Comparison of immobilization yield in plasma and laser assisted processing of silver nanoparticles on polyethyleneterephthalate

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Abstract: Immobilization of nanoparticles on the surface of soft polymeric materials belongs to current issues of material science. Such altered polymeric platforms exhibit desired properties suitable for broad spectrum of industrially important applications ranging from catalysts over textile industry up to medicine. In this work we compare efficiency of immobilization process of silver nanoparticles on the surface of polyethyleneterephthalate accomplished by (i) plasma and (ii) laser treatment. Changes in chemical composition and surface structure of polymer after particle immobilization were studied in detail.

Keywords: Silver nanoparticles, plasma, laser, immobilization efficiency.

1. Introduction

Dating back to beginnings of this millennium nanoparticles (NPs) of different chemical composition and diverse morphologies, initiated technological revolution covering almost all fields of human activity. Application potential of these new entities spread out into such heterogeneous areas as catalysts [1,2], energy storage devices [3], medicine and health care industry [4], cosmetics [5] or textile industry [6]. Precise control over nanoparticle shape, size and composition promotes them for utilization in desired applications. Especially in catalysis, however, the immobilization process represent important technological step crucial to right component functionality in other fields too [7,8].

In this study we compare the immobilization yield of silver nanoparticles (AgNPs) on the surface of polyethyleneterephthalate (PET), performed by two different approaches; (i) plasma treatment-activated PET coated with biphenyl-4.4'-dithiol (BPD) active interlayer with high affinity to silver and (ii) laser assisted mediatorplain NPs immobilization of silver NPs (see Fig. 1a,b).



Fig. 1 Scheme of (a) plasma treatment activation process of PET with grafting of BPD interlayer and subsequent immobilization of silver NPs and (b) laser assisted mediator-plain immobilization process of silver NPs.

Electrochemically synthesized silver NPs were immobilized from their water solutions. Both techniques allowed activation of polymer surface, resulting in successful particle immobilization, however, the laser assisted approach eliminated the need of chemical mediator. Moreover, detected concentrations of silver were approximately twice higher when using laser assisted immobilization. Changes in chemical composition and surface structure of polymer after particle immobilization were examined by XPS, EDX, AAS, ICP-MS, TEM, and AFM techniques. Performed analyses showed that silver NPs were firmly immobilized in the thin surface layer of the polymer, homogeneously distributed and strongly resisted the release into surrounding media, however, majority of monitored parameters indicated the benefit of the laser immobilization method compared to plasma approach.

2. Materials, methods 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, current150 mA). DC voltage was applied to the silver bars immersed in electrolyte for 30 min under vigorous magnetic stirring at elevated temperature of 60°C. 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. Finally, concentration of silver in prepared colloid NP solution was determined by atomic absorption spectroscopy.

Biaxially oriented PET foil (density 1.3 g cm⁻³, 50 μ m thick, supplied by Goodfellow Ltd., UK) was used in this study. The samples were treated in Ar⁺ plasma on Balzers SCD 050 device; the exposure time was 240 s, the discharge power 8.3W, gas purity 99.99%, flow rate 0.3 l s⁻¹, pressure 10 Pa, electrode distance 50 mm and its area 48 cm², chamber volume approx. 1000 cm³, plasma volume 240 cm³ and treatment was accomplished at the

laboratory temperature. Immediately after the plasma treatment the samples were inserted into methanol solution of biphenyl-4.4'-dithiol $(1x10^{-4} \text{ mol } 1^{-1}; \text{ BPD};$ Sigma-Aldrich Corp.; US) for 24 h. After this step the samples were inserted into colloidal solution of AgNPs (average diameter of 23.1 ± 5.9 nm, concentration of 60 mg 1^{-1}) for 24 h. Finally the samples were rinsed in methanol and then dried under N₂ flow. Samples were kept under laboratory conditions in desiccator.

Immobilization of silver NPs was carried out using KrF excimer laser (COMPex Pro 50F, Coherent, Inc., wavelength 248 nm, pulse duration 20–40 ns, repetition rate 10 Hz, laser fluence 32 mJ.cm⁻²). Strip of PET foil (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 centred in the middle of the cuvette. Afterwards, 3 ml of colloidal silver NPs 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 mm².

Concentration of silver in prepared colloid NP solution was determined by atomic absorption spectroscopy (AAS) on VarianAA880device (Varian Inc.,USA) using a flame atomizer at 242.8 nm wave-length. Typical uncertainty of concentration determined by thismethod 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.

Elemental analyses were performed using an energy dispersive spectroscopy analyzer (EDS) with a 20 mm² 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 centre plane of a sample. Compositional changes of polymer carrier were measured by X-ray photoelectron spectroscopy (XPS) by Omicron Nanotech-nology ESCAProbeP spectrometer. The atomic concentrations of silver Ag(3d) and sulphur S(2p) in plasma and laser immobilized 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 bondstrength 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. 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%.

3. Results and Discussion

TEM image of electrochemically synthesized silver NPs is shown in Fig. 2. The image refers to nanoparticles immediately after the synthesis process. It is obvious, that electrochemical synthesis provides faceted, round-shaped silver NPs with pretty narrow size-distribution. Average diameter of silver NPs derived from TEM images was (23.1 ± 5.9) nm.



Fig. 2 TEM image of silver nanoparticles used in the process of immobilization.

Concentration of silver in NPs solution, which was further used in the process of nanoparticle immobilization on the PET surface was determined by AAS to 60.0 mg I^{-1} . With respect to density of bulk silver and nanoparticle size derived from TEM, one can estimate the number of particles in 1 ml of colloid solution to about 6.0×10^9 .

Results from AFM analysis providing detailed information about the vertical proportions are shown in Fig. 3. Fig. 3a refers to surface morphology of PET after

plasma activated silver NPs immobilization utilizing BPD interlayer, whereas Fig 3b shows surface morphology of the sample with immobilized silver NPs in laser assisted manner. While plasma approach does not significantly affect surface morphology of polymer, in the case of laser approach dramatic change of surface morphology takes place (see corresponding scale bar). This may be caused by the presence of BPD interlayer, which may smooth the surface roughness. Moreover, one can clearly see a fine microstructure (Fig. 3a,b) superimposed on the original PET morphology, suggesting the presence of silver NPs.



Height Sensor 600.0 nm Fig. 3 AFM images of PET after plasma (a) and laser (b) immobilized silver NPs on its surface.

Distinctive microstructure visible in the AFM images (Fig. 3) is most likely associated with the immobilization of AgNPs in a thin surface layer of polymer. To confirm this, XPS and EDX analyses were conducted. Atomic concentrations of elements derived from XPS spectra Ag(3d), S(2p) are summarized in Table 1. The measurement was conducted on plasma activated samples in two steps; (i) after BPD grafting and (ii) after silver whereas at laser NPs immobilization, assisted immobilized samples in one step only (after mediatorplain silver NPs immobilization process). Therefore, concentration of sulphur (S) refers to the success of BPD grafting in plasma approach.

Table 1 Concentration of silver Ag(3d) and sulphur S(2p) in silver NPs immobilized PET.

PET Sample	Concentration of Elements (at. %)	
-	Ag	S
Plasma/BPD/AgNPs	2.9	7.3
Laser/AgNPs	9.1	-



Fig. 4 Records from EDX analysis showing the map of silver distribution. Corresponding concentrations of silver are $c^{Ag}_{Plasma} = 3.3 \%$, $c^{Ag}_{Laser} = 9.5 \%$.

Additionally to XPS, EDX analysis was performed to confirm the homogeneity of silver NPs distribution regarding to both immobilization methods. Outputs from EDX are summarized in Fig. 4. It shows silver mapping over the examined area after plasma assisted immobilization (upper image) and after laser assisted approach (bottom image). It is obvious that immobilized silver is uniformly distributed over the entire surface area in case of both methods. Different shades of blue colour are attributed to the signal from Ag. Atomic concentrations of elements (after excluding Au, $c^{Ag}_{Plasma} = 3.3 \%$, $c^{Ag}_{Laser} = 9.5 \%$) are corresponding to those acquired by XPS (see Table 1). Slight discrepancy is more likely due to the difference of penetration depth of primary radiation, which is in case of EDX three orders of magnitude higher.

Immobilization of particles onto polymers seems to be very promising in catalysis and medical related applications. Presented approaches, especially laser assisted approach lacking a chemical mediator open up new possibilities in the development of the next generation catalytic media or cell-conform antimicrobial coatings of polymeric materials, since the bound strength is expected to be strong enough to prevent particle release into the surrounding environment. Particle release capability into distilled water was examined by ICP method coupled with mass spectroscopy detector. Performed analysis showed, that practically no Ag was detected in the leachates even after vigorous sample sonication. Concentration of Ag detected in plasma and laser immobilized samples was 22.6 and 9.8 ng l-1, respectively. These findings are pretty closed to the value of Ag background in the distilled water itself.

4. Conclusions

Electrochemically synthesized silver NPs were successfully immobilized on the surface of PET foil by plasma and laser assisted approaches. Pronounced changes in the surface morphology of polymer were observed solely in the case of laser immobilization, which is probably due to the absence of chemical interlayer and higher energy of laser radiation. Broad spectrum of analytical methods proofed the presence of silver NPs onto the polymer surface regardless of specific method used, however, detected concentrations of Ag were about three-times higher in case of laser assisted approach compared to plasma one. ICP-MS proofed that AgNPs were firmly immobilized in the thin PET layer which prevented them to release into water environment even after vigorous sample sonication. Polymer immobilized nanoparticles are believed to open up new possibilities in the development of the next generation catalytic media or cell-conform antimicrobial coatings

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6. References

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