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Nanoparticle-decorated ceramic as substrate in surface enhanced Raman spectroscopy

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ABSTRACT

Laser-assisted method for fabrication of nanoparticles on the surface of ceramic substrate is presented. The method is based on laser dewetting of thin metal film deposited on the substrate. Using this technique, gold nanoparticles on alumina ceramic surface are fabricated. It is shown that the processing parameters can influence the properties of the fabricated structure, as at certain conditions a homogeneous cover of nanoparticles with narrow size distribution can be achieved. The processed surfaces are tested as substrates in surface enhanced Raman spectroscopy of a standard dye. The efficiency of the substrates is estimated by the ability of detection of the dye at nM concentration and it is compared to that of thin gold film on ceramic substrate. The strongest enhancement is observed for the sample where Au film is not completely decomposed and the structure consists of thin film and nanoparticles aggregates. The proposed method has potential application in fabrication of cheap and reliable substrates for Raman spectroscopy analysis with high sensitivity and also in catalysis.

1. Introduction

The metal nanoparticles and their ensembles continue attracting much attention last years, due to the complex and unusual properties that they express and do not exist in bulk material. Due to the high surface to volume ratio and the high catalytic activity, these structures become a basis in catalysis, where the benefit of their use can be seen even at ambient temperature or less [1]. A classical example is the oxidation of CO at temperature less than 0 °C in the presence of nanosized Au particles supported on a metal oxide substrate [2]. The high efficiency of the metal nanoparticles in controlling the velocity of chemical reaction also is a fundament of development of technologies for pollution control, as air quality monitoring and improvement, water treatment [3], development of materials with bactericidal effect [4], clean hydrogen production, and fuel cell development [1].

In addition to the specific intrinsic properties of the metal nanoparticles, a large number of their applications are related to their response to external interactions. Most of these relays on the specific properties of the interaction between nanoparticles and electromagnetic field. For noble metal nanoparticles this interaction is related to the ability of efficient plasmon excitation in near UV–Vis spectral range that drastically changes their optical properties [5,6]. At resonance conditions the absorption and scattering coefficients are strongly enhanced as the values can be more than several orders of magnitude higher compared to the organic dyes used in photothermal and photodynamic therapy [7]. Furthermore, the field intensity in close vicinity of the nanoparticle surface can be strongly enhanced in so called “hot spots”. This enhancement is the basis of surface enhanced Raman spectroscopy (SERS) that is able to detect even single molecule [8]. The theoretical and experimental studies on the optical properties of noble metal nanoparticles [5,6] show that they can be efficiently modified since the plasmon resonance frequency depends on the size, shape, and orientation of the particle with respect to the polarization of the incident irradiation, dielectric properties of the environment, geometry of the irradiation.

The unique properties of nanoparticles are even more exciting when multidimensional ensembles are considered [6,9]. These structures may include composite materials consisted of nanoparticles or nanoparticle architectures formed on desired surface. In such structures the optical spectra expresses more complex structure that results from electromagnetic coupling of neighbouring particles [9–11]. When the interparticle distance is less than the particle diameter near field coupling is realized and field intensity in strongly localized in the gap between particles. For particles

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separated at larger distances far field coupling is realized as it is influenced by the interference of the scattered light from neighbouring particles. From application viewpoint the 3D nanoparticle systems are shown to be more efficient substrates in SERS than single particles and 2D arrays [12]. Composite nanoparticle-consisted materials and nanoparticle ensembles on different substrates also found application in light harvesting systems [13].

Fabrication of multidimensional nanoparticles systems with desirable parameters on a substrate is still a significant challenge. The developed nanolithography and template synthesis techniques usually include slow and costly processes; the chemical methods require multi steps and usage of hazardous materials [14]. Recently, different methods based on processing of thin films that can lead to large-area nanostructuring have been shown. As a promising one for fabrication of nanoparticle arrays is thermally induced dewetting of metal films deposited on oxide substrates. The homogeneous heating of the samples or local heating by laser treatment may result in decomposition of the thin metal films directly into 2D nanoparticle arrays [15–18]. The properties of the formed arrays depend on both the properties of the deposited films and the characteristics of the heating process. Furthermore, the interparticle distance and the size of the formed particles depend on the film thickness. The experiments in the field show that the process can be realized also on corrugated surface, where the chemical potential difference between convex and concave regions leads to selective positioning of the formed nanoparticles into the surface valleys [19].

In this paper we propose simple and efficient method for fabrication of metal nanoparticles on alumina ceramic surface. The method is based on laser-assisted dewetting of metal film deposited on the surface. The ceramic material being composed of crystallites has a porous structure with large surface area. The homogeneous cover of nanoparticles on such surface, combined with the high mechanical strength, the chemical inertness, and the low cost of this type of ceramic, makes the proposed structure an efficient candidate in catalysis applications and sensor devices.

2. Experimental setup

The proposed method for nanoparticle decoration of the alumina ceramic surface consists of two steps. In the first one, thin metal film of gold is deposited on the substrate. This is realized by pulsed laser deposition technique, by ablating Au (99.99) target at ambient pressure of $\sim 10^{-3}$ Pa. The substrates are alumina ceramic (Balzers, 99.9%) with thickness of 1 mm. Nd:YAG laser system operating at wavelength of 355 nm is used to ablate the target material. Pulse duration of the delivered laser pulses is 15 ns and the repetition rate is 10 Hz. The laser fluence used for film deposition is 1.5 J/cm^2. The deposition time is 3 min. The thickness of the produced gold film at these conditions is about 80 nm measured by AFM on polished crystalline Al_2O_3 substrate.

The second fabrication step is laser annealing of the as-deposited films. This is performed using the same laser system applied in the deposition process. The laser fluence and the number of the applied laser pulses are varied in order to investigate their influence on the observed thin film modifications. The surface morphology of the samples is studied by SEM (JEOL, JSM 6390). The optical properties of the fabricated structures are analyzed on the basis of transmission spectra taken by HR 4000 spectrometer (Ocean Optics). The obtained samples are used as active substrates for SERS measurements. For this experiment (Delta Nu) Raman system operated at 785 nm is applied. The excitation laser power used is 80 mW and the acquisition time is 10 s. The enhancement of the Raman signal of a standard dye Rhodamine 6G is estimated.

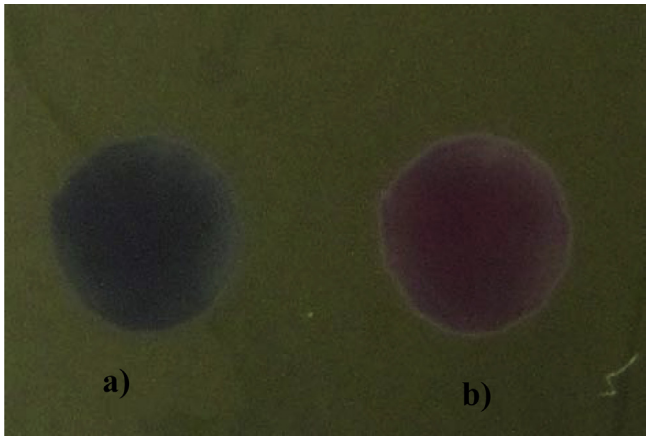

Fig. 1. Optical image of the laser processed areas on Au film deposited on alumina ceramic. The laser fluence in both cases is 0.3 J/cm^2. The number of the applied laser pulses is 1 in. (a) and 5 in. (b). The wavelength of the laser radiation is 355 nm.

3. Results and discussion

The alumina ceramic used in the presented experiments consists of Al_2O_3 crystallites with sizes varied in the range of 500–3000 nm. The deposition of the gold film results in clear change of the sample colour from white to yellow-grey. Fig. 1 represents an optical image of the ceramic substrate after laser treatment with (a) single, and (b) five laser pulses with fluence of 0.3 J/cm^2. The application of a single laser pulse leads to appearance of a dark grey spot in the processed area. A pink coloured spot is clearly observed after irradiation with 5 consecutive laser pulses. The optical properties of the produced structures can be also seen in their transmission spectra. Fig. 2 represents the spectra taken in the two spots shown in the optical images in Fig. 1. In the case of single pulse irradiation a flat spectra in the visible spectral region is observed. The transmission of the sample is in the range of 30–40% compared to the native alumina ceramic. The effect is related to the uncompleted decomposition of the Au film. The transmission spectrum of the area formed after irradiation with 5 laser pulses, shows clearly expressed dip in the transmission with minimum at 560 nm. This band can be attributed to the plasmon excitation in nanoparticle system formed at presented conditions.

The performed SEM analysis of the processed area confirms the change of the structure of the Au film. Fig. 3(a) and (b) shows the

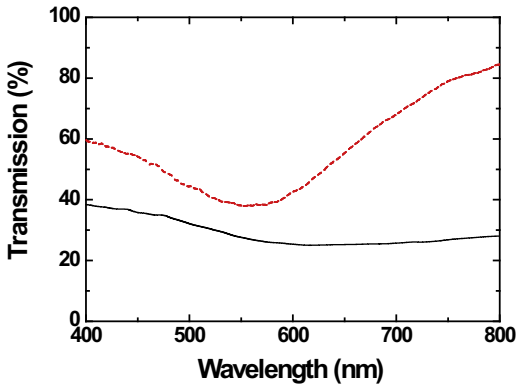

Fig. 2. Transmission spectra of the laser processed areas on Au film deposited on alumina ceramic. The black solid line represents the spectrum for the structure produced after irradiation with single laser pulse, and the red dashed line corresponds to the structure produced after irradiation with 5 laser pulses. The laser fluence in both cases is 0.3 J/cm^2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)