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The effect of laser radiation on the properties of platinum nanoparticles produced in a gas discharge

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Abstract. This study is devoted to the investigation of the effect of laser radiation of different wavelengths (355, 527 and 1054 nm) on the morphology, structure and optical properties of platinum nanoparticles synthesized in a gas discharge. The results confirmed that all three types of lasers can be used to modify platinum nanoparticles and to change their sizes. The best modification that is shape transformation from aggregates to individual nanoparticles is achieved by using an infrared laser (1054 nm). It was shown that all obtained nanoparticles have a maximum of plasmon resonance in the ultraviolet region in the wavelength range from 200 to 300 nm, which is similar to the additionally simulated calculations based on the theory of Mie absorption spectra of monodisperse platinum particles with sizes from 5 to 120 nm.

Keywords: Platinum nanoparticles (Pt NPs), spark discharge, laser radiation, reshape, plasmon resonance, ultraviolet (UV)

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Влияние лазерного излучения на свойства наночастиц платины, полученных в газовом разряде

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Аннотация. Данное исследование было посвящено влиянию лазерного излучения различных длин волн (355, 527 и 1054 нм) на свойства наночастиц платины, синтезированных в газовом разряде. Результаты подтвердили, что все три типа лазеров могут быть использованы для модификации наночастиц платины и изменения их размеров. Было показано, что все полученные наночастицы обладают максимумом плазмонного резонанса в ультрафиолетовой области в диапазоне длин волн от 200 до 300 нм, что находится в согласии с дополнительно смоделированными по теории Ми спектрами поглощения монодисперсных частиц платины с размерами от 5 до 120 нм.

Ключевые слова: наночастицы платины, газовый разряд, лазерное излучение, модификация, плазмонный резонанс, ультрафиолет (УФ)

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Introduction

The catalytic and optical properties of Pt NPs make them applicable to a wide range of scientific and engineering industries, such as optics, electronics, medicine and fuel cells [1, 2]. There are many physical and chemical methods for the synthesis of platinum nanoparticles, for instance, laser ablation in liquids, polyol and green synthesis [1, 3] and gas phase methods [4]. One of the most future-oriented method to produce nanoparticles with high purity chemical composition and ability to control the size is suggested to be gas discharge generation [5]. The power of additional laser radiation and variation of gas flow rate in gas discharge setup can adjust the particle size distribution and morphology of aerosol nanoparticles [4, 6]. Pure platinum nanoparticles (Pt NPs) with various sizes can be fabricated by gas discharge [7] with a theoretically presumable plasmon resonance in the ultraviolet region with a peak maximum at a wavelength of 200–500 nm depending on the particle size [8]. This study presented the results of the effect of laser radiation on the morphology, structural and optical properties of aerosol nanoparticles of metallic platinum by exposing the aerosol flow of nanoparticles to laser radiation of wavelengths 355, 527 and 1053 nm, as well as theoretical and experimental extinction spectra of Pt NPs of various diameters.

Materials and Methods

Primary Pt NPs were synthesized in the spark discharge during the electrical erosion of the electrodes in an atmosphere of high purity argon (99.9999%). Excess gas pressure was 0.6 atm and the aerosol flow varied from 50 to 600 ml/min. The electrodes used in the work were made of Pt a purity of 99.9999% and had a shape of hollow cylinders with an outer diameter of 8 mm (Plaurum Group, Verhnyaya Pyshma, Russia) the thickness of the cylinder wall was 1 mm.

The interaction of radiation with aerosol nanoparticles was carried out in a laser modification cell developed by our laboratory, which combines an aerosol flow with a laser beam along its length [12]. The experimental setup is shown in Fig. 1. In a such system, nanoparticles absorb a fraction of the radiation energy, which is converted into heat and spent on partial or complete modification, practically without heating the environment. In the experiments, we used pulsed lasers with the wavelength of 355, 527 and 1054 nm (TECH-1053, “Laser-export” Co. Ltd., Moscow, Russia) with a pulse duration of about 40 ns and controlled pulse repetition rates in the range of 10 Hz–10 kHz.

Four samples of Pt NPs, obtained in spark discharge generator with gas flow rate 50 ml/min, gap voltage 1.3 kV, capacity 107 nF, frequency of discharge 330 Hz without radiation and using lasers 355 nm (230 mW), 527 nm (90 mW), 1054 nm (230 mW) were investigated by the transmission electron microscope (TEM) JEM-2100 (JEOL, Ltd., Tokyo, Japan). Extinction spectra of colloids prepared from platinum nanoparticles in chromatographic isopropanol with additional ultrasonication for 30 minutes were measured on a JASCO V-770 spectrophotometer. Measurements of the size distribution of nanoparticle agglomerates were carried out using a particle mobility analyzer (TSI Inc, SMPS 3936 aerosol spectrometer).

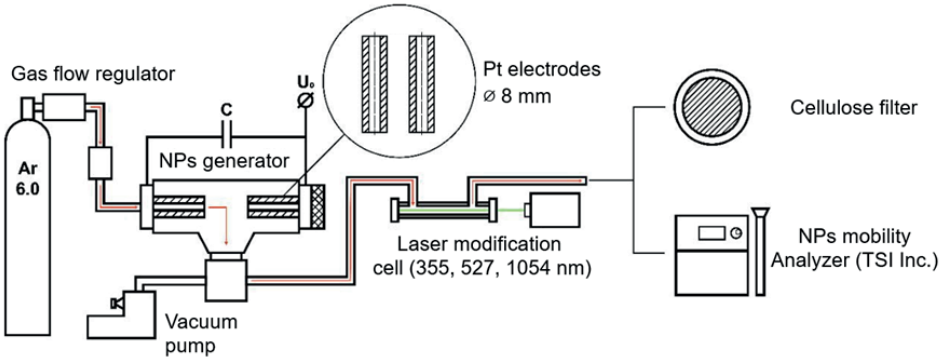

Fig. 1. Scheme of spark discharge synthesis of Pt NPs

Results and Discussion

According to the TEM images (Fig. 2, *a-d*), primary particles of platinum nanoparticles with an average size of 5.9 ± 2.4 nm, forming large aggregates of nanoparticles, were obtained in the gas discharge. Interaction with laser radiation with a wavelength of 355 nm leads to a partial increase in primary nanoparticles to an average size of 22.6 ± 11.8 nm and the appearance of spherical particles up to 190 nm in size. Laser radiation with wavelengths of 527 nm and 1054 nm increases the average particles sizes to 27.2 ± 14.2 nm and 44.2 ± 34.5 nm respectively, and individual spherical nanoparticles up to 250 nm in size were observed. Size distributions of nanoparticles are approximated by a lognormal function and shown in Fig. 2, *e*. During the analysis of electron diffraction patterns (Fig. 2, *f*), it was revealed that the nanoparticles were crystallized in the phase of crystalline platinum of Fm3m space group.

Fig. 2, *g* shows the investigated dependence of the average size of platinum agglomerates on the aerosol flow. In this experiment, one can observe how the degree of particle reduction during laser modification changes depending on the carrier gas flow. For two lasers with wavelengths of 355 and 1054 nm with maximum output powers of 250 and 400 mW, respectively, the particle sizes were obtained before and after interaction with the lasers. It was found that with an increase in the gas flow from 50 to 600 ml/min, a decrease in the size of agglomerates by 20% (from 295 to 235 nm) is observed without the use of a laser. During the interaction between nanoparticles agglomerates and UV laser, the size increases by a factor of 2 (from 95 to 190 nm) while the flow

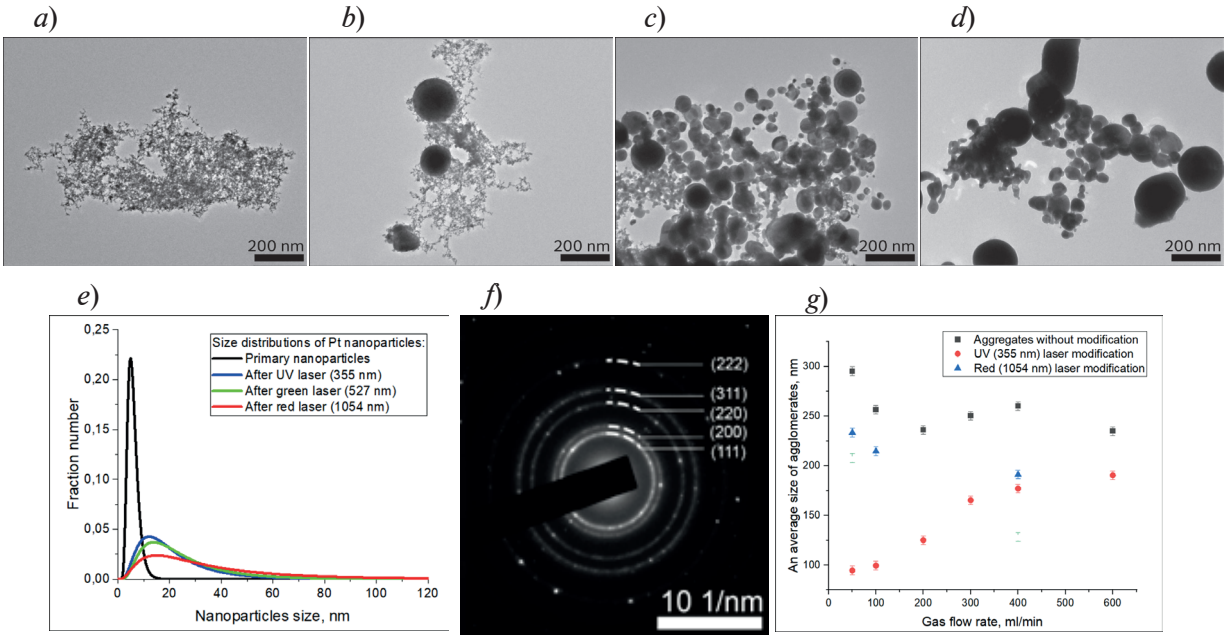

Fig. 2. TEM images of primary Pt NPs (no laser) (*a*); after UV laser (*b*); green laser (*c*); infrared laser (*d*); size distributions of Pt NPs before and after laser radiation (*e*); electron diffraction pattern (*f*); graph of the dependence of the average size of platinum agglomerates on the aerosol flow (*g*)

rate is enhanced. Thus, at high aerosol flow rates, the effect of laser modification of nanoparticle's morphology reduced. With an increase in gas flow from 50 to 400 ml/min, a decrease in the size of modified particles by red laser is observed approximately 18 % (from 233 to 191 nm). Thus, the size drop during the modification by laser with wavelength of 1054 nm is negligible and similar to the changes in size of primary agglomerates.

With laser modification, there is a change in the modification of nanoparticles occurs, namely, large particles appear, but agglomerates are also present as before the interaction with the laser. The expected result, as with the modification of silver and gold [4, 6], that completely spherical large platinum particles would appear did not occur, apparently due to insufficient laser power. The largest number of individual spherical sintered particles was observed by TEM images of nanoparticles after interaction with an infrared (IR) laser (the average size changed by almost 10 times), while green and UV laser radiations increase the average size by about 4–5 times.

Within the framework of the Mie formalism, a physicomathematical model has been implemented to calculate the spectral dependence of the absorption and extinction cross sections for spherical platinum nanoparticles. The extinction cross-section spectra of nanoparticles with diameters of 5–120 nm in isopropanol have been calculated using the dispersion of complex dielectric function determined by W.Werner et.al. [9]. The model extinction spectra are shown in the Fig. 3, *a*. It was found that monodisperse platinum particles are described by spectra with several peaks, one of which located in the ultraviolet region in the range from 230 to 315 nm, the second peak is in the UV region for particles less than 50 nm and in the visible and IR part of the spectrum (420–890 nm) for particles with diameter more than 80 nm. The absorption peak of monodispersed Pt NPs in isopropyl alcohol with sizes less than 50 nm has three peaks: first considerable one disposes in the middle UV region from 235 to 260 nm, second weak peak located in the range from 290 to 310 nm and third substantial one at the border with the visible region comprised between 380 and 390 nm. Notably, that the plasmon peaks shifts for larger wavelengthes with the growth of a NPs' diameter, and the increase of the Pt NPs diameter upper 60 nm the quadrupolar mode becomes prominent on the absorption spectra, while the intensity of the dipolar mode is decreased. This phenomenon is known to be common for various types of metal nanoparticles [10, 11].

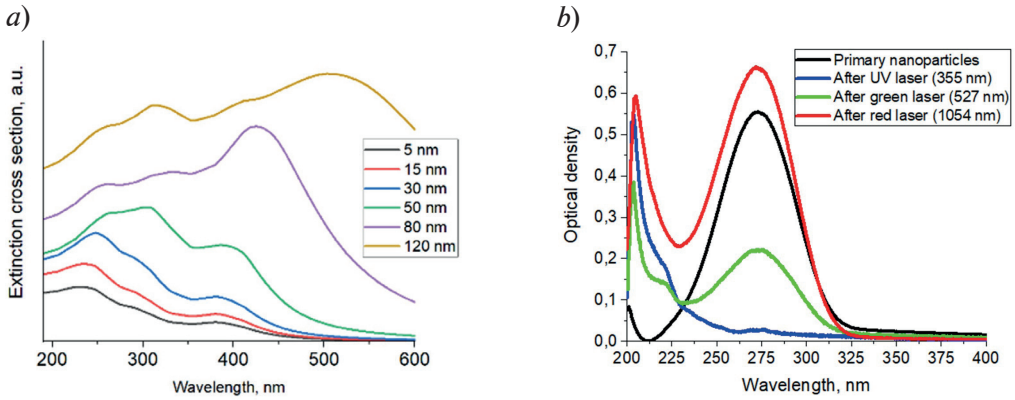

Fig. 3. Simulated (*a*) and experimental (*b*) extinction spectra for platinum nanoparticles with size meanings from 5 to 120 nm

Fig. 3, *b* shows the experimental extinction spectra of colloids of platinum nanoparticles in isopropanol in the ultraviolet range. For the primary nanoparticles without laser interaction (black line) one substantial plasmon peak were detected at a wavelength of 272.5 nm, for particles after interaction with the UV laser in gas stream (blue graph) peaks are located at wavelengths of 203.6 nm, 221.2 nm, 273.9 nm, for particles after the green laser modification (green graph) – at wavelengths of 203.3 nm, 220.8 nm, 272.9 nm, and for aggregated nanoparticles undergo the red laser interaction the maximums of extinction at wavelengths of 204.7 nm, 215.6 nm and 273.2 nm were observed.

Plasmon peak located at 273 nm is observed in all samples, while additional short-wave peaks of about 200 nm occur only in samples affected by laser interaction. This fact intuitively does not

correspond to the data on simulated spectra for monodisperse platinum particles. However, with a large particle size distribution, as in our case, the extinction spectra may differ significantly from the absorption of monodisperse nanoparticles with a similar average size [10, 11].

Comparing our results to the literature, we found, that Bigall et.al. [2] had showed the experimental and calculated spectra for Pt NPs with diameter of 29 and 73 nm with plasmon peak located at 250 and 375 nm, correspondingly. Several researches [12, 13] simulated and measured extinction cross section area only in visible interval from 450 to 1000 nm and showed the results similar to presented in this work.

Pt nanoparticles, obtained in these experiments can be applied for fabrication of plasmon nanostructures to enhance photoluminescence in ultraviolet range [14] and SERS (Surface enhanced Raman spectroscopy) signals [15].

Conclusion

Platinum particles with different morphologies and sizes from 5 to 250 nm were obtained in a gas discharge using additional laser modification in a gas flow at different wavelengths. The resulting particles have a wide particle size distribution with average diameters ranged varies from 22 to 44 nm depending on the laser wavelength and an extinction peak in the UV region. It is shown that the best modification (shape transformation from aggregates to individual particles) is achieved by using green and infrared laser. The calculations carried out according to the Mie theory showed that several peaks appear in the extinction spectra of monodisperse platinum particles with sizes from 5 to 120 nm, one of which lies in the ultraviolet region in the range from 230 to 315 nm.

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