Synthesis of COOH-functionalized plasma polymer nanoparticles

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Abstract: In this work, we utilized a gas aggregation cluster source for the synthesis of carboxyl-functionalized nanoparticles (NPs) with tailor-made characteristics by polymerization of acrylic acid in radio-frequency plasma operated in continuous wave and pulsed mode. The aspects of gas phase NP synthesis as well as tailoring NP morphology and chemical composition are discussed.

Keywords: plasma, acrylic acid, nanoparticles, functionalization

1. Introduction

Over the last few decades, remarkable attention was drawn to plasma polymerization of acrylic acid to fabricate carboxyl-functionalized coatings. These novel materials are expected to be attractive for many biomedical applications and biosensor manufacturing [1].

Carboxyl functional groups are able to support adhesion and proliferation of different kinds of cells and, therefore, they can be used as immobilization agents for biomolecules [2]. The process of immobilizations is based on covalent binding via dehydration reaction between carboxylic group and primary amines (N-termini) of biomolecule. Moreover, these groups are quite sensitive to pH changes of the solution they are immersed in [3]. This type of behaviour could be applied in design of drug delivery systems exploiting the idea of releasing a certain amount of a payload, a drug, in an environment that possesses a specific pH.

It was shown that carboxyl-rich coatings can be successfully produced by means of acrylic acid plasma polymerization. However, all of the existing studies in this field deal with thin films, not with nanoparticles (NPs), although such NPs might be a substantial solution to a number of challenges in controlled drug/gene delivery system design. Efficiency and durability of these systems depend on strength of bio-load attachment to the NPs surface which is influenced by many various parameters such as total area of the interface, morphology, density of carboxyl functional groups, etc.

In this work, we utilized a gas aggregation cluster source (GAS) for the synthesis of COOH-functionalized NPs by plasma polymerization of acrylic acid (ppAA NPs).

2. Experimental

The experiments have been carried out using a deposition system comprised of a gas aggregation cluster source (GAS) mounted in the vertical position onto a deposition chamber (Fig.1).



Fig. 1. Experimental scheme of the GAS used for ppAA NPs.

The GAS consisted of a water-cooled vacuum chamber of cylindrical form with a conical lid and an orifice (1 mm \emptyset) in the end. It was equipped with a planar RF copper electrode (2 inches \emptyset). A flask containing a liquid monomer (Sigma-Aldrich, purity 99%) was connected to the GAS via a needle valve (Swagelok) which enabled the precise control of the monomer vapour flow rate. The automatic flow controller (MKS Instruments) was used to adjust the flow rate of a carrier gas (Ar). The monomer vapours were mixed with Ar and the mixture was injected into the aggregation chamber. The overall pressures in the aggregation and deposition chambers were maintained to be 100 Pa and 1 Pa, respectively. An RF generator (Cesar Dressler) operated in both continuous wave (CW) and pulsed mode was used to ignite the discharge. In the CW mode, the discharge power was the varying parameter whereas, in the case of the pulsed mode, duty cycle (DC), average power and pulse repetition frequency (PRF) were varied. The NPs formed in the aggregation chamber were collected onto silicon substrates placed on the substrate holder inside the deposition chamber.

3. Results and Discussion

The ppAA NPs were successfully synthesized both in the CW and in the pulsed mode, yet with a different size and flux which is defined as the number of the NPs deposited per unit area per time. Larger NPs with smaller flux are produced in the CW mode whereas the pulsed mode results in the yield of larger amounts of smaller NPs.



Fig. 2. SEM images of ppAA NPs deposited at different monomer flow rate at constant power of 40 W and various power in CW and pulsed mode at constant flow rate of 4.7 sccm. Deposition time: 30 s.

Fig. 2 shows the examples of the SEM images of the ppAA NPs in dependence on the monomer flow rate at constant average power, and on average power at fixed flow rate. The mean size of the NPs tends to grow from 24 nm to 99 nm with increasing of the monomer flow rate.

The NP size and flux were obtained for all average power values studied and are summarized in Figure 3. For both operational regimes, the trend is confirmed that the NP size decreases and the flux increases with increasing average power at constant duty cycle (DC). The changes in NP size and mass flux are more prominent in the case of the CW mode, whereas the behavior of the NP flux in the case of the pulsed mode is less explicit. The mean size of the NPs ranges from 15 nm to 100 nm in the CW mode, and from 22 nm up to 50 nm in the pulsed mode at constant DC of 50%. The NP flux in both modes demonstrated the saturation after 60 W.



Fig. 3. Dependence of the ppAA NP diameter, flux and mass flux on the average power in the CW and the pulsed mode.

The chemical composition of the ppAA NPs was analyzed by XPS and FTIR in dependence on the effective power in order to investigate an influence of the power input on the retention of the carboxyl functional groups. The NPs were prepared using both CW and pulsed mode at constant duty cycle of 50% and pulsed repetition frequency of 20 kHz (pulse period T_{pulse} of 50 µs). The C1s spectra (Fig. 4) resemble the spectra obtained for thin films of plasma polymerized acrylic acid.



Fig. 4. C 1s XPS spectra of ppAA NPs deposited at various discharge power in the CW mode.

The C1s envelope of the analyzed samples can be decomposed into four distinct peaks: a peak at 285.0 ± 0.1 eV associated with the C-C and C-H bonds, a peak at 286.5 ± 0.1 eV due to the C-OH and C-O-C functional groups, a peak at 288 ± 0.1 eV corresponding to the C=O and O-C-O bonds and, finally, a peak at 289.1 ± 0.1 which is attributed to the carboxyl and/or ester (-COOR) groups. Recently, carboxyls were distinguished from esters in plasma polymer films by performing chemical derivatization with trifluoroethanol (TFE) [4, 5]. The results confirmed that the contribution of the carboxyl groups to the peak at 289.1 exceeds 90% and, therefore, the peak can be mainly associated with the COOH functionalities.

For the ppAA NPs presented here, a decay of the concentration of the COOH groups is observed with an increase of the discharge power for both operational regimes. The most prominent loss of the carboxyl groups occurs in the plasma operated in the CW mode. The theoretical maximum of the carboxyl group concentration is 33 at. % (as is the case of conventional polyacrylic acid). The maximal values obtained for the ppAA NPs were 16 at. % for 25 W pulsed plasma and only 10 at. % for the CW mode. The minimal retention was observed for 80 W in both types of plasma without any significant difference between the operational modes.

Apart from XPS, the ppAA NPs deposited at different operational conditions were analysed by FTIR. The normalized IR-spectra are shown in Fig. 5. The most intensive peak (corresponding to the C=O bond) was used as reference for the normalization.

Generally, the spectra are similar to those recorded for the plasma polymerized AA in the form of thin films. The spectra show the expected bands of hydroxyls (2500-3500 cm⁻¹), hydrocarbons (2900-3000 cm⁻¹), and carbonylbased bonds (1700 cm⁻¹). The higher power results in the weaker signal from the carbonyl-based species which we associate with the poor retention of the carboxyls.



Fig. 5. Normalized FT-IR survey spectra of the ppAA NPs deposited at different power in the CW and the pulsed mode.

The ratio of the area under the C=O stretching band to the area under the C-H stretching band was used to estimate the efficiency of the carboxyl retention from the FTIR spectra. The ratio was obtained for five samples prepared in the CW and the pulsed mode at different power supplied to the plasma.

In both operational regimes (CW and pulsed), the C=O/C-H ratio decreases with increasing average discharge power. The obtained results are in close agreement with XPS data, suggesting that the increase of the power and, therefore, the average energy supplied per molecule, leads to the loss of the original monomer structure. High energy delivered to the monomer molecule causes a severe monomer fragmentation and, therefore to low carboxyl group concentration in the resulted NPs.

Duty cycle was found to be a powerful parameter to control the size, the flux and the chemical composition of the NPs at constant power. Under $P_{eff} = 40$ W, the NP size varied in the range of 30 nm to 100 nm, while the NP flux tended to decay with increasing DC. At high values of

DC, only individual NPs were formed whereas coagulation of the NPs into larger agglomerates was observed at low DC region. The phenomenon suggests that the accumulation of electric charge on the NPs during the on-time and its loss during the off-time are the concurring mechanisms that determine the resultant morphology.

The concentration of carboxyl groups in the resulted plasma polymer NPs was found to pass through minimum with varying DC from 100% to 32%. The maximal concentration of 12 at. % was reached at the lowest DC value of 32%.

4. Conclusion

Acrylic acid can be plasma polymerized with the formation of spherical NPs with the mean size controlled within 15 -100 nm. The NP size decreases and their number increases with the rise of the effective power at constant duty cycle (DC), or with the decreasing DC at constant P_{eff} . The flow rate of the monomer contributes to the size of NPs as well. However, the dependence is rather complicated. Higher energy causes more intensive monomer fragmentation and, therefore, a lack of the monomer structure retention in the resulted plasma polymer network. The COOH group concentration as well as the C=O/C-H ratio in the NPs significantly decreases with the increase of P_{eff}. In the large duty cycle regime, energetic collisions of positive ions with the growing NPs result in the detachment of low mass species at the expense of the retention of the COOH groups. In the small duty cycle regime, radical-induced opening of the double bond and chain propagation through the addition of intact monomer molecules becomes dominating.

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5. References

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