



Original Research Paper

Physicochemical investigation of nanopowders prepared by laser ablation of crystalline silicon in water



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ABSTRACT

In this work, an investigation of SiO_x nanopowders synthesised by the laser ablation of crystalline silicon in water, evaporation of solvent and heat treatment is presented. The material is obtained for the first time by laser ablation in large quantities, which allows the use of a variety of physicochemical methods. The chemical composition and structure of the nanopowders were analysed before and after calcination in air and/or argon from 200 to 1000 °C. The particles prepared by laser ablation of a silicon target in water contain an amorphous and/or crystalline silicon core and a silicon oxide shell. Calcination results in the disappearance of crystalline silicon reflections in diffraction patterns and the appearance of oxygen vacancies in the silica. These materials are potentially important for such applications as optics, sensors and catalysis.

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1. Introduction

Laser ablation of bulk targets in liquids is a unique method for the synthesis of nanoparticle dispersions of a wide range of materials [1]. Additional chemical reagents (including reducers and precipitators) are not needed, which, along with mechanical effects, implying contact with equipment, allows yield of pure nanomaterials. Moreover, the high reactivity of small particles and high temperature of the synthesis promote chemical processes, including oxidation at the surface with participation of solvent molecules and gases dissolved within. Thus, for example, oxide, hydroxide and carbonate nanoparticles [2,3] and materials of much more complicated compositions [4], including core@shell structures [5–7], can be obtained from metal targets. An important feature of nanoparticles obtained by high-energy laser ablation is their defect structure, leading to new optical, antibacterial and catalytic [8] properties.

Of the many types of nanoparticles obtained by laser ablation, silicon materials are of central interest. “Green” synthetic methods in water allow use of the obtained particles in medicine and biology, for example, for generation of singlet oxygen [9,10]. Other potential applications of such particles are related to sensors and

catalysis, where oxidised silicon particles can be employed as a support.

To date, there have been many studies devoted to the ablation of crystalline silicon [11–17] by laser radiation with different durations and spectral compositions both in water and organic solvents. The composition of the obtained materials is defined by the type of reaction medium, laser radiation settings, and duration and conditions of the ablation process. However, systematic studies by a variety of physicochemical methods have not yet been conducted; therefore, the various results presented by different authors are often contradictory and insufficient.

One problem of laser ablation is poor productivity, which requires considerable time and energy to obtain a sufficient amount of sample for further investigation in the solid state (powder) and restricts the application of nanomaterials synthesised in this way. The quantities of nanoparticles obtained in all known literature works do not exceed 10 mg. In one previous study [18], the preparation of several grams of nanoparticles in 1 h was reported, but the authors obtained not more than 1 mg of nanoparticles by themselves.

As our previous experiments have shown, laser ablation allows preparation of colloids with particle concentrations of 0.1–1 g/l, depending on the target material and solvent; the optimisation of the ablation process with application of a multichannel system and flow reactor can lead to a rate of approximately 0.1 g/h. Such

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rates allow synthesis of enough material for investigation in the solid state and definition of abilities for future applications. In this study, the first results of a physicochemical investigation of nanopowders obtained by laser ablation of single-crystal silicon in water via irradiation with an Nd:YAG laser before and after calcination are presented. The obtained results indicate silicon oxide nanoparticles whose structures have a high concentration of defects, which may allow for the application of such materials as catalyst supports [19,20].

2. Materials and methods, experimental equipment

2.1. Synthesis of dispersions and powders

The laser ablation method in liquids was used to obtain silicon-containing dispersions. In this work, focused nanosecond-pulsed radiation of the main harmonics of an Nd:YAG laser LS-2131M (LOTIS TII, Belarus) with wavelength $\lambda_{\text{las}} = 1064$ nm was used. The excitation pulse energy was less than 180 mJ, and the pulse width was 8 ns with a 20 Hz repetition rate. Radiation was divided into two equal beams by a prism. Each beam irradiated the surface of a single-crystal silicon target with arbitrary orientation and dimensions of $12 \times 25 \times 5$ mm, which was placed into a glass cylindrical reactor with distilled water as the solvent. Radiation was introduced through the reactor side wall. Focusing was adjusted during illumination so that the surface pulsed power density of radiation was $1\text{--}2$ g W/cm². The target was moved automatically in-plane orthogonal to the pumping beam by means of two linear translators model 8MT173-30 (Standa Ltd., Lithuania) for uniform irradiation.

Radiation with wavelength of 1064 nm for which scattering (compared with less wavelength) and secondary interaction of radiation with nanoparticles were minimal was used. Such radiation was used, for example, in Refs. [13,14]. The duration of radiation was several nanoseconds. It is also optimal for nanoparticles productivity compared with pico- and femtosecond pulses. Short focused lens ($F = 40$ mm) was used. It allows to decrease a secondary interaction with nanoparticles. Sufficiently large power density on the target was utilized. It increases a size of obtained nanoparticles but at the same time improves a productivity. System of solution pumping (~ 0.5 ml/min) permits constantly to substitute a solution with nanoparticles for fresh without process shutdown. Therefore, particles are situated in the reactor for a short period of time compared with time in works [11–16] and their secondary interaction with laser radiation is minimal. Utilization of two equal channels from one pumping laser allows to increase a productivity since laser power is enough. Productivity of laser ablation device was ~ 12.5 mg/h.

The obtained dispersions were dried at 50 °C until the solvent evaporated. Material obtained by this method was designated SiO_x. Dried powders were mechanically mixed and kept in an muffle furnace SNOL 30/1100 (AB Umeqa, Lithuania) ($T_{\text{max}} = 1100$ °C, temperature range 5 °C). Samples were calcined at 200, 550, 700, 900 and 1000 °C in air for 12 h. Powders of SiO_x treated in this way were denoted SiO_x200, SiO_x550, SiO_x700, SiO_x900 and SiO_x1000, accordingly. Moreover, one sample was annealed at 1000 °C in Ar (designated SiO_x1000Ar).

2.2. Physicochemical methods

The absorption and photoluminescence characteristics of the initial dispersions and powders in the UV and visible range were investigated in reflection mode by a Cary 100 spectrophotometer (Varian, USA) with diffuse reflectance attachment and CM2203 spectrofluorimeter (SOLAR, Belarus) with solid sample holder.

The effect of particle structure and composition was studied using FTIR spectroscopy (Nicolet 6700, Thermo Fisher Scientific, USA). The samples were examined using the diffusion reflection method. Reflection spectra were converted by Kubelka–Munk transformations. Processing and spectra decomposition were performed using OMNIC software (Thermo Fisher Scientific, USA).

An electron microscopy study of Si/SiO_x nanoparticles was carried out using a JEM-2010 (JEOL, Japan) microscope with 0.14 nm resolution along the lines and an accelerating voltage of 200 kV.

Sample structure was determined by an XRD 6000 diffractometer (Shimadzu, Japan) using Cu K α radiation over an angular range of 10–70° with scanning pitch of 0.02°. Sample phase analysis was carried out using the PDF4 database, and quantitative phase distribution and particle size were determined using Powder Cell 2.4.

The elemental composition, presence of carbon and silicon/oxygen ratio of the samples were detected by a Lab Center XRF 1800 sequential X-ray fluorescent spectrometer (Shimadzu, Japan). The calibration used silica gel (for chromatography) and spectrally pure graphite; accuracy was 1×10^{-2} at.%.

X-ray photoelectron spectra (XPS) were recorded using a KRATOS Ultra Axis DLD electron spectrometer (Kratos Analytical Ltd., UK). An aluminium anode with a monochromator (photon emission energy was 1486.6 eV) was used as the radiation source. To determine a qualitative chemical composition and presence of impurities, survey spectra were registered in the range of 0–1100 eV with 1 eV energy steps using a constant analyser pass energy of 160 eV. To detect concentrations of elements and their oxidation states at the sample surface, narrow spectral regions of the most intense lines for each element were recorded at an analyser pass energy of 20 eV with 0.1 eV steps. The quantitative chemical composition was calculated from peak area ratios, accounting for atomic sensitivity factors [21]. The spectra were calibrated relative to the maximum of carbonic amorphous deposits on the sample surface with $E_b(\text{C1s}) = 284.8$ eV. Spectra processing, smoothing procedure, background subtraction and the decomposition of lines into individual components were carried out using the special software XPS-CAI, which has been successfully used for many other systems [22–24].

Processes occurring in powders during heat treatment in air and in argon were investigated by synchronous thermal analysis with thermogravimetry (TGA) and differential scanning calorimetry (DSC) using a STA 449 F3 Jupiter thermal analyser (Netzsch, Germany) below 1000 °C with a heating rate of 10 K/min.

The specific surface area and porosity of silica samples were estimated by a TriStar II automatic gas adsorption analyser (Micromeritics, USA). Specific surface areas were determined from low-temperature nitrogen physisorption isotherms.

3. Results

Laser ablation of silicon targets in water at the conditions described above lead to the formation of stable water dispersions of silicon-containing particles.

Investigation by HRTEM showed (Fig. 1) that amorphous nanoparticles with an average diameter of 7 nm (Fig. 1, a) are formed in the course of ablation. Additionally, an insignificant number of larger particles with diameters as large as 30 nm is observed. The particle size distribution is presented in the inset of Fig. 1, a. The sample also contains spherical single particles with sizes of approximately 100 nm (Fig. 1, b). These particles have a crystalline core and amorphous surface layer, thus representing a “core–shell” structure. Interplanar spaces from particle cores measured on high-resolution photos correspond to crystalline silicon. Moreover, an intense Si K α signal from these particles is observed, with no oxygen O K α signals.

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