Heterogeneous nanoparticles for preparation of nanocomposites

A.Shelemin[1], D. Nikitin[1], M. Vaidulych[1], R.Stefanikova[1],M. Cieslar[2], O. Kylian[1]
A. Choukourov[1], H. Biederman[1]

[1]*Department of Macromolecular Physics, Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic*
[2]*Department of Physics of Materials, Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic*

Abstract: The three techniques for preparation of heterogeneous nanoparticles plasma polymer and Cu or Ag are introduced. The application of gas aggregation cluster source is described: 1) DC magnetron sputtering of Ag into high pressure of Ar+HMDSO, 2) RF magnetron sputtering of composite target Cu/Nylon and 3) the two magnetrons - RF for Nylon and DC for Ag sputtering. SEM, HRTEM and XPS characterization of nanoparticles was performed. Basic optical and electrical properties of nanoparticle films were studied.

Keywords: nanoparticles, gas aggregation cluster source, nanocomposite films.

1. Introduction

Gas aggregation cluster source became very popular for nanoparticles preparation [1-3]. In the most cases metal NPs were investigated. Later composite targets were used for heterogeneous NPs preparations, followed by adding one more or two magnetrons. Metallic core@shell NPs were successfully obtained. However, plasma polymer/metal NPs were attempted only in several cases [4-6]. In this contribution we would like to present several techniques that can be utilised for production of such NPs: mixing Ar and organic gas, e.g. HMDSO, composite target metal-nylon and two magnetrons DC for metal and RF for nylon inserted into one aggregation chamber.

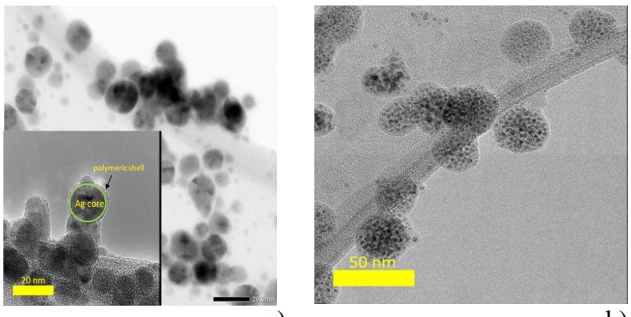
2. Experimental part

Gas aggregation cluster source (GAS) designed in our group was described in detail elsewhere (e.g. [7]). In short it is composed from the planar magnetron 3 inch in diameter placed in water cooled aggregation chamber 10 cm in diameter and 15 cm long ended by a conical piece with the exit orifice. The sputtering takes place in an Ar at a pressure from 30 to 100 Pa and flow 1 to 30 sccm. In one type of experiment DC magnetron was used with Ag target and Ar+n-Hexane or HMDSO vapours were introduced into the GAS. In the other experiment RF magnetron was used in the GAS using nylon target 3 mm thick with a strip of Cu sheet 2 cm bright and 2 mm thick placed over the Nylon centre. In the last set of experiments experimental set-up with the two magnetrons in one aggregation chamber was used. RF magnetron (applied RF power 40 W) with nylon 6,6 target from the side and DC magnetron with Ag target from the bottom. The pressure in the aggregation chamber was 122 Pa that corresponded to the Ar flow 28 sccm.

3. Results and discussion

In the first set of experiments the DC magnetron (3 inch in diameter) with Ag target in the GAS was operated in Ar+HMDSO working gas mixture at a pressure 150Pa and magnetron current 600 mA. The increase of the HMDSO percentage from 0 to about 5 % caused the increase of magnetron voltage from around 300V to 440V.

The XPS analysis showed that the signal from Ag 3d deteriorated with increasing of the monomer concentration. This evoked the assumption that a polymeric deposit appeared on the metallic NPs (cores). This was further proved by HRTEM. Introducing the monomer HMDSO into the Ar leads to the formation of smaller (~10 nm) Ag NPs enveloped in a thin plasma polymer (ppHMDSO) shell (Fig.1a). Moreover, under about 4% of HMDSO the NPs of the mean size 30 nm were composed of many small Ag cores (mean size 3 nm) encapsulated in a plasma polymer. This means that so-called Ag multicore/ppHMDSO shell NPs were deposited (Fig.1b). Nanocomposite films were prepared. These revealed PPR resonance effects in the UV-VIS region of light (anomalous absorption peak at a 380 nm wavelength). The electrical conductivity became very low when HMDSO concentration increased over 1% suggesting thus low Cu filling factor. I-V characteristic was as usual non-linear (parabolic or exponential).

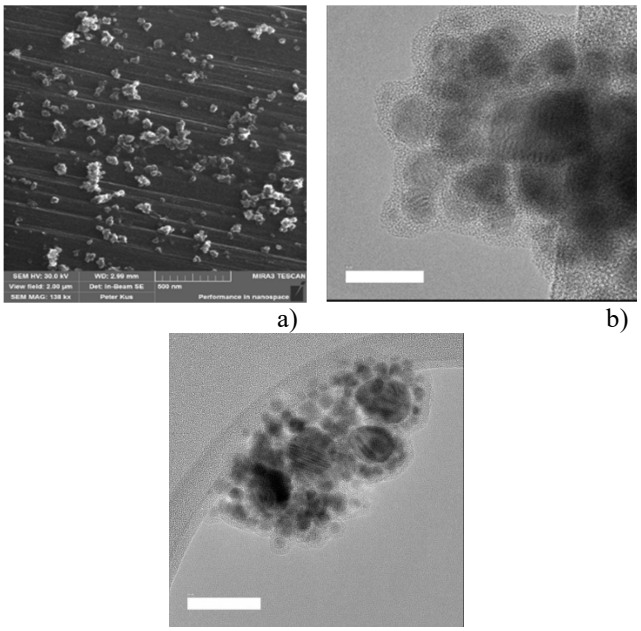


a) b)

Fig 1. HRTEM of the samples prepared at 1 % (a) and 4% of HMDSO in the working gas mixture.

In the second set of experiments the composite nylon/Cu target was RF sputtered in the GAS at an experimental conditions : flow of Ar 22 sccm; pressure 133 Pa, applied RF power 80W. The two basic groups of NPs were observed. Small ones with the size from 20 nm to 30 nm and then agglomerates of Cu NPs covered by plasma polymer. In Fig 2. It seems that central Cu nanoparticle about 40 nm in diameter is enveloped by a plasma polymer that contains again many small Cu NPs about 10 nm in diameter. Nanocomposite Cu/plasma

polymers films were obtained with the properties as above.



a) b) c)

Fig.2 SEM and HRTEM pictures of Cu/nylon like NPs.

In the last experiment the RF magnetron for Nylon and DC magnetron for Ag sputtering were used in order to fabricate heterogeneous NPs: plasma polymer with Ag NPs of the similar structure. Please, see Fig.3. It seems that the ”central“ Ag NP about 50 nm in size is encapsulated in a plasma polymer that contains smaller Ag ~ 10 nm nanoparticles and in addition very small ones (~ 3 nm in size). Nanoparticle films revealed PPR effects in transmitted UV-VIS light.

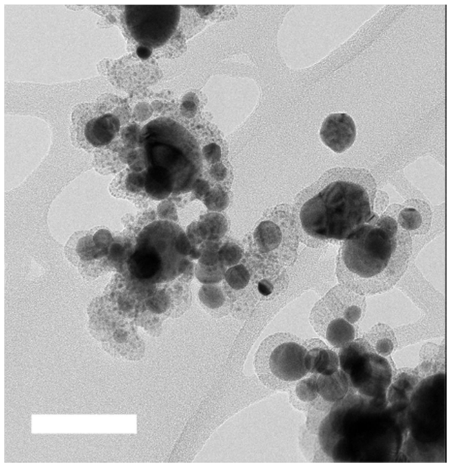


Fig.3. An example of HRTEM micrograph of nylon like NPs coated by silver.

4. Conclusions

It has been shown that heterogeneous NPs composed of a plasma polymer and Cu or Ag can be prepared by the three described ways and can be used for preparation of nanocomposite films. However, only the first technique proved to enable longer time stable deposition of heterogeneous NPs and therefore reproducible deposition of nanocomposite films.

5. Acknowledgements

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6. References

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