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PLASMA-BASED NANO-STRUCTURING OF SURFACES

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Abstract
Fabrication of nano-structured surfaces by plasma-based methods is discussed with special attention paid to deposition of nano-particles by gas aggregation particle sources. Combination of different nano-particles as well as their embedding into supporting matrices is shown to open diverse possibilities for controllable tuning of functionality of resultant films.

Ключевые слова: плазма, наноструктуры, поверхность, частицы, газ

Introduction

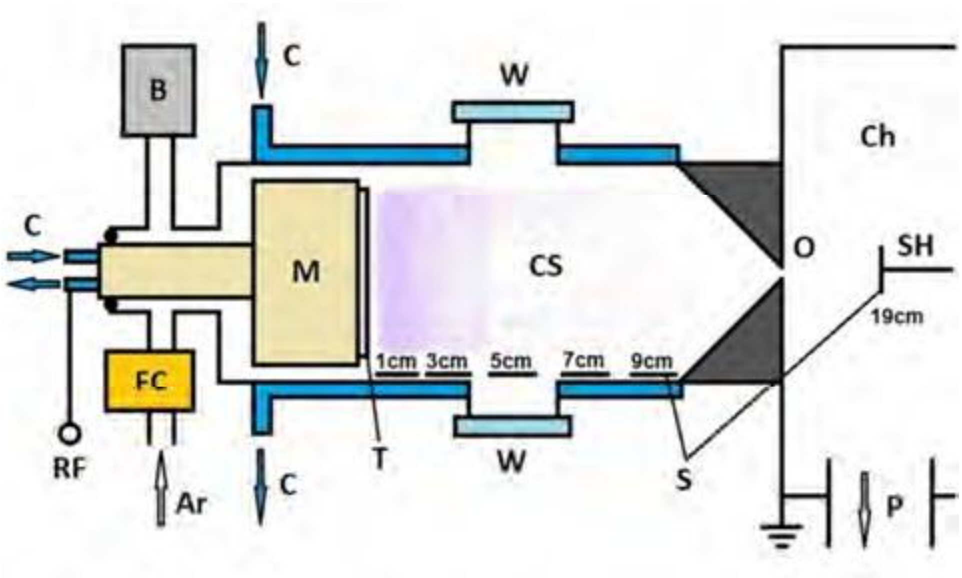
Vacuum deposition of pre-formed nanoparticles (NPs) onto solid supports has gained significant scientific as well as technological interest. This is given by the ability to produce NPs of a great variety of materials with adjustable size distribution, to study their atomic/molecular structure and possible hierarchic self-organization. Fabrication of novel NP-based materials with advanced functionality has also attracted a great deal of attention.

Regardless the diversity of NP sources developed up to date, all of them contain a region where supersaturated vapors of the material are confined. First sources used simple heating of metals above their melting point with subsequent ejection of metal vapor through a nozzle into a cooled region containing a rarefied inert gas [1]. The use of cooled rare gas favored condensation of vapors into NPs which were then extracted through a series of apertures into a high-vacuum chamber. Later, the thermal source was replaced by a DC magnetron with a sputtered target which allowed fabrication of NPs of refractory metals with higher fluxes [2]. Furthermore, a significant portion of NPs were ionized as they were formed and travelled through the magnetron discharge zone. This opened the possibility to manipulate the beam by application of electromagnetic fields. Further development involved utilization of planar magnetrons which were driven either by DC or by RF generators. The magnetron was placed in the gas aggregation chamber at elevated pressure which was separated from the high-vacuum main deposition chamber via a nozzle as shown in Figure 1. The use of RF driving voltage allowed sputtering of non-conducting materials and broadened the palette of produced NP. The results presented below were obtained using this type of the particle source.

Results and discussion

Generally, stable fabrication of NPs depends on a number of parameters including pressure and flow rate (both defining the residence time of NPs in the aggregation chamber), the magnetron power and the type of the material to be sputtered. The presented NP source proved to be fairly universal as different types of NPs were successfully fabricated with the corresponding adjustment of deposition parameters. The entire palette of NPs produced so far includes metallic (Au, Ag, Pt, Cu, Ti, Al) NPs as well as NPs of plasma polymers produced by plasma polymerization of hexane [3] or by RF sputtering of PTFE [4] and nylon [5]. Figure 2 shows the examples of Pt, Ti, Al and C:H NPs obtained [3,6–8], others not shown for simplicity. Obviously, NPs with different size may be deposited with Pt giving the smallest ones (average size is 4 nm) followed by

Ti (22 nm), Al (60 nm) and C:H (110 nm). Thus, the surface roughness can be tuned in a wide range merely by choosing the appropriate type of NPs.



C-cooling water, B-pressure gauge,
FC-flow controller, M-magnetron,
T-target, W-window,
CS-gas aggregation source, S-substrates,
SH-substrate-holder,
O-orifice,
Ch-main deposition chamber,
P-pumping

Fig. 1 – The typical scheme of a gas aggregation particle source

Under the typical experimental conditions, the NPs arrive onto the surface in the soft-landing regime and therefore they are held on the surface by mere physical adsorption. Weak anchoring may limit their possible applications and one may consider additional fixing of NPs by overcoating them with a thin film. This brings further advantage of independent control of the surface roughness and chemical composition. The example in Figure 3 shows the NPs of C:H plasma polymer deposited on silicon and overcoated by flat films of C:H plasma polymer (top) or titanium (bottom). In both cases, the NPs were effectively buried in the overcoat, the roughness of the surface was retained but its chemistry completely changed.

Similar strategy can be used for fabrication of surfaces with controllable wettability [9]. Ti NPs similar to those shown in Figure 2 can be allowed to deposit for different periods of time, thus resulting in roughening of the growing front. As it is shown in Figure 4, the RMS roughness measured from the 5 μm AFM scans increases from 0.4 nm to 12.0 nm with deposition time. The particles can be afterwards overcoated either with hydrophobic plasma polymerized hexane or with hydrophilic plasma polymer produced by sputtering of nylon. According to the Wenzel law, the increase of the roughness enhances hydrophobicity of hydrophobic surfaces and hydrophilicity of hydrophilic ones. In the particular case in question, the water contact angle (WCA) increases from 90° to 130° for the plasma polymer of hexane and decreases from 45° to 25° for the nylon-sputtered plasma polymer.

High value of WCA and their low hysteresis measured on hexane-plasma-polymer-covered Ti NPs implies that the surface is slippery and can be characterized by a Cassie-Baxter model in which air pockets are assumed to be captured in the voids between the surface bumps. Such air pockets prevent a direct contact between water and the surface and a droplet easily rolls off the surface. A recent research found that dual- and multi-scale nano-structure may help to provide hydrophobic state of the surface, yet at the same time with a high adhesive force to water [10].

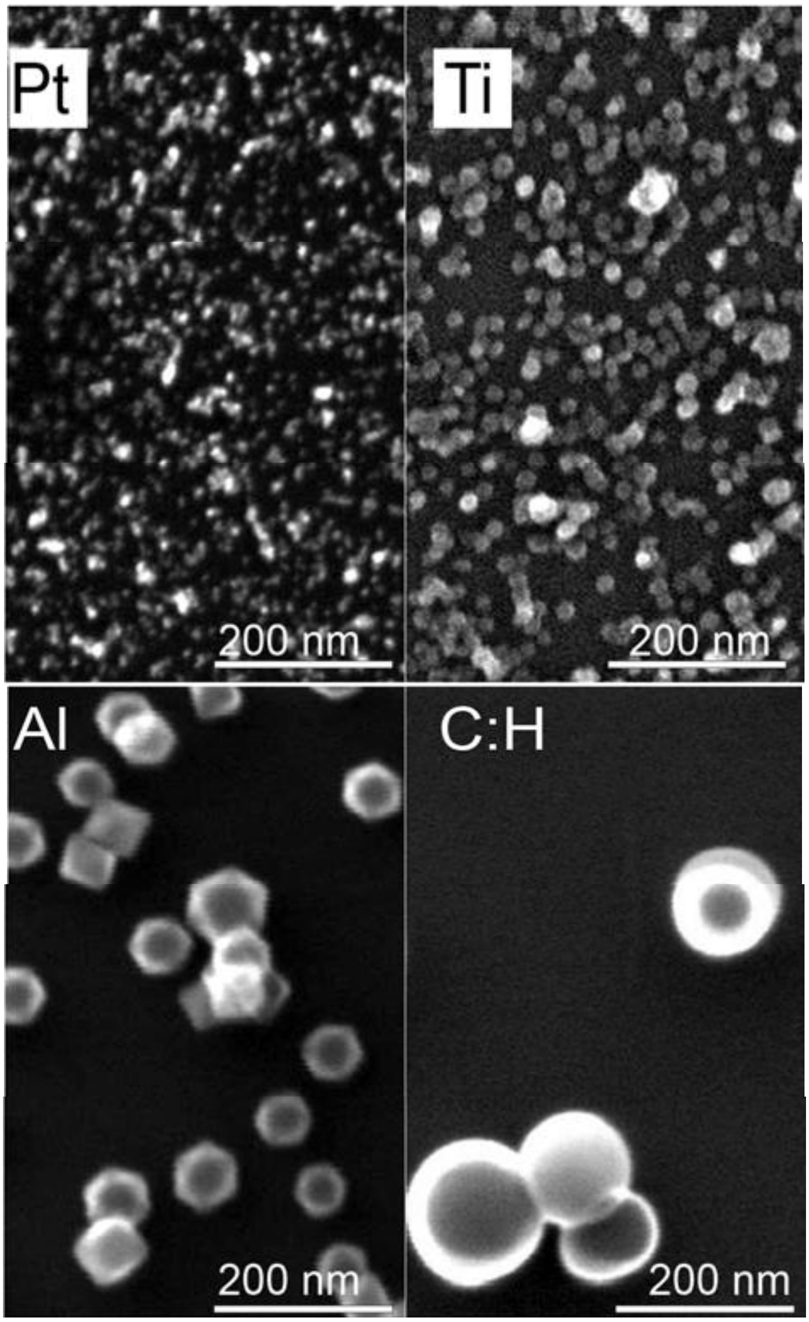


Fig. 2 – The SEM images of NPs produced by the gas aggregation source:
Pt 4 nm, Ti 22 nm, Al 60 nm, C:H 110 nm

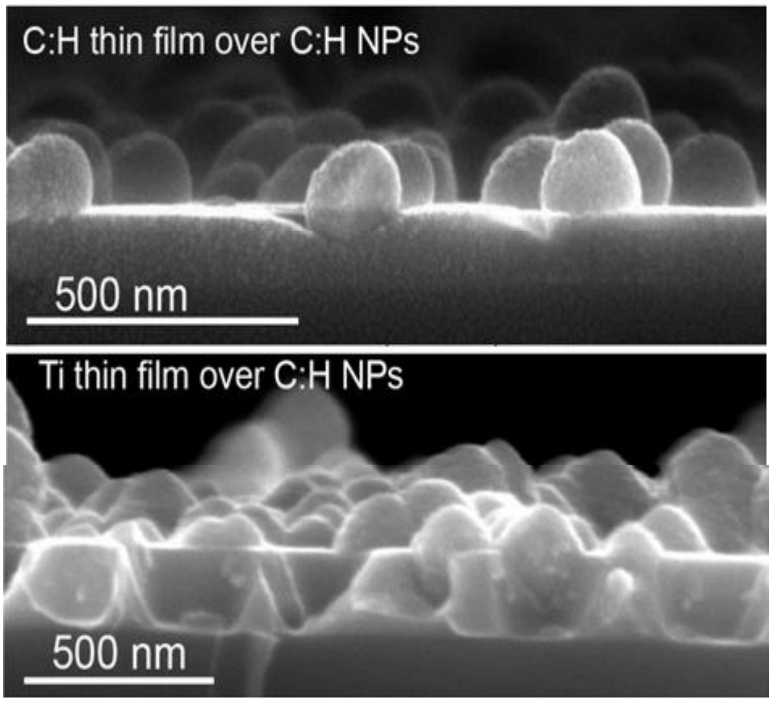


Fig. 3 – Cross-section of the C:H NPs overcoated by thin films of C:H plasma polymer (top) and Ti (bottom).

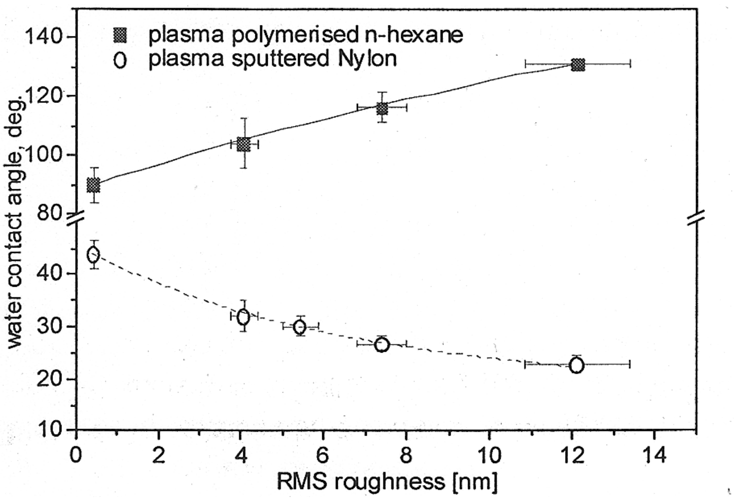


Fig. 4 – The dependence of water contact angle on roughness for the Ti NPs overcoated with plasma polymers of hexane and sputtered nylon

Such scenario was called the impregnating Cassie-Baxter regime to emphasize that water in this case penetrate in between the larger structures whereas smaller nano-structure still remains impenetrable. Deposition of different ensembles of clusters onto the same surface may readily satisfy the condition of dual scale roughness. Figure 5 shows the examples of the 200 nm C:H (top image) and 20 nm Cu (middle image) NPs deposited over flat silicon substrates.

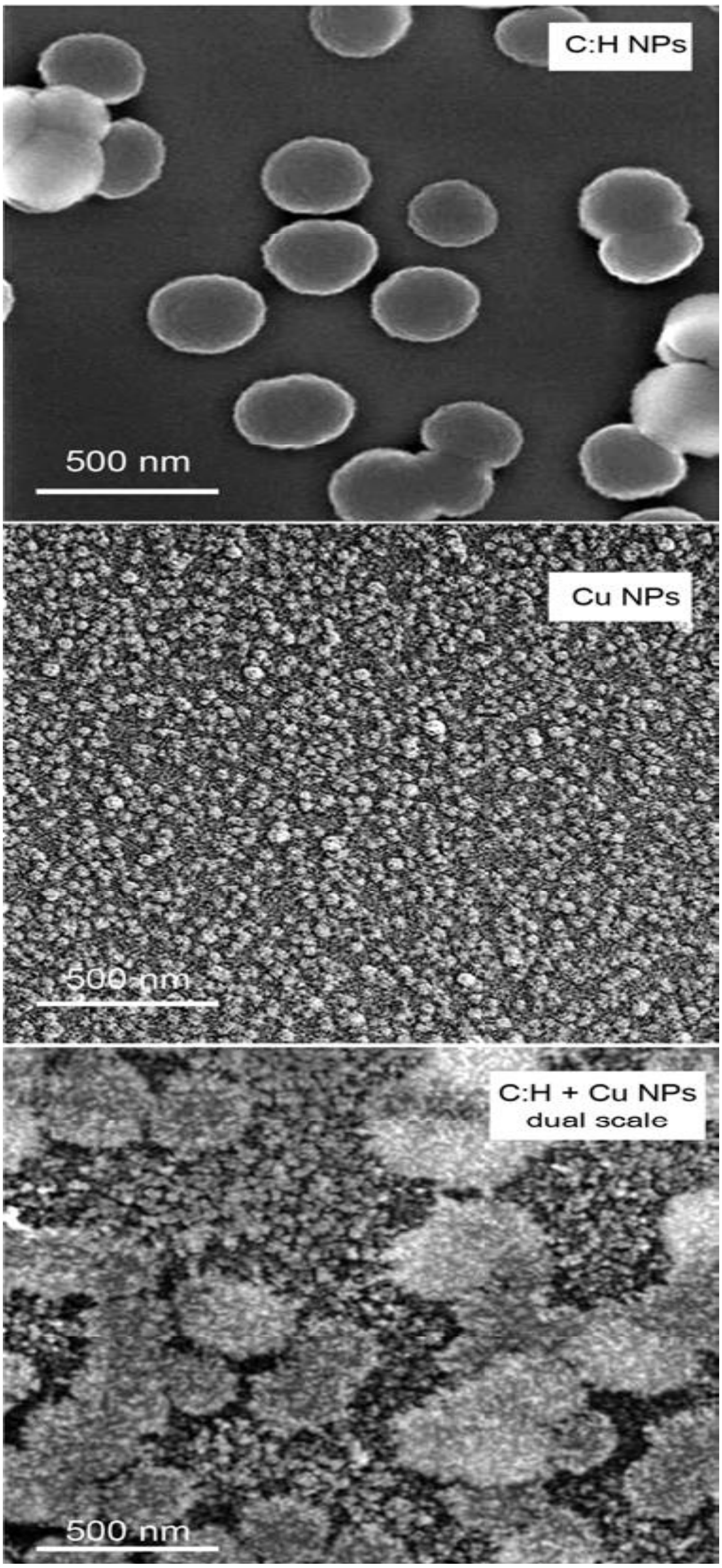


Fig. 5 – The SEM images of the large C:H NPs (top), small Cu NPs (middle) and the combination of the C:H and Cu NPs (bottom) yielding the dual-scale roughness

The bottom image of Figure 5 represents the coating produced in result of sequential deposition of the C:H and Cu NPs over the same Si substrate. Apparently, there exist two characteristic length scales on such surface which correspond to smaller Cu and bigger C:H NPs, respectively. The packing density of both types of NPs can be tuned by the proper adjustment of their deposition time and, thus, triggering between the classic and the impregnating Cassie-Baxter regime should be achievable.

The above examples dealt with sequential deposition of a layer of NPs and subsequent overcoating with another material. Further modification of nanocomposite fabrication may involve simultaneous deposition of NPs and embedding matrix. In this case, an auxiliary magnetron is mounted in the main deposition chamber and the position of the substrates is changed in a way to accept simultaneously the beam of NPs coming out of the gas aggregation source and the flux of the embedding material coming from the auxiliary magnetron. The concentration of NPs in the nanocomposite (filling factor) can be controlled by varying the operational conditions during the same deposition process.

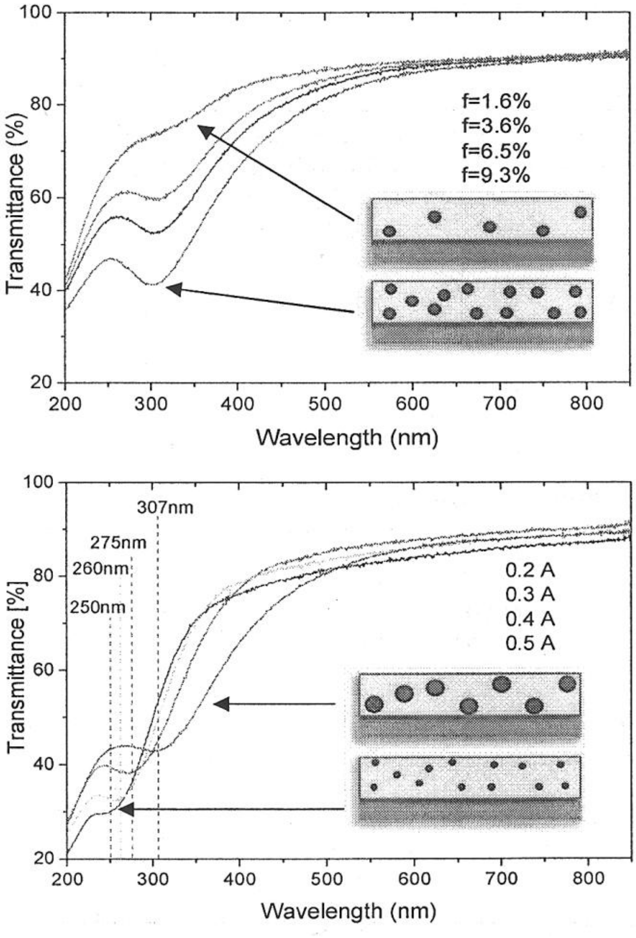


Fig. 6 – The UV-Vis spectra of the Al/C:H nanocomposites prepared with different filling factors (top) and different size of Al NPs (bottom)

The top graphs of Figure 6 show the UV-Vis spectra measured on the nanocomposite Al/C:H thin films which were fabricated by simultaneous deposition of the 60 nm Al NPs and the matrix of C:H plasma polymer [8]. The amount of the matrix was fixed for all the samples but the amount of the NPs was changed. This led to the fabrication of the films with filling factor (f) ranging from 1.6 to 9.3% (the insets in Figure 6 demonstrate schematically the structure of the nanocomposites in question). All the samples exhibit a characteristic plasmon resonance peak. Its position remains constant at 307 nm for all the nanocomposites but its intensity expectedly increases with filling factor. The position of the plasmon resonance can be tuned in a certain range by changing the size of the NPs. The Al/C:H nanocomposites were prepared at different currents on the Al target which resulted in fabrication of the NPs with the size ranging from 30 nm (0.2 A current) up to 60 nm (0.5 A current). The deposition of the C:H matrix was held at fixed parameters for this set of the samples. The UV-Vis spectra given in the bottom image of Figure 6 show the shift of the plasmon peak towards higher wavelengths with increasing the NP size. Hence, utilization of NPs produced by the gas aggregation source is feasible also for fine tuning of optical properties of the nanocomposites.

Another influence on the optical properties of resultant coatings can be expected if two types (or more) of NPs are used. Figure 7 shows the UV-Vis spectra taken on the sandwich-type nanocomposites in which several layers of 12 nm Ag NPs and/or 20 nm CU NPs were separated by the C:H matrix of plasma polymer. (It is worth noting that simultaneous deposition from two gas aggregation sources in a single-step process is also possible). The Ag NPs alone reveal the plasmon resonance around 400 nm (top image) while the Cu NPs exhibit such peak red-shifted to about 600 nm (middle image). The combination of both types of the NPs results in the spectrum which is characterized by two absorption maxima corresponding to the Ag and Cu NPs, respectively (bottom image). Thus, this technology can be perspective for fabrication of advanced optically active coatings.

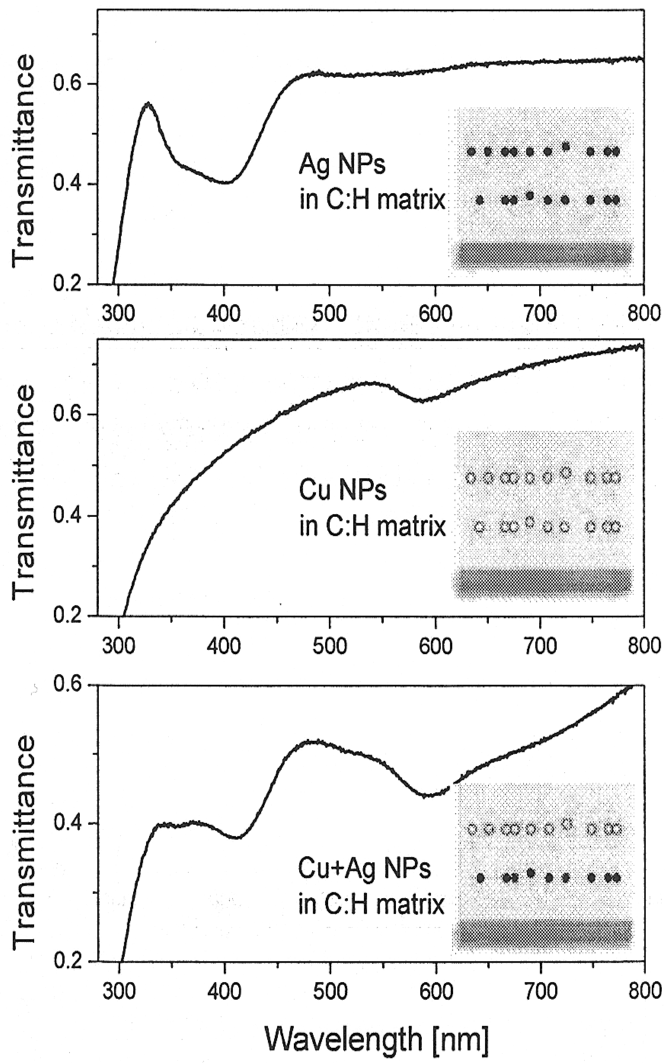


Fig. 7 – The UV-Vis spectra of the Ag/C:H (top), Cu/C:H (middle) and Ag/Cu/C:H (bottom) nanocomposites

Conclusions

Fabrication of NPs by gas aggregation sources is highly attractive both from the fundamental and applied point of view for solventfree, fast and relatively simple nanostructuring of surfaces. Diverse combination of the particle sources and auxiliary plasma-based techniques may provide a novel platform for fabrication of the coatings with advanced functionality.

Acknowledgements

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ПЛАЗМЕННОЕ НАНО-СТРУКТУРИРОВАНИЕ ПОВЕРХНОСТИ

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Аннотация
Обсуждается получение наноструктурированных поверхностей плазменными методами. Особое внимание уделяется осаждению нано-частиц из газа, как источника частиц. Показано, что сочетание различных наночастиц, а также их встраивание в матрицу, открывает различные возможности для управления функциональной перестройкой полученных пленок.

ПЛАЗМА БЕТІНІҢ НАНОҚҰРЫЛЫМДЫ

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Аннотация
Плазмалық әдістермен наноқұрылымды беттерді алу қарастырылады. Газдан нанобөлшектердің қалыптасуын бөлшектердің келу қайнары ретінде басты назарға аламыз. Түрлі нано-бөлшектердің бірігуі, сондай-ақ оларды матицияға енгізу,алынған қабыршықтарды функционалдық бағыттау үшін әр түрлі мүмкіндіктерін ашу көрсетіледі.