13], which is based on citrate reduction of chloroauric acid $H[AuCl_4]$. The table contains the characteristics of the colloidal solutions: the plasmon resonance peak wavelengths λ_{max}; the gold particle sizes corresponding to the plasmon resonance peak, taken from [13]; and the gold particle sizes obtained in this study.

The extinction spectra of the colloidal solutions (the samples were 1 mm thick) were recorded on a Shimadzu UV-3600 spectrophotometer in the wavelength range of 300–1600 nm (Fig. 1). One can see that the spectra contain the plasmon absorption band of gold nanoparticles, and that the absorption is close to zero near λ = 1064 nm.

Table 1.

Sample No.	λ_{max}/nm	Average particle diameters/nm [13]	Average particle diameters/nm, obtained in this study
1	519	13	12.2 ± 0.4
2	527	30	23.8 ± 0.6
3	532	40	34.6 ± 1.4
4	536	50	46.3 ± 2.1

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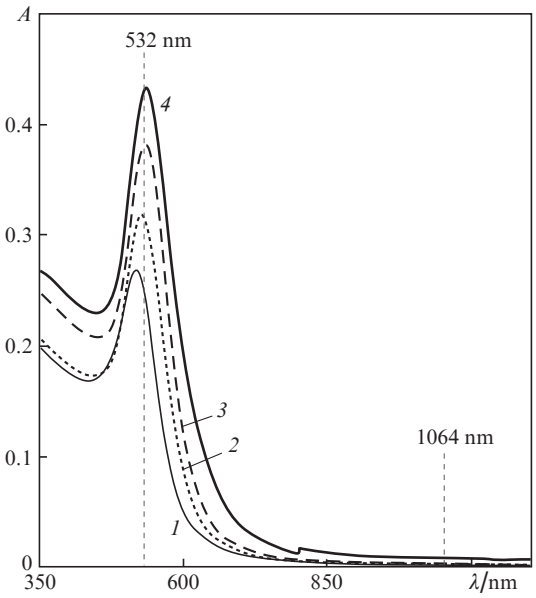

Figure 1. Extinction spectra of the colloidal solutions of gold nanoparticles. The numbers of the curves correspond to the numbers of samples in the table.

Micrographs of gold nanoparticles were obtained by transmission electron microscopy (TEM), and nanoparticle size distribution histograms were constructed (Fig. 2).

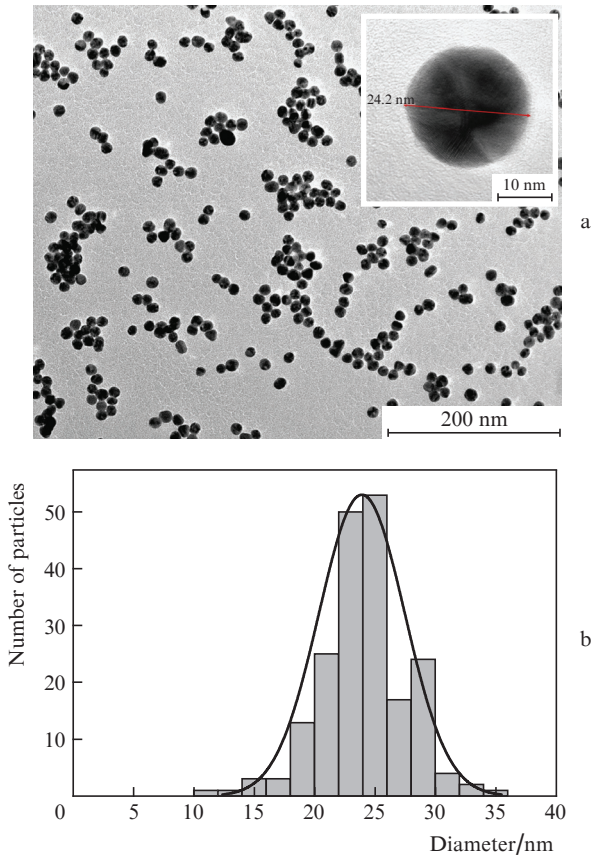

Figure 2. (a) TEM photograph and (b) size distribution histogram for gold particles (data for sample 2 from the table).

A PETN sample with inclusions of gold nanoparticles was prepared in the following way. A weight (400 mg) of PETN powder with a maximum particle size ranging from 1 to 2 μm was poured with hexane and placed in an ultrasonic bath. Then an aqueous colloidal solution of gold nanoparticles of necessary volume (the nanoparticle content in the solution was 0.15 mg mL^{-1}) was added (upon continuous stirring) in 1-mL portions. The possibility of preparing homogeneous mixtures of the objects of study was established after numerous experiments, because PETN powder is poorly wetted with water. The mixture was exposed to ultrasound for about 30 min. Then it was dried to the air-dry state and pressurised (using a special mold) into a hole 3 mm in diameter in a 1-mm-thick copper plate. Thus we obtained samples in the form of pellets 3 mm in diameter and 1 mm thick, having a density of 1.73×0.03 g cm^{-3} (the PETN single crystal density is 1.77 g cm^{-3}).

Figure 3 shows the extinction spectra of the pellets. It can be seen that the spectra contain the plasmon absorption band characteristic of gold nanoparticles. Thus, the presence of gold nanoparticles in the PETN matrix was confirmed.

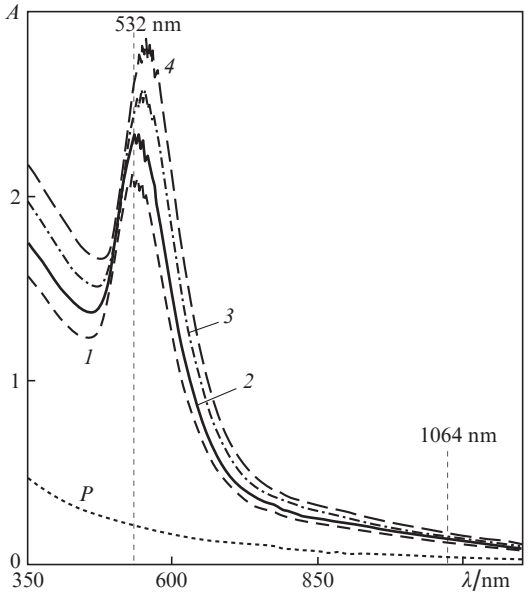

Figure 3. Extinction spectra of PETN samples with inclusions of gold nanoparticles (concentration 0.1 wt.%). The numbers of the curves correspond to the numbers of colloidal solutions (table) from which the PETN–gold mixtures were prepared (sample thickness 0.3 mm); *P* is the extinction spectrum of 'pure' PETN polycrystal.

The second harmonic of a neodymium laser (λ = 532 nm) is fairly close to the peak of the plasmon absorption band.

It is noteworthy that the absorption peak is slightly red-shifted with respect to the peaks of colloidal solutions. This shift for different samples is 10–14 nm. Figure 4 illustrates this effect. In this stage of studies, it can be explained by the difference in the refractive indices of water (1.33) and PETN (1.56) and, possibly, the stronger interaction between gold nanoparticles and surrounding particles in the PETN–gold nanoparticle composite.

As well as in colloidal solutions, absorption in the vicinity of 1064 nm is practically absent in PETN–gold mixtures. However, intense absorption at the wavelength of the second harmonic of a neodymium laser (532 nm) occurs in both

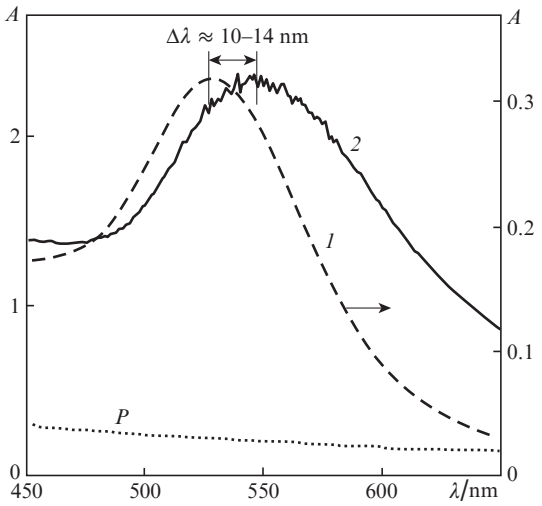

Figure 4. Extinction spectra of (*1*) sample 2 and (*2*) the PETN–gold mixture fabricated on its basis; *P* is the extinction spectrum of 'pure' PETN polycrystal.

cases. Obviously, gold nanoparticles are responsible for this selective absorption.

3. Photoacoustic study of the material

The results of the spectrometric study of PETN with inclusions of gold nanoparticles are presented in Section 2. It is shown that the spectra of both the initial samples of colloidal gold and the composite of PETN with inclusions contain a strong surface plasmon resonance band at 520–540 nm. The second harmonic of a pulsed neodymium laser (532 nm) fits well in this range.

However, when the objects of study are samples with a thickness exceeding 0.5 mm and a mass concentration of gold nanoparticles above 0.05%, their spectrometry is hindered because of the high optical density of these samples.

Taking into account these considerations and trying to find out how the energy of high-intensity (in comparison with the emitter energy used in the spectrometric method) pulsed laser radiation behaves (is absorbed or scattered) with a change in the concentration of gold nanoparticles in PETN samples, we applied the photoacoustic method, which makes it possible to determine absorbed energy profiles and extinction coefficients in both absorbing and scattering media [14].

The measurement of the photoacoustic characteristics (extinction coefficient k_{eff} and photoacoustic signal amplitude U) by the pulsed photoacoustic method was performed in the scheme with direct detection of photoacoustic signals [14] (Fig. 5).

Photoacoustic signals were excited by a pulsed Q-switched LQ929 YAG:Nd laser (SOLAR Laser Systems, Minsk) (*1*) with a pulse width of 14 ns. We used the first (λ = 1064 nm) and second (λ = 532 nm) harmonics. The pulse energy density was 30 mJ cm^{-2}. This radiation intensity did not lead to a significant sample damage during the pulse and, at the same time, was sufficient to record acoustic response oscillograms. The laser energy was measured using a PE50BF-C pyroelectric energy meter (Ophir® Photonics). The instability of the initiating pulse energy did not exceed 3%. A major part of radiation was focused by lens (*3*) onto sample (*4*) (inserted in a copper plate). The laser beam cross section on the sample

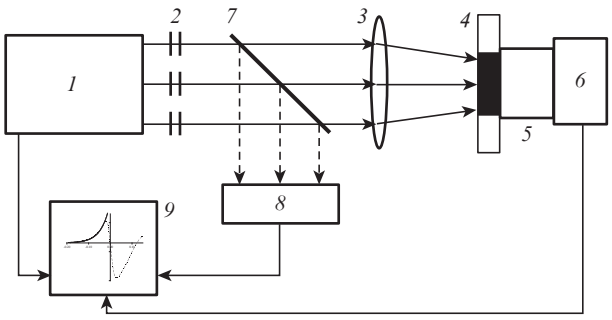

Figure 5. Schematic of the experimental setup:
(*1*) YAG:Nd laser; (*2*) neutral light filters; (*3*) focusing lens; (*4*) sample in copper holder; (*5*) acoustic delay; (*6*) piezoelectric transducer; (*7*) beam splitter; (*8*) photodiode; (*9*) oscilloscope.

surface was close to rectangular, corresponding to a beam diameter of 2 mm. The sample was brought [through duralumin delay (*5*)] into acoustic contact with piezoelectric transducer (*6*), made of PZT-19 ceramics (8 mm in diameter, 4 mm thick, with deposited silver electric contacts). To monitor the pulse energy, part of laser radiation was directed by beam splitter (*7*) to a calibrated photodiode. The radiation affected only the open surface of the samples. The signal from the piezoelectric transducer was recorded using a LeCroy WJ332A *9* digital oscilloscope (transmission band 350 MHz, sampling rate 2 GHz). The elements of the system were synchronised using the internal generator of the laser control unit.

Using the photoacoustic method, we obtained the extinction coefficients of the samples on the first (λ = 1064 nm) and second (λ = 532 nm) neodymium laser harmonics. Typical photoacoustic signals are presented in Fig. 6.

Based on the character of these signals, one can conclude the following. Under the pulsed laser irradiation of the samples

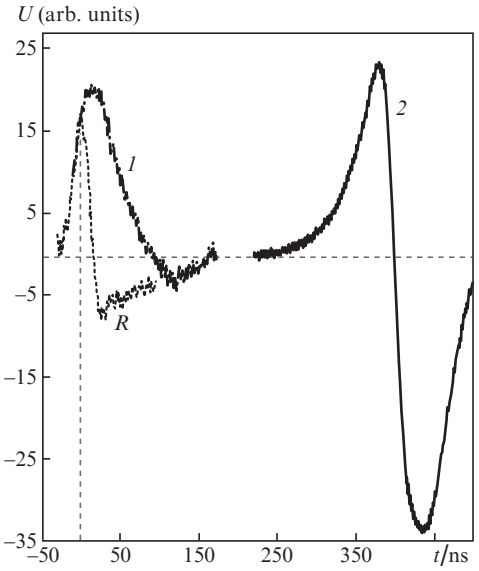

Figure 6. Typical photoacoustic signals from a sample exposed to the (*1*) first and (*2*) second laser harmonics. The sample is PETN with inclusions of 0.1 wt.% gold nanoparticles (colloidal solution 2). *R* is the reference signal in the absence of sample. Zero time is considered to be the instant at which the signal *R* reaches a maximum. The intensities of signals *1* and *R* are increased by a factor of 4. The laser energy density is 30 mJ cm^{-2}.

(with the energy densities in use), the second harmonic is absorbed more efficiently than the first one. It can be seen that, in the case of the first harmonic, the laser beam, being hardly absorbed, passes through the sample to affect the piezoelectric sensor [Fig. 6, curve (*1*)]. For the second-harmonic irradiation, a sound wave is generated according to the thermo-optic mechanism [15]*.

According to [14], the temporal profile of the photoacoustic signal leading edge is described by the expression

$$U(t) \sim \exp(t/\tau), \quad (1)$$

where $\tau = (kc_0)^{-1}$, c_0 is the speed of sound in the sample, and k is the extinction coefficient. According to our measurements, the speed of sound in the PETN–gold nanoparticle composites is 2500 ± 200 m s^{-1}. The photoacoustic signal leading edge was approximated to calculate the extinction coefficient k of the samples.

We investigated the acoustic response to the laser irradiation of the samples with nanoparticle contents of 0.03, 0.075, 0.1, and 0.2 wt.% (the photoacoustic signal is not recorded at lower concentrations, while at higher concentrations the technique is inapplicable because of the violation of the linearity condition).

Pressed PETN samples free of inclusions have a zero acoustic response. In other words, within the sensitivity of the measuring system, the absorption of light and light-to-heat conversion are not observed; i.e., the medium is weakly absorbing. On the contrary, the samples with nanoparticle inclusions yield well-detectable signals.

The experimental values of $(kc_0)^{-1}$ were used to determine the k values for different concentrations of nanoparticle inclusions. The results are presented in Fig. 7. It can be seen that k linearly depends on the nanoparticle concentration. This fact suggests that the nanoparticles in the samples mainly absorb rather than scatter laser radiation [14].

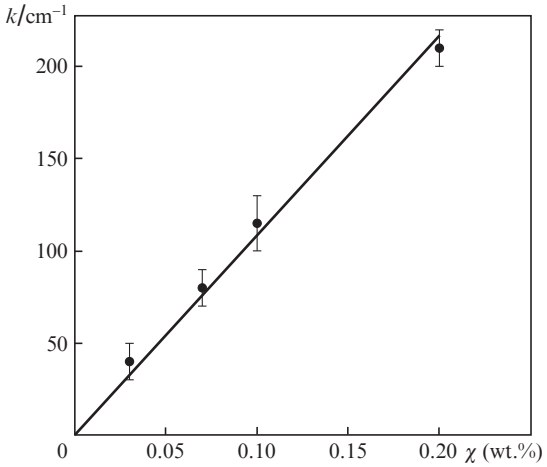

Figure 7. Dependence of k on the concentration χ of gold nanoparticle inclusions in sample. Each point corresponds to a measurement averaged over five samples. The confidence interval is calculated by the Student method with a confidence probability of $\alpha = 0.95$.

*The laser irradiation does not lead to any visible changes throughout the entire sample volume. In addition, the extinction spectra measured before and after the irradiation are reproduced well.

4. Conclusions

The following conclusions can be drawn based on the results obtained.

(i) A technique for introducing gold nanoparticles in form of a colloidal solution into an energy-related material (PETN) was developed.

(ii) The extinction spectra of a mixed composition of PETN with gold nanoparticle inclusions were investigated. It was found that this material can selectively absorb 532-nm light, in contrast to 'pure' PETN (without inclusions).

(iii) It was shown by the photoacoustic method that inclusions of gold nanoparticles in the samples mainly absorb rather than scatter the second-harmonic radiation of pulsed neodymium laser.

To conclude, we should note that the fundamental possibility of fabricating a material with necessary optical properties (the position of the optical absorption band peak) for application in special-purpose devices was implemented in this study.

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