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Synthesis of Au-Si and SiO_2 Nanoparticles by Pulsed Plasma in Liquid Method, Characterization and Study of Their Thermal Annealing Behaviors

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Abstract-Au-Si and SiO_2 nanoparticles were synthesized by Pulsed Plasma in liquid method, using the gold-silicon (Au-Si) and silicon-silicon (Si-Si) as electrodes, submerged in water and diluted $HAuCl_4$ acid solution as liquid mediums. Objective of this work is to present novel synthesis of Au-Si and SiO_2 nanoparticles by pulsed plasma in liquid method, their characterizations and study of their thermal annealing behavior. One of superior advantages for pulsed plasma in liquid is opportunity to easy achieving of metastable phase nanomaterials comparing to other conventional methods. Pulsed plasma in liquid allows obtaining broad scale of nanomaterials structures, morphology and properties. Au-Si and SiO_2 nanoparticles were obtained by varying the electrode type and surrounding liquid composition. Thermal annealing was applied to detect appropriate structural, morphological and phase changes in Au-Si and SiO_2 nanoparticles. After serial annealing and XRD analyses, changes in full width half maximum (FWHM) of Au-Si and SiO_2 nanoparticles were detected and calculated. HRTEM observations revealed Au-Si and SiO_2 crystalline nanoparticles with size from 4-17 nm.

Keywords- *synthesis, nanoparticle, pulsed plasma*

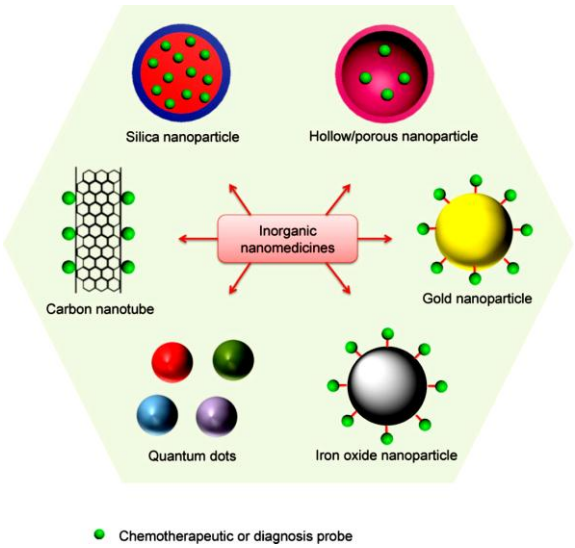

Figure 1. Examples of inorganic nanomedicines for cancer diagnosis and therapy (Reprinted from Nano Today, 8 /3, Li Tang et al., Nonporous silica nanoparticles for nanomedicine application / Review, p.290-312., Copyright (2013), with permission from Elsevier).

I. INTRODUCTION

Since discovery of fluorescence phenomena outgoing from Si and Au nanoparticles, in the last decades, SiO_2 and Si-Au nanoparticles are of great interest, due to their important applications in energy sources, electronic, catalysis, sensor and biomedical device manufacturing [1] and unique properties, including, biomedical [2], optical [3], photoluminescence [4], photoconductivity [5], photodynamical diagnostics and therapy [6]. Recently, Si and Au nanoparticles have been used as inorganic nanomedicines for cancer diagnosis and therapy (Fig. 1). One of the valuable properties exhibited by SiO_2 nanoparticles is their surface modification and protein binding abilities. Silica nanoparticles after surface modification are able to function at dual-mode. Also dye-doped silica nanoparticles are used for cellular imaging.

Several techniques and methods in these latter days were described for synthesis of silicon and silicon-gold nanoparticles, such as: ultrasonication by sol-gel method [7], green synthesis [8], wet chemical synthesis [9], and so on. Turkevich method was reported for synthesis of Au nanoparticles, to fabricate the SiO_2@Au and TiO_2@Au core-shell nanostructures [10]. Synthesis of Si nanoparticles embedded in Graphene sheets was also reported [11]. Core-shell structured nanoparticles of Au and Si [12], and direct silica coated Au nanoparticles [13] were likewise described. There is no doubt that above works performed, have their definite and aimed objectives in synthesis of Si and Si-Au nanoparticles. However, most of they are based on multitude chemicals usage, and slightly complicated synthesis steps.

Among these and other reported works, our work presents synthesis of Au-Si and SiO_2 nanoparticles by Pulsed plasma in

liquid process [14-16], which is described in experimental section of this work. Basic simplicity of pulsed plasma in liquid method is its originality and actuality in the Nanotechnology. Beside of synthesis process, the scope of this work was aimed to characterizations, study of structural and morphological changes happened during serial thermal annealing of Au-Si and SiO_2 nanoparticles. It is well known, that reduction of nanomaterials crystallite size (or any other structural entities) below a threshold value, results in drastic change of their physical properties [17], this factor is also a key issue in determination of nanomaterials quality and applications. Consideration of nanomaterials properties is always mean of metastability, which is defined by consequence of high energy load. Achieving the metastable phases of nanomaterials during their synthesis process is very important tool for study, and discovery of new phase materials and new property materials. Application of pulsed plasma for synthesis of SiO_2, Si-Au nanoparticles is one of interesting challenges in our practice. It was observed, that full width half maximum (FWHM) and particle sizes for SiO_2, Si-Au nanoparticles were changed after each annealing.

Also, increase and decrease in the Au phase was detected in regard to nanoparticles fraction. Increase in the Si phase was observed after final annealing at 600 °C. Formation mechanism of Au-Si and SiO_2 nanoparticles was described by using the Atomic emission spectra, collected from the plasma discharge zone during synthesis experiment. Si I, II, III, IV atoms, H I and O II atoms were detected by spectroscopical set up fixed and installed inside the experimental chamber.

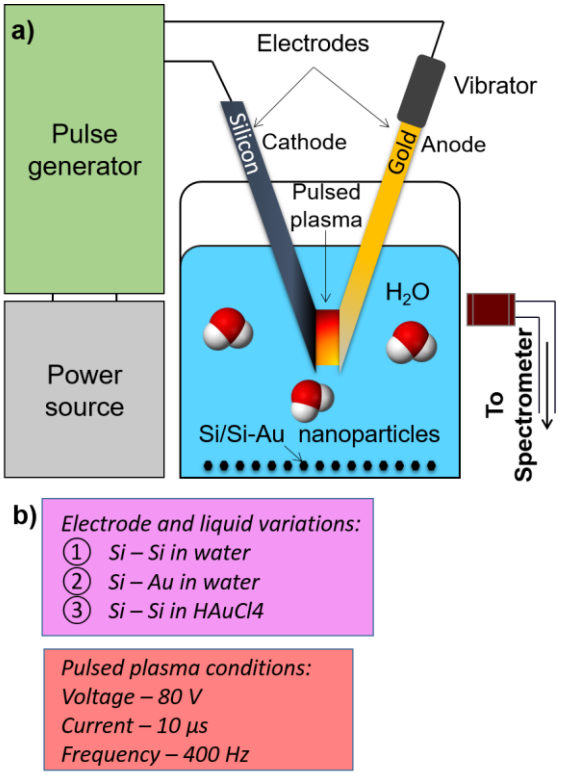

Figure 2. a) Schematics of experimental set up designed for synthesis of SiO_2 and Si-Au nanoparticles by pulsed plasma; b) Electrode and liquid variations with electrical conditions during synthesis.

II. Experimental Set up

Experimental set up for pulsed plasma in liquid process was also reported in our previous works [14-16]. There were no significant modifications in set up used for synthesis of SiO_2, Si-Au nanoparticles by pulsed plasma in liquid method (Fig. 2). Connection and adjustment of Si pieces with the power source was performed by fixation of pin clip attachments. Si pieces with purity of 98.99 % were purchased from Alfa Aesar, Au metal rods with purity of 99.99 % and diameter of 3 mm were purchased form Rare Metallic Co., and $HAuCl_4$ acid with concentration of 99.0 %, purchased from Kanto Chemical Co. Inc.

A. Synthesis of SiO_2 nanoparticles.

Achieved by use of two Si pieces fixed tightly with the power source, inserted in a Pyrex beaker, which was filled with 200 ml of distilled water. Electrical voltage of 180 V, and electrical current of 10 microseconds (µs) were applied.

The duration of pulsed plasma synthesis was one hour.

B. Synthesis of Au-Si nanoparticles.

Carried out by the same set up. For this experiment, source of Au was provided by two ways. In the first way, pure Au metal electrodes were adjusted within the experimental setup; pulsed plasma was generated between Si and Au electrodes, which were submerged in distilled water. Second way was based on the use of two Si pieces submerged in $HAuCl_4$ diluted acid solution. All experiments were carried out with duration of one hour, and this time was quite enough to get an appropriate amount of nanoparticles for further characterizations and annealing studies. As it is seen from Fig. 2a), d), two electrodes were adjusted and fixed stable to conduct electricity, thus, providing synthesis of nanoparticles. Optical spectrometer SEG-2000 UV-vis. was used to collect atomic emission spectrum peaks for separating atoms from electrodes during pulsed plasma. Emission spectrum peaks were identified by NIST Database [18].

X-ray diffraction characterizations of as-synthesized nanoparticles were carried out on a Rigaku RINT 2500HV diffractometer with Cu-α radiation on wavelength 0.15406 nm, with tube voltage of 40 kV, and current of 200 mA. Size, shape and morphology characteristics were observed by Philips Technai F20 S-Twin high resolution electron microscope including X-ray spectroscopy EDX detector for elemental analysis at 200 keV.

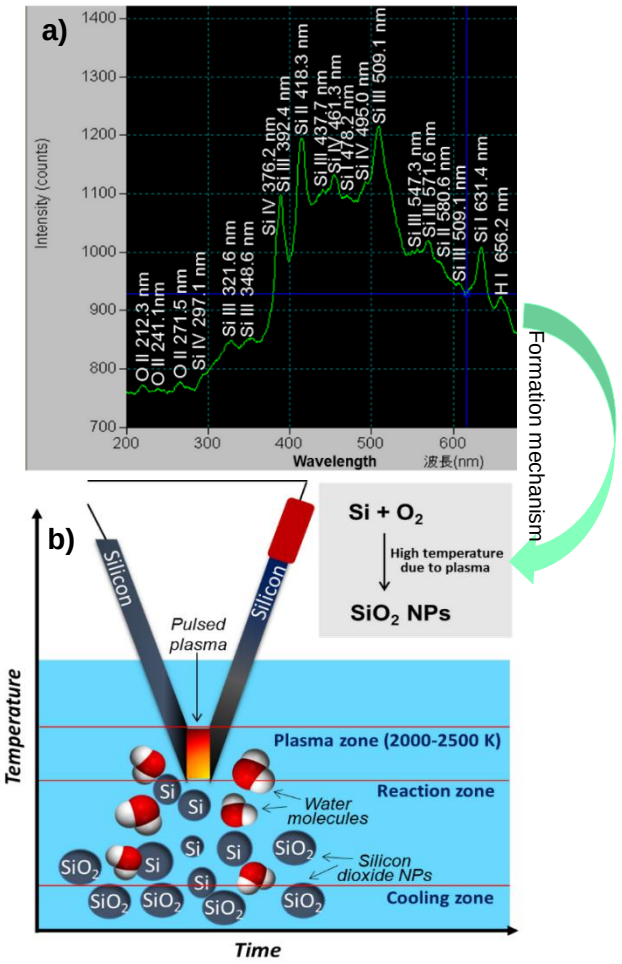

Figure 3. a) Atomic emission spectrum collected form the pulsed plasma discharge zone; b) Formation mechanism of SiO_2 nanoparticles by pulsed plasma in liquid method.

C. Formation mechanism.

Formation of silica nanoparticles during pulsed plasma discharge is shown in Fig. 3. a), the atomic emission spectra peaks collected from plasma discharge zone are identified using the NIST Database. Chemical reaction caused between Si atoms released from Si pieces, and oxygen atoms released from surrounding water medium, will provides formation of Si nanoparticles, which are sedimenting in the bottom of the beaker (b).

III. RESULTS AND SICUSSIONS

HRTEM analyses revealed size, shape and morphology of Au-Si and SiO_2 nanoparticles synthesized by pulsed plasma in liquid method. Fig. 4 shows HRTEM photograph of gold (Au) nanoparticle with size of 17 nm; b) is HRTEM photograph of randomly located Au and Si nanoparticles atoms; c) enlarged image taken form the Au nanoparticle at 1 nm scale, yellow line was drawn for set of neighboring atoms, to determine the inter atomic distance (d/nm) between them; d) showing the FFT image for Au nanoparticle in a), with *hkl* parameters of (111), (200) and (220); e) EDX spectrum taken from nanoparticles synthesized by pulsed plasma in liquid; f) Peak profile chart generated from the yellow line drawn in c). It is shown that interatomic distance (d/nm) is in agreement with the XRD characterization data.

A series of X-ray Diffraction analyses were carried out after annealing the SiO_2 and Si-Au nanoparticles at 400, 500 and 600 °C, respectively. X-ray diffraction analyses performed to analyze the phase compositions and structures of as-synthesized SiO_2, and Si-Au nanoparticles, also revealed high intensity peaks for SiO_2, Si and Au phases. Fig. 5 a) shows XRD pattern for nanoparticles before annealing, right after synthesis; b) XRD pattern for samples obtained after annealing at 400 °C, for 2 hours; c) XRD pattern for samples obtained after annealing at 500 °C, for 2 hours; d) XRD pattern for samples obtained after annealing at 600 °C, for 2 hours. It was observed, that quantity and intensity of SiO_2 peaks was increased after annealing of samples at 600 °C for sample named S1. Further annealing of samples at 400, 500 and 600 °C inhibited intensity of Au phase in S4 sample. But changes in size and the FWHM peaks derived from the X-ray diffraction analyses had shown different values. Table 1 presents full width half maximum (FWHM) and particle size (D/nm) for SiO_2, Si-Au NPs calculated by using the Scherer's equation (1). The full width half maximum (FWHM) and particle size (D/nm) for Si, Si-Au NPs were calculated by using the Scherer's equation (1), and tabulated. According to Scherer's equation

$$D = k\lambda / \beta\cos \qquad (1)$$

where, D is particle size, k is the constant of 0.94, and λ is radiation (Cu Kα), equal to 1.54 for diffractometer type, particle sizes were calculated by multiplication of kλ and their division by FWHM of most intensive peak from the X-ray diffraction profile. As it is shown in the Table 1, phase composition of sample 1 (S1) was revealed as SiO_2. Phase compositions of S2 and S3 are Si and Au nanoparticles. S4, S5 and S6 showed mainly Au composition. Right after pulsed plasma synthesis, all samples obtained according to electrode and liquid variations, were kept sediment for separation of nanoparticle fractions. During sedimentation of nanoparticles synthesized by adjusting the Si and Si electrodes in distilled water (named as S1), only the bottom fraction of liquid contained the nanoparticles of SiO_2, which is detected by XRD analysis. No upper fraction was available for separation. Before annealing, the particle size for SiO_2 was calculated to be 42.3 nm. After annealing at 400 °C and 500 °C, it was observed that SiO_2 particle size was decreased to 41.37 nm and 26.4 nm, respectively. This might be due to evaporation of excess water amount in samples, and also due to volatilization of impurities. Presence of water is caused by liquid medium during the pulsed plasma synthesis. After annealing at 600 °C, particle size was increased up to 32 nm, which is supposed as result of agglomeration at higher temperature.

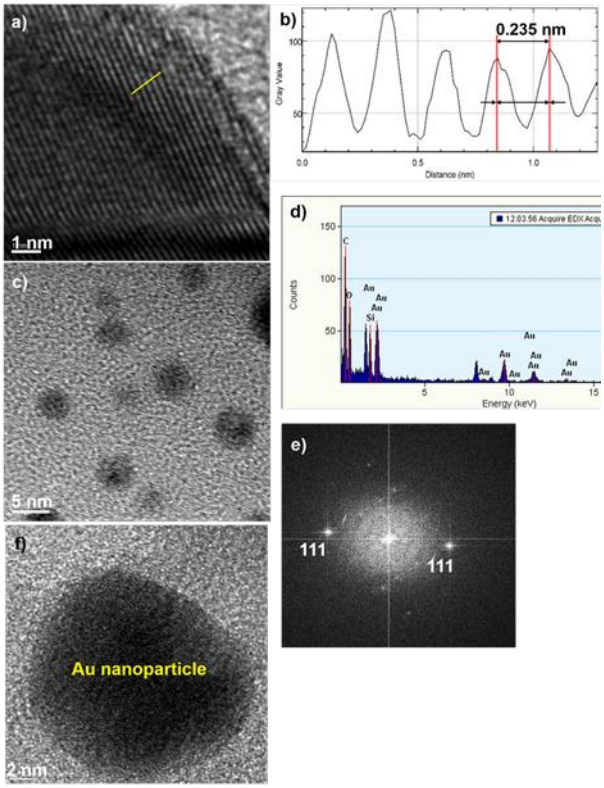

Figure 4. HRTEM characteristics of Au Si nanoparticles synthesized by pulsed plasma: a) HRTEM photograph taken at 2 nm scale for Au nanoparticle, with size of 17 nm; b) randomly located Au Si nanoparticles synthesized by pulsed plasma in liquid method; c) Enlarged photograph taken at 1 nm scale, with yellow line drawn for obtaining plot profile and interatomic distance determination; d) FFT image showing *hkl* parameters for Fm-3m (225) gold nanoparticle; e) EDX chart showing Au and Si nanoparticles synthesized by pulsed plasma in liquid; f) Plot profile showing 0.235 nm distance between the neighboring atoms in Au nanoparticle synthesized by pulsed plasma.

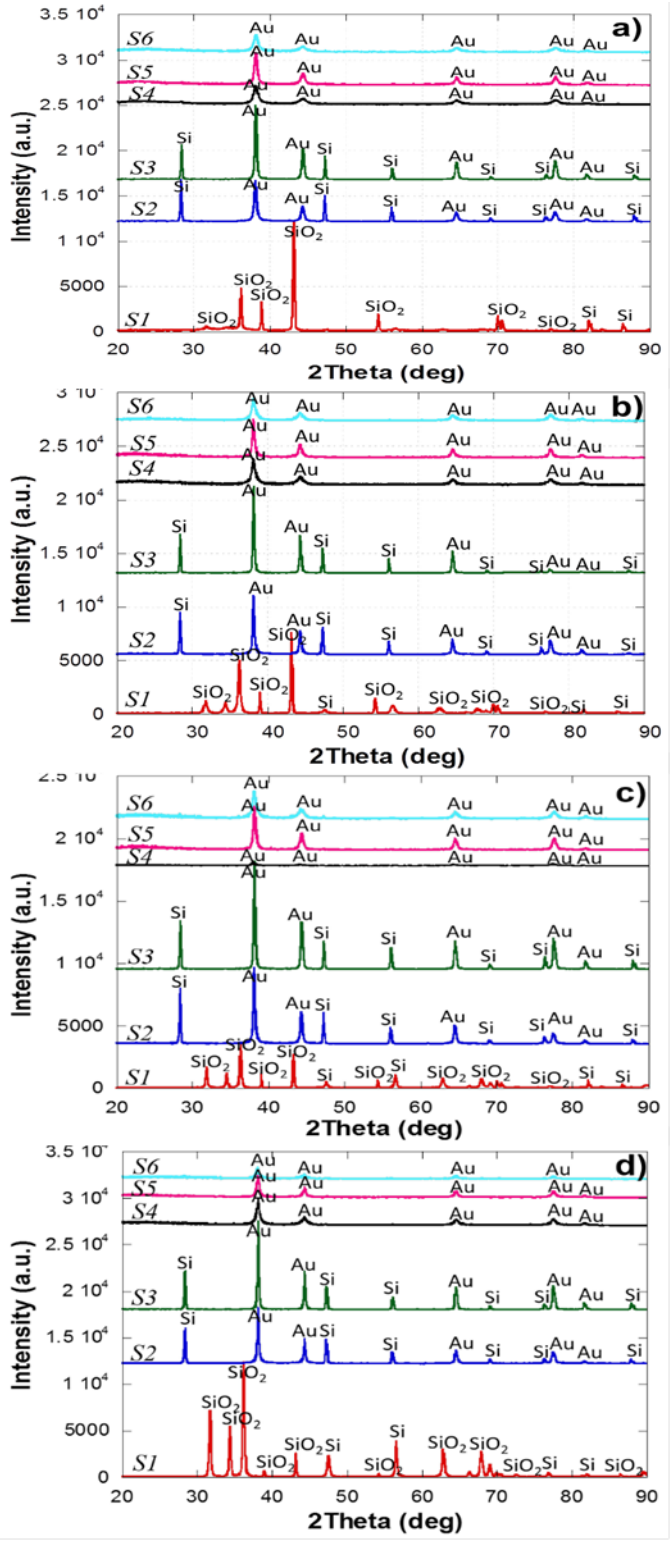

Figure 5. a) XRD pattern for samples obtained right after synthesis, before annealing; b) XRD pattern for samples obtained after annealing at 400 °C, for 2 hours; c) XRD pattern for samples obtained after annealing at 500 °C, for 2 hours; d) XRD pattern for samples obtained after annealing at 600 °C, for 2 hours.

For nanoparticles synthesized by adjusting the Si and Au electrodes in distilled water, during sedimentation, two of fractions, upper S2 and bottom S3 were observed. These upper and bottom fractions were revealed by XRD analysis as mixture of Si and Au nanoparticles. Before annealing, Si nanoparticles in the upper fraction S2 showed particle size of 42.4 nm, while Si NPs in the bottom fraction are 43.9 nm. Particle size for Au nanoparticles in the upper S2 fraction before annealing was detected as 27.6 nm, which is smaller than Au nanoparticles size, 32.2 nm in the bottom fraction. This phenomenon is also based on gravitation: as heavier particles have higher sedimentation speed, and lighter particles have lower sedimentation speed. After annealing at 400 °C and 500 °C, Au NPs in the S2 fraction showed increase in particle size, and decrease after annealing at 600 °C. Particle size of Si NPs in this fraction, increased to 43.6 nm after annealing at 400 °C, and decreased to 10.7 nm after annealing at 500 °C, which might be cause of volatilization of impurities. Again, increase in particle size of Si NPs, up to 20.3 nm after annealing at 600°C considered as reason of agglomeration. Bottom S3 fraction also showed the analogous results, increase and decrease at given temperatures, due to agglomeration and volatilization phenomena, respectively.

In case of nanoparticles synthesized by adjusting the Si and Si electrodes in $HAuCl_4$ acid diluted solution, during sedimentation, the three fractions of nanoparticles, S4 upper, S5 middle and S6 bottom were observed. XRD analyses revealed high intensity peaks in the middle fraction for Au nanoparticles. Before annealing, particle size of Au nanoparticles in S4 fraction was calculated to be 17.34 nm. After annealing at 400 °C, the particle size was decreased to 14.65 nm, caused by evaporation of water and volatilization of impurities.

TABLE I. FULL WIDTH HALF MAXIMUM (FWHM) AND PARTICLE SIZE (D/NM) CHARACTERISTICS FOR AU-SI AND SiO_2 NPS CALCULATED BEFORE AND AFTER ANNEALING AT 400°C, 500°C AND 600°C.

Condition	Before	annealing	Annealed	at 400 °C	Annealed	at 500 °C	Annealed	at 600 °C
Character	FWHM	D/nm	FWHM	D/nm	FWHM	D/nm	FWHM	D/nm
Sample 1	SiO_2 (0.21)	SiO_2 (42.3)	SiO_2 (0.21)	SiO_2 (41.3)	SiO_2 (0.33)	SiO_2 (26.4)	SiO_2 (0.27)	SiO_2 (32)
Sample 2	Au (0.309) Si (0.203)	Au (27.6) Si (42.4)	Au (0.304) Si (0.206)	Au (28.8) Si (43.6)	Au (0.220) Si (0.085)	Au (40) Si (10.07)	Au (0.358) Si (0.421)	Au (24.8) Si (20.3)
Sample 3	Au (0.278) Si (0.194)	Au (32.2) Si (43.9)	Au (0.193) Si (0.257)	Au (32.7) Si (45)	Au (0.253) Si (0.278)	Au (34.6) Si (32.7)	Au (0.252) Si (0.203)	Au (36) Si (42.35)
Sample 4	Au (0.508)	Au (17.3)	Au (0.554)	Au (14.6)	Au (0.046)	Au (19.04)	Au (0.429)	Au (20.57)
Sample 5	Au (0.400)	Au (21.1)	Au (0.373)	Au (23.56)	Au (0.175)	Au (51.42)	Au (0.364)	Au (24)
Sample 6	Au (0.539)	Au (16.4)	Au (0.515)	Au (17.14)	Au (0.511) Si (0.133)	Au (17.14) Si (65.45)	Au (0.222) Si (0.127)	Au (40) Si (68.57)

After annealing at 500 °C and 600 °C, particle size of Au NPs was slightly increased to 19.04 nm and 20.57 nm, respectively, due to agglomeration. For Au NPs in S5 middle fraction, particle size before annealing was calculated to be 21.17 nm, then, after annealing at 400 °C, 23.56 nm. After annealing at 500 °C and 600 °C, particle size for S5 fraction was calculated to be 57.42 nm and 24 nm, respectively. Final S6 fraction showed particle size calculated to be 16.45 nm, before annealing. After annealing ate 400 °C and 500 °C, particle size was increased up to 17.14 nm. After annealing at 600 °C, increase in Au nanoparticles size up to 40 nm was observed. Additionally, after annealing at 500 °C and 600°C, XRD peaks for Si nanoparticles with particle sizes of 65.45 nm and 68.57 nm were detected. Such appearance of Si phase can be explained by the removal of impurities in S6 fraction during annealing.

IV. CONCLUSION

Synthesis, characterization and thermal annealing behaviors of Au-Si and SiO_2 nanoparticles was described in this work. Simple and one-step pulsed plasma in liquid method (PPL) was applied for above nanoparticles synthesis between electrodes submerged in a liquid media. Several types of nanomaterials obtained by using the PPL were described and reported in our previous works. Current work was focused on the phase composition, size, shape and morphologies of as-synthesized Au-Si and SiO_2 nanoparticles by PPL method. Thermal annealing behaviors were detected after serial annealing at 400, 500 and 600 °C have been reported. Depending on the synthesis conditions (initial chemical material type variation), changes on FWHM and D/nm parameters were also calculated and described.

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She has published number of works related to synthesis of various nanomaterials by using the pulsed plasma in liquid method in peer-reviewed international journals. Her book named Nano and Biomaterials: compounds, properties, characterization and applications, by Wiley-VCH, Verlag GmbH & Co. KgaA is under publication process.

Prof. Abdullaeva is a member of Japanese Ceramic Society, Materials Research Society and European Society of Biomaterials.