Applied Surface Science 420 (2017) 661–668

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full length article

Laser-assisted immobilization of colloid silver nanoparticles on polyethyleneterephthalate

Jakub Siegel[a,*], Oleksiy Lyutakov[a], Markéta Polívková[a], Marek Staszek[a], Tomáš Hubáček[b], Václav Švorčík[a]

[a] Department of Solid State Engineering, Institute of Chemical Technology, 166 28 Prague, Czech Republic
[b] Biology Centre CAS, SoWa National Research Infrastructure, Na Sádkách 7, České Budejovice, Czech Republic

ARTICLE INFO

Article history:
Received 20 February 2017
Received in revised form 15 May 2017
Accepted 17 May 2017
Available online 26 May 2017

Keywords:
Silver nanoparticles
Polyethyleneterephthalate
Excimer laser
Immobilization

ABSTRACT

Immobilization of nanoobjects on the surface of underlying material belongs to current issues of material science. Such altered materials exhibits completely exceptional properties exploitable in a broad spectrum of industrially important applications ranging from catalysts up to health-care industry. Here we present unique approach for immobilization of electrochemically synthesized silver nanoparticles on polyethyleneterephthalate (PET) foil whose essence lies in physical incorporation of particles into thin polymer surface layer induced by polarized excimer laser light. Changes in chemical composition and surface structure of polymer after particle immobilization were recorded by wide range of analytical techniques such as ARXPS, EDX, RBS, AAS, Raman, ICP-MS, DLS, UV–vis, SEM, TEM, and AFM. Thorough analysis of both nanoparticles entering the immobilization step as well as modified PET surface allowed revealing the mechanism of immobilization process itself. Silver nanoparticles were physically embedded into a thin surface layer of polymer reaching several nanometers beneath the surface rather than chemically bonded to PET macromolecules. Laser-implanted nanoparticles open up new possibilities especially in the development of the next generation cell-conform antimicrobial coatings of polymeric materials, namely due to the considerable immobilization strength which is strong enough to prevent particle release into the surrounding environment.

1. Introduction

In the beginning of this century nanostructured materials, especially nanoparticles (NPs), initiated technological revolution in almost all areas of human activity. They have been successfully applied in catalysts [1–4], energy storage devices [5–7], healthcare industry [8,9], cosmetics [10,11] or textile industry [12–14]. Numerous techniques have been developed to produce those man-made entities since the first pioneering studies in the early 1960′s [15]. Nowadays shape controlled NPs with complex morphologies can easily be synthesized by means of chemical or physical methods, giving us basic building blocks tailored for specific applications. The successful synthesis itself, however, does not often lead to desired functional product. It is an indispensable step, but another must be followed to give rise to a novel functional material or component having desired properties. Especially in catalysis, textile or healthcare industry the immobilization of NPs onto the carrier substrate represent important technological step crucial to the success of developed product in the view of their long-term functionality [16–18].

Immobilization of nanoobjects on the surface of underlying material can be accomplished by different ways, depending on the bounding strength which is needed for specific application. Currently, in the case of NPs, most widespread immobilization approaches are: (i) anchoring of functionalized NPs to the surface by the mean of covalent chemical bond [19], which often suffers from low yields, (ii) electrostatic immobilization of NPs on oppositely charged surfaces [20], being extremely sensitive to the properties of surrounding medium, (iii) simple physisorption of NPs on the rough surface [21], which is generally very weak; particles can be spontaneously released into the environment, and finally (iv) embedding of NPs into the entire volume of material [22], which dramatically reduces the concentration of particles on the very surface. In summary, each of above listed approaches for NPs immobilization deal with the obstacles that either reduce the efficiency of the process itself or impose special requirements on the treatment of bounded particles.

---

[*] Corresponding author.
E-mail address: jakub.siegel@vscht.cz (J. Siegel).

http://dx.doi.org/10.1016/j.apsusc.2017.05.151

Latest progress in the field of optomechanical manipulation with nanoscale materials [23], seems to give interesting alternative to commonly used techniques of NPs immobilization. The coupling of optical and mechanical degrees of freedom is the underlying tool for many investigations of small forces in the micro- and nanometer range. Especially developments in determination of the forward-directed scattering force, that dominates for incident light of a wavelength close to the plasmon resonance of metal nanopatricle, is of essential importance in utilization of targeted transport of particles in liquids [24]. Even though such forces are in the range of tens of femtonewtons [24] to hundreds of piconewtons [25], they may induce collective motion of particles in the direction of excitation radiation. Moreover, since the round-shaped nanoparticles with radius <20 nm excite primarily dipole plasmon resonance mode [26,27], polarization of laser prior to irradiation multiplies acting force increasing the pushing effect in order of magnitude.

In this paper we introduce unique approach for immobilization of silver nanoparticles (AgNPs) on the surface of polyethyleneterephthalate (PET). Electrochemically synthesized AgNPs were immobilized from their water solution by the action of polarized excimer laser light. Laser light stimulated both the polymer causing transformation of its surface into worm-like structure and AgNPs which were excited enough to incorporate into the activated PET surface. Performed analyses showed that AgNPs were firmly immobilized in the thin surface layer of the polymer, were homogeneously distributed and strongly resisted the release into surrounding environment.

2. Experimental

2.1. Materials, apparatus and procedures

AgNPs were prepared electrochemically from two silver electrodes (silver bars, dimensions of 40 x 10 x 1 mm, purity 99,99%, supplied by Safina a.s., Czech Republic) immersed in sodium citrate electrolyte (0.016 wt.%, volume 200 ml, supplied by Sigma-Aldrich Co., USA) and powered by DC power supply (voltage 12 V, current 150 mA). DC voltage was applied to the silver bars immersed in electrolyte for 1 h under vigorous magnetic stirring at room temperature. Afterwards, the silver electrodes were carefully removed to avoid the dispersion of silver agglomerates from the cathode, caused by imperfect transport of formed NPs into the liquid volume. The beaker containing the solution was kept for 24 h in darkness to complete AgNPs formation. The AgNPs solution was then decanted and filtered to remove macroscopic impurities. For more details about the synthesis procedure see [28]. Finally, concentration of Ag in prepared colloid NP solution was determined by atomic absorption spectroscopy.

Immobilization of AgNPs was carried out using KrF excimer laser (COMPex Pro 50F, Coherent, Inc., wavelength 248 nm, pulse duration 20–40 ns, and repetition rate 10 Hz). Strip of polyethyleneterephthalate (PET) foil (Goodfellow Ltd., UK, thickness50 μm, dimensions 30 x 8 mm) was cut and placed vertically into high precision spectro-optics cell (HellmaAnalitics GmbH, Germany, type No. 100-QS, light path 10 mm) so that the polymer strip was centered in the middle of the cuvette. Afterwards, 3 ml of colloidal AgNPs solution was added using automatic pipette. The laser light was linearly polarized with a UV-grade fused silica prism (model PBSO-248-100). Irradiation was performed perpendicularly to the PET surface, using an aperture with an area of 5 x 10 mm^2.

2.2. Analytical methods

Concentration of Ag in prepared colloid NP solution was determined by atomic absorption spectroscopy (AAS) on VarianAA880 device (Varian Inc.,USA) using a flame atomizer at 242.8 nm wavelength. Typical uncertainty of concentration determined by this method is less than 3 %.

Silver NPs were analyzed by transmission electron microscopy (TEM). Drop of colloidal solution was placed on a copper grid coated with a thin amorphous carbon film on a filter paper. The excess of solvent was removed. Samples were air-dried and kept under vacuum in a desiccator before placing them on a specimen holder. TEM characterization of the samples was performed on JEOL JEM-1010 (JEOL Ltd., Japan) operated at 400 kV. Particle size was measured from the TEM micrographs and calculated by taking into account at least 500 particles.

The particle size and size-distribution was determined by Zetasizer ZS90 (Malvern Instruments Ltd., England) in the dynamic light scattering (DLS) regime equipped with an avalanche photodiode for detecting the signal. Diode pumped solid state laser (50 mW, 532 nm) was used as a light source. The measurements were performed in polystyrene cuvettes at room temperature.

Surface morphology was investigated using scanning electron microscopy (SEM) with a field emission electron gun on FIB-SEM TESCAN LYRA3GMU (Tescan a.s., Czech Republic) at acceleration voltage of 5 kV. Elemental analyses were performed using an energy dispersive spectroscopy analyzer (EDS) with a 20 mm^2 SDD detector (X-MaxN, Oxford instruments). Data evaluation was performed using AZtecEnergy software. To conduct the measurements, the samples were fixed by a carbon conductive tape and additionally deposited with 20 nm thick gold layer to ensure sample discharging. SEM-EDS measurements were carried out using a 10 kV electron beam.

Surface morphology and roughness was measured also by atomic force microscope (AFM) on DimensionIcon (Bruker Corp., USA) in ScanAsyst-Air mode. Silicon Nitride tip for ScanAsyst mode (Bruker Corp., USA) was used operating near its resonant frequency of 70 kHz (spring constant 0.4 N·m^{-1}). The scans were acquired at the line scanning rate of 0.5 Hz. Surface roughness, characterized by the mean roughness value (R_a), represents the arithmetic average of the deviation from the center plane of a sample.

The RBS spectra were measured on a 3 MV Tandetron MC 4130 accelerator using 2.0 MeV ^{4}He$^+$ ions at a laboratory scattering angle of 170° in the Cornell geometry. The Ultra-Ortec PIPS detector solid angle was 2.612 mSr, the spectrometer energy resolution for 2.0 MeV ^{4}He$^+$ ions was FWHM = 12 keV and the beam spot area on the sample was 1×1 mm^2. The typical beam current was 5 nA.

Compositional changes of polymer carrier were measured by X-ray photoelectron spectroscopy (XPS) by Omicron Nanotechnology ESCAProbeP spectrometer. The atomic concentrations of silver Ag3d, carbon C1 s and oxygen O1 s in laser irradiated/AgNPs immersed samples were analyzed. The X-ray source, monochromated at 1486.7 eV with the step size of 0.05 eV, was used. The spectra evaluation was carried out by CasaXPS software. The uncertainty of the measurement was less than 3%.

Inductively coupled plasma with mass spectroscopy detector (ICP-MS) was used to determine the bond-strength of immobilized nanoparticles on PET surface. The samples were immersed in 10 ml of distilled water and sonicated at 24 °C for 24 h. The trace element analysis of Ag leachates was conducted by using Agilent 8800 triple-quadrupole spectrometer (Agilent Technologies, Japan) connected to auto-sampler. Sample nebulization was performed using a MicroMist device equipped with a peristaltic pump. To minimize the interference of an analyte with PtH adduct, we used a collision cell (He collision gas) operating in a high-energy mode. The uncertainty of the measurement was less than 3%.

Raman scattering was measured on Nicolet Almega XR Raman spectrometer (laser power 15 mW) with 470 nm excitation wavelength (Thermo Scientific, France). Spectra were collected through