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Formation and applications of polymer films with gas-phase aggregated nanoparticles: A brief review

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ABSTRACT

Nanoparticles (NP) of different types, especially metal ones, are of high interest for research and industry due to a wide spectrum of unique physical and chemical properties. Among various synthesis methods, the gas-phase aggregation of clusters/NPs is a technique providing a number of advantages in tailoring the composition, structure and spatial arrangement of materials on the nanoscale. Depositing or embedding the NPs on/in polymer films can improve the key functional properties and bring additional convenience in practical use. Therefore, there has been an active research on the development of such composite films in the past decade. The paper overviews the main approaches for covering and filling the thin polymer films with NPs produced by gas aggregation sources and provide brief review on several application areas of such composite materials, where the capabilities to control surface roughness, wettability, optical and electrical properties play an important role. The review is finalized by the discussion of current challenges of the method and prospective ways of the development.

1. Introduction

During the last couple of decades, nanomaterials have become an integral part of a wide range research and industrial applications. A tremendous number of papers about different types of nanostructures and methods of synthesis has been published. In this review, the focus is put on one of the approaches, which has reached maturity relatively recently, namely the gas-phase aggregation of clusters (GAC), also known as the cluster beam technique [1–4]. In this content, cluster is an atomic aggregate ranging from a few up to many thousands of constituents, i.e. varying in size from a fraction of nanometer to some tens of nanometers. Therefore, words “cluster” and “nanoparticle” (NP) are used as synonyms in this work.

Cluster sources can be based on different principles of material vaporization utilizing heating, laser ablation, arc discharge, ion and magnetron sputtering as well as matrix assembly [2,5–8]. Overall, the GAC approach provides a number of advantages compared to other physical and chemical means of nanoscale synthesis [9] making this method to be a unique tool in many research areas. Among the advantages, there is a very good control of composition because ultra-pure targets are used and the particles are aggregated in vacuum. Formation of not only homoatomic but alloy and compound clusters with tunable structure and shape (core@shell, Janus- and dumbbell-like, spherical or cubic etc.) is possible [10–16]. Adjusting the aggregation parameters allows for NP size tuning [17]. Adding mass-filtering systems brings a capability of very precise selection, especially for small clusters, where a size control of ±1 atom can be reached [18]. Kinetic energy can be tuned, thus, allowing to vary the cluster-surface interaction mechanism from soft-lading to energetic impact (implantation or sputtering) [19]. One more advantage is control of the cluster beam flux enabling to provide required surface coverage or volume filling factor of NPs. Finally yet importantly is a capability to form patterned nanostructured films or coatings with gradients of NP surface density [20–23].

A lot of potential is seen in utilizing the GAC technique for the formation of nanocomposite materials. Polymers are very attractive hosting or supporting media for NPs due to plasticity, flexibility, easy processing, low weight and cost. Hence, use of polymers allows to improve or even add required functionality, for instance, to vary electrical and optical properties in a wide interval, while utilizing plasticity or porosity provided by the substrate in order to build elastic electrodes, actuators or sensors [24]. Incorporation of NPs into the organic matrix paves a way for biocompatibility or/and utilizing bactericidal properties [25,26]. It should be stressed that in the current review, the focus is put only on the polymer films with NPs produced by gas-phase aggregation method.

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2. Covering and filling of polymer films with NPs

Common polymers are materials with relatively low density (between 900 and 1500 kg/m^3) and low surface energy γ (between 20 and 80 mJ/m^2). NPs made of semiconductors, metals and their compounds have much higher density and also higher surface energy (on J/m^2 scale). These differences define the dynamics of NP behavior on a polymer surface. For a rigid particle on a surface of soft material, the following inequality condition is valid [27]

$$\gamma_{NP} > \gamma_{pol} + \gamma_{NP/pol}, \tag{1}$$

where γ_{NP}, γ_{pol} and $\gamma_{NP/pol}$ are the surface energies (tensions) at the interfaces of NP/air, polymer/air and NP/polymer, respectively. This condition requires the NP to immerse until the equilibrium is reached

$$\gamma_{NP} = \gamma_{NP/pol} + \gamma_{pol}\, cos\varphi, \tag{2}$$

where φ is the contact angle as shown in Fig. 1. Considering this equilibrium and geometry of a spherical in shape particle with radius r, height of the towered part h can be calculated as [28]

$$h = r(1 + \cos\varphi). \tag{3}$$

However, NP embedding into a solid-state polymer requires creation of a void. In terms of thermodynamics, the Gibbs free energy of the system must be changed fulfilling the work of adhesion requirement. One of the straightforward ways to add the energy is heating of the polymer. Bellow the glass transition temperate (T_g) the immersion process is slow, while above the T_g it becomes faster and the embedding velocity vs temperature follows Arrhenius plot [29]. Thus, varying the annealing temperature and time allows to control the immersion depth. An example of copper NPs deposited on polystyrene (PS) and annealed to facilitate the embedment is shown in Fig. 2 [28]. Similar results were obtained for other metal species and different polymers [30–32].

It is worth mentioning that the above-described scenario of a NP immersion into a polymer is idealized for an arbitrary rigid particle and homogeneous amorphous soft material. In fact, majority of real polymers can contain ordered regions where the chains fold together, thus, representing materials with some degree of crystallinity. Tendency to crystallize depends on the chemical composition, molecular weight of chains, structural details and temperature [33]. In most of bulk polymers, an increase of the crystal growth rate is observed for the temperature interval between the glass transition and melting points. However, in the case of a thin film, the nucleation is often found below T_g. Thus, the NP immersion will be site-dependent; the embedding rate would be different for amorphous areas compared to more rigid crystalline domains and the difference would become more pronounced with the temperature increase especially above the T_g value. Additionally, the thin near-surface layers of polymers were found to have higher molecular mobility and lower T_g, hence, affecting the immersion process [34]. These phenomena cause a difference in immersion dynamics of individual NPs leading to deviations in the depth of embedding, which can be seen in example presented in Fig. 2b.

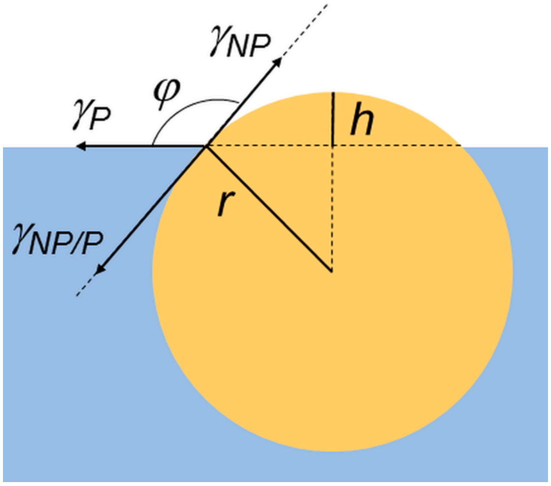

Fig. 1. Schematic picture of a NP with radius r towered above a polymer surface for height h. See text for the details.

Increase of NP kinetic energy on interaction with a polymer is another way to provide embedding. This approach was realized for small Pd NPs, which were collimated into a supersonic beam (mean velocity of 1000 m/s) and implanted into polymethyl(methacrylate), PMMA, to the depth up to 50 nm [35]. There are two important factors driven the implantation. On the one hand, the impact energy is lower (fraction of eV/atom) than the cohesive energy of the metal cluster (several eV/atom), therefore, the aggregates stay intact during the implantation. On the other hand, the total energy delivered at the impact spot is high because a NP consists of hundreds/thousands of atoms. It was theoretically calculated that an Au_{6000} cluster impacting polydimethylsiloxane (PDMS), with energy of 2 eV/atom leads to heating up to 600 K along the track [36]. The energy transfer causes the vibrational excitation of the polymer atoms on the time scale of 10^{-14} – 10^{-12} s [37] followed by the energy conversion into thermalization around the track on the time scale of some tens-hundreds ps [36]. The cluster penetration to the depth of several tens of nm is momentum driven. This simple model provides reasonable explanation of the cluster implantation to certain depth but one should consider that the real process is more complicated. The polymer may possess a high degree of crystallinity, thus, leading to inhomogeneity of the energy transfer and of viscoelastic properties. The penetrating cluster can cause scission of polymer chains or initiate cross-linking. The scission would lead to the change of polymer composition, for example, through the degassing of volatile compounds, while the cross-linking to the structural alteration. These degradation phenomena are well studied for ion implantation of polymers [38,39] but unfortunately not yet properly addressed in the literature for energetic clusters. Nevertheless, empirical adjustment of cluster implantation parameters provides an efficient way for filling of thin polymer films and formation of functional composites.

Polymer coatings with NPs can also be produced combing the GAC method with either plasma enhanced chemical vapor deposition or radio-frequency sputtering both allowing to form so-called plasma polymers [40]. The NPs deposition can be carried out simultaneously with the polymer formation or sequentially. The latter brings a capability to produce sandwich structures (see Fig. 3) [25]. Thus, one can build layers with well-controlled thickness, NP filling factor and arrangement of NPs inside the film, which can be based on various polymers (a-C:H, C:F, C:H:N:O, nylon etc.) and be filled with required nanoscale species (metals, metal oxides, semiconductors, core@shell structures etc.) [10,40,41].

To emphasize a high flexibility of GAC technique, a few recent advances towards synthesis of metal/polymer composite films should be mentioned. One of them is formation of metal core@polymer shell NPs; the metal NPs were produced by magnetron sputtering and then coated by an evaporated polymer during their flying time to the substrate inside the vacuum chamber [42]. Using this method, parameters of the core and shell can be independently tuned providing good flexibility in engineering the final structure and, thus, properties. Another example is formation of heterogeneous metal/polymer particles by adding a precursor gas (hexamethyldisiloxane) into the chamber where aggregation of the Ag NPs was occurring; the resulting structures showed multi-core@shell arrangement, several small metal cores became embedded into the polymer "envelope" [43]. The core and envelope parameters were found to be adjustable through the control of aggregation conditions.

Thus, using the cluster deposition/implantation on/in polymers or combining the cluster beam method with *in situ* polymer formation provide flexible technological approaches for the production of

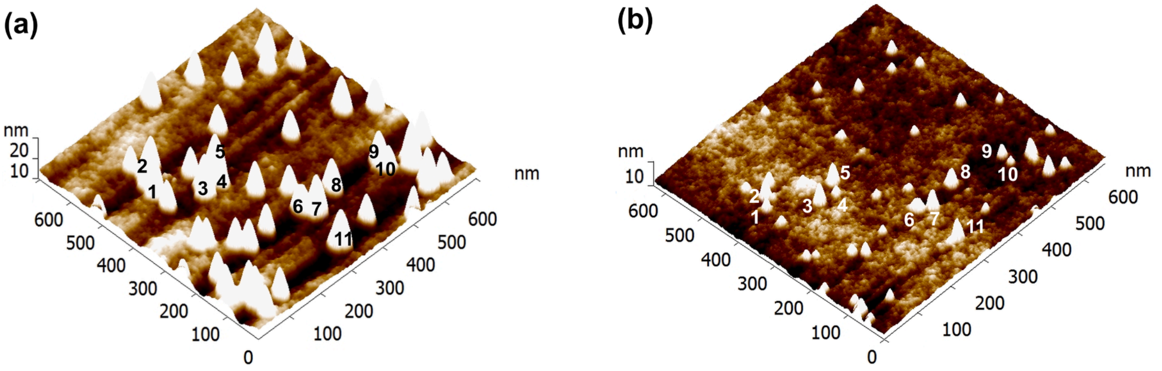

Fig. 2. Atomic force microscopy (AFM) images of Cu NPs on PS (a) directly after the deposition and (b) after annealing at 125 °C (above T_g) for 7 min. Some NPs are numbered to easier follow the immersion. Reprinted with permission from Bonde et al. [28].

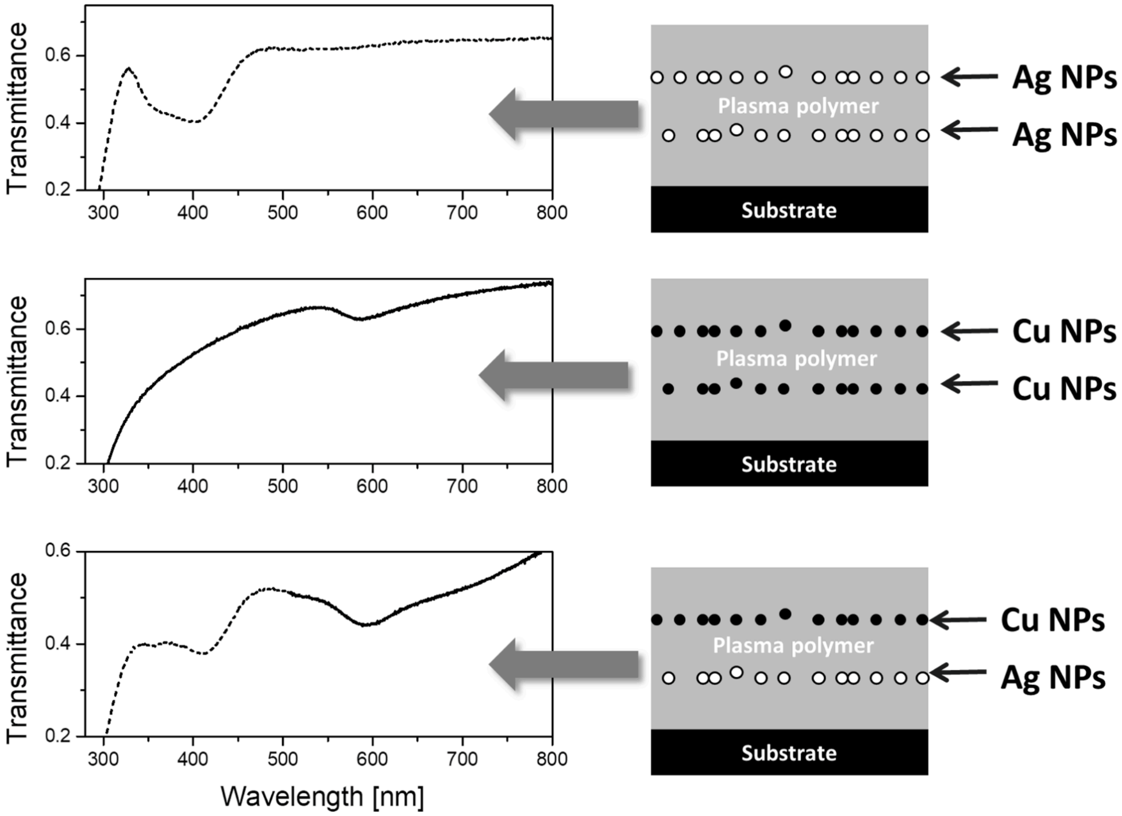

Fig. 3. Optical transmittance spectra of Ag (top), Cu (middle) and Ag/Cu (bottom) nanocomposites. Matrix material is C:H plasma polymer, thickness of C:H interlayers is 10 nm. Reprinted with permission from Kylián and Popok [25].

composite films, layers and coatings with unique functional properties.

3. Applications of polymer composite films with NPs

Polymer films with deposited or embedded NPs can be considered for a number of applications. These applications can be conditionally divided into several main groups, namely, utilizing (i) surface, (ii) electrical and (iii) optical properties of the composites. Functionalization of polymer surfaces through the nanoscale roughness control allows to tailor wettability and biocompatibility. At the same time, utilizing the NPs of certain metals and metal oxides can add the bactericidal properties. Controllable filling of polymer films with metal NPs paves the way for tuning the resistance and fabrication of devices in which the conductivity can be varied by elastic deformations or change of conductivity due to different external factors can be used for sensing. Embedding metal NPs into flexible polymer films also opens possibilities to fabricate devices with tunable optical properties.

3.1. *Tuning the roughness and wettability of polymer coatings with NPs for bio-applications*

Adding NPs on the surface or into the near-surface layer of a polymer film with controlled coverage or filling factor provides the way to tailor the roughness on the nanoscale. One can either enlarge the contact area between the composite surface and liquid droplet or limit the surface-liquid contact (by making protrusions with air pockets in between), thus, tune the wettability in a very wide range from super-hydrophilic to super-hydrophobic [25]. It is worth mentioning that an interplay between the surface energy of the NP and particular polymer also plays an important role, as already discussed in Section 2.

One of the ways to vary the roughness is through the control of polymer layer thickness at the constant particle coverage level. It was shown for 14 nm-sized Ag NPs, that at the initial stage of covering them by the plasma polymer (thickness below 20 nm), the composite film was porous leading to heterogeneous wetting of the surface with water contact angle (WCA) close to 135°, i.e. to super-hydrophobic state [44]. Increasing the polymer thickness caused the change of roughness and transition to the homogeneous wetting scenario.

The surface roughness can be adjusted by another approach, namely, by varying the cluster coverage and then depositing the polymer film of certain thickness. This way was tested using Ti NPs and two different polymers: sputtered nylon and plasma polymerized n-hexane [45]. These two polymers are known for different wetting properties when prepared as smooth films; nylon has hydrophilic character, while n-hexane is of hydrophobic nature. Increasing the roughness by the NP deposition caused two opposite trends. WCA of the Ti/n-hexane film increased making the coating super-hydrophobic, while WCA of the Ti/nylon film decreased showing good wetting conditions with WCA down to 16° at high roughness (see Fig. 4).

It was also shown that preparing the samples with gradient of NP coverage across the surface enables to gradually change the roughness and, thus, wetting properties as demonstrated for the deposited Ag NPs covered by poly(tetrafluoroethylene) prepared by magnetron sputtering [46]. The wetting can also be controlled by fabrication of nanocomposite coatings with multilayer structure of metal NPs. Such "sandwiches" allow to increase the metal filling factor without drastic change of the chemical composition also controlling the surface roughness. Layers of Cu NPs formed by magnetron sputtering were separated by 40 nm thick nylon "spacers" made by plasma sputtering in a sequential deposition process [47]. The composite films were found to increase hydrophilicity (to decrease WCA) due to the roughness increase with the number of embedded layers of Cu NPs (see Fig. 5).

One more example is the case when the NP/polymer coatings can be used to preserve wetting properties of technologically important films like for example SiO_2. It was shown in [48] that growth of silicon oxide films utilizing substrates with Ag NPs helps to keep them in super-hydrophilic state for 2 years while similar films grown on the substrates without NPs were observed converting towards higher WCA on the scale of days.

The above-discussed control of the surface roughness and wetting are very important issues for materials bioengineering providing a route for the formation of biocompatible polymer coatings mimicking topography of bones and other natural tissues. At the same time, embedded NPs of certain metals or metal oxides, such as Ag, AgO, Cu, Cu_2O, TiO_2 and some other metal combinations can promote bactericidal effect of the coatings [44,45]. Oxidation of metals can be achieved *in situ* by adding oxygen into the aggregation chamber or by in-flight oxygen plasma processing as well as *ex situ* directly after the NP deposition using oxygen plasma or ultraviolet(UV)-ozone treatment [51,52]. Combining the GAC method with the above-mentioned approaches of the polymer film growth provides a high flexibility to form coatings with appropriate wetting, antibacterial and cytotoxic properties. Leaching of metal ions (i.e. bactericidal vs cytotoxic effect) can be controlled through filling factor of metal NPs, their arrangement inside the film as well as through the type of polymer and its thickness. Some of the strategies are summarized in schematic pictures presented in Fig. 6 showing the cases of the film randomly filled by NPs of one or different species, bi-layered structures, film with towered NPs, composite film overcoated by non-fouling polymer and etched films. These strategies were recently applied and tested in bio-applications [49,50,53–55].

3.2. Polymer films with metal NPs for advanced optical applications

Nanoscale metal structures are well known for the phenomenon of localized surface plasmon resonance (LSPR) [56]. Gold, silver and copper NPs are among the most popular species providing the resonance in the spectral interval between near UV and near infrared. Aluminum nanostructures are attractive for the cases requiring maximal extinction in low UV range. These metal species are widely utilized in plasmonic-based sensing and surface enhanced Raman spectroscopy

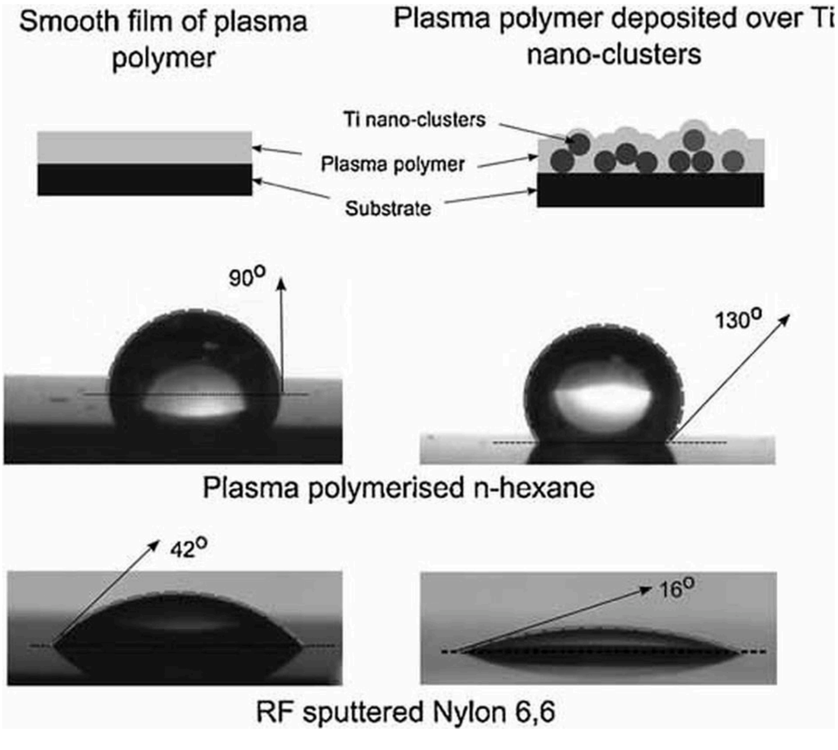

Fig. 4. Schematic pictures of the smooth plasma polymer film (top left) and the one with embedded Ti NPs (top right) as well as photos of measuring WCA on them, respectively, for n-hexane and nylon. Reprinted with permission from Kylián et al. [45].

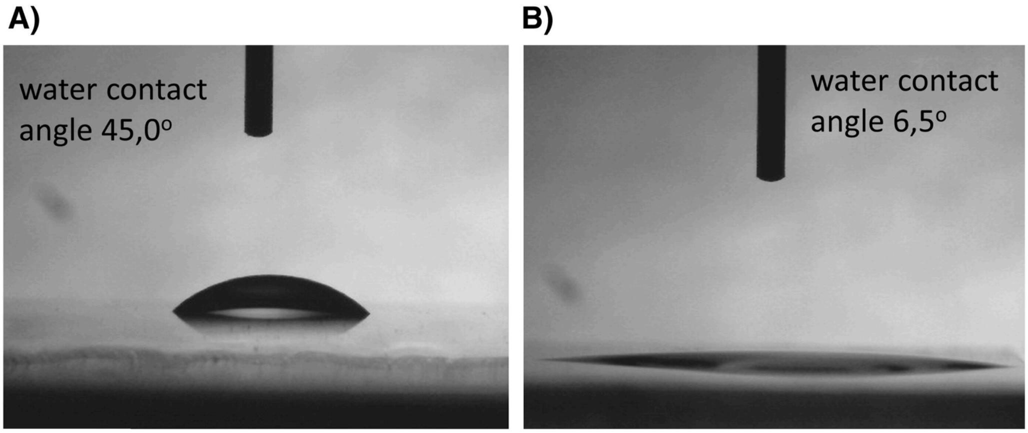

Fig. 5. Pictures of WCA measuring on (a) smooth plasma sputtered nylon and (b) nylon composite film with 5 layers of embedded Cu NPs. Reprinted with permission from Kylián et al. [47].

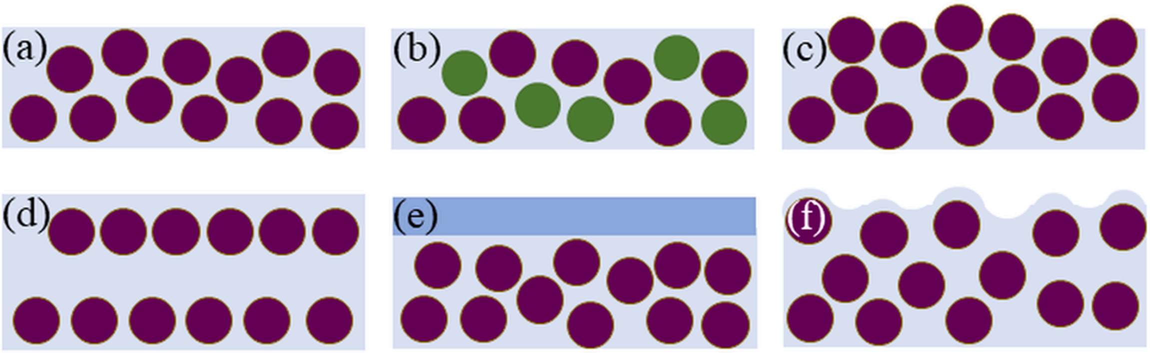

Fig. 6. Schematic pictures of different arrangements of NPs in polymer films: (a) film with randomly filled NPs of the same species; (b) film with randomly filled NPs of two different species; (c) film with towered NPs; (d) film with bi-layer filling of NPs; (e) film with NPs covered by non-fouling polymer layer; (f) nanorough composite film produced by oxygen etching.

(SERS) [57]. For the applications, it is important to adjust the plasmon resonance wavelength to that of the used laser. From this point of view, GAC method provides very good flexibility in tuning the resonance parameters by controlling the particle size and interparticle distance. For example, it was shown for Ag NPs that the resonance wavelength can be shifted for ca. 20–25 nm by changing the mean size from 12 to 24 nm [58] or it can be tuned from 400 to 570 nm by increasing the surface coverage (decreasing the interparticle distance) [59]. Making alloy NPs, for example of Ag and Au, allows to change the LSPR wavelength by adjusting the metal ratio [12].

Forming the polymer composites with NPs significantly widens tunability of the plasmonic properties. For instance, filling of polymer films with well separated layers of two different types of NPs, for example of Ag and Cu as shown in Fig. 3, provides a composite with two resonance bands. Embedding of NPs into a polymer film plays an important role in stabilizing them on the substrate (improving adhesion), which is an important issue for sensing of analytes in liquid phase [60,61]. Overcoating of NPs with polymers, however, has a drawback because the sensing efficiency decreases exponentially with distance. On the other hand, polymers have higher dielectric constant compared to air. Thus, NPs in organic matrix show an increased plasmon band intensity [30]. Hence, transducers represented by plasmonic NPs overcoated by the nm-thick polymer layer still enable to ensure good detection capabilities of biological analytes [62].

In SERS applications, arrays of NPs are often used to form so-called “hot spots” in order to obtain higher enhancement factor and approach single molecule detection [63]. Combining the cluster beam deposition on polymers with electron beam lithography was found to be an effective way to fabricate such arrays of Ag and Cu NPs [32]. In Fig. 7a, one can see a schematic picture of the procedure involving the spin coating of standard photoresists (polymethylglutarimide, PMGI) and PMMA, patterning and lift-off, NP deposition, annealing to facilitate NPs immersion into PMGI and finally one more lift-off to remove PMMA. As a result of these operations, the stripes of Ag NPs are obtained as shown in Fig. 7b.

Metals such as Cu and Al are prone to oxidize in ambient conditions. Therefore, their practical applications typically require passivation or overcoating. One of the recently-suggested original methods to preserve plasmonic properties of Cu NPs was UV-ozone treatment utilizing standard UV-ozone cleaners. Processing of Cu NPs for 20–30 min leaded to the formation of 2-3 nm thick Cu_2O shell around the metallic core which effectively protected it against following oxidation in ambient conditions [52]. UV-ozone processed Cu NPs were shown to preserve the intensive LSPR band for at least 5–6 months of storing in ordinary laboratory conditions (see Fig. 8). While been embedded into thin PMMA film, the UV-ozone processed Cu NPs also provided good time-stability of LSPR [31]. UV-ozone treatment of thin continues Cu films was shown to have the same protection effect promoting the open-air plasmonic applications [64].

One of the polymer properties, which is of importance for optical applications, is plasticity. Filling the polymer films with metal NPs opens a way for easy tuning the optical characteristics by the film stretching, compressing or bending, which change the interparticle distances. For the case of gold and silver NPs implanted into PDMS films, nanocomposites with stable plasmonic tuning properties and gratings with characteristics varying by stretching were fabricated [65,66].

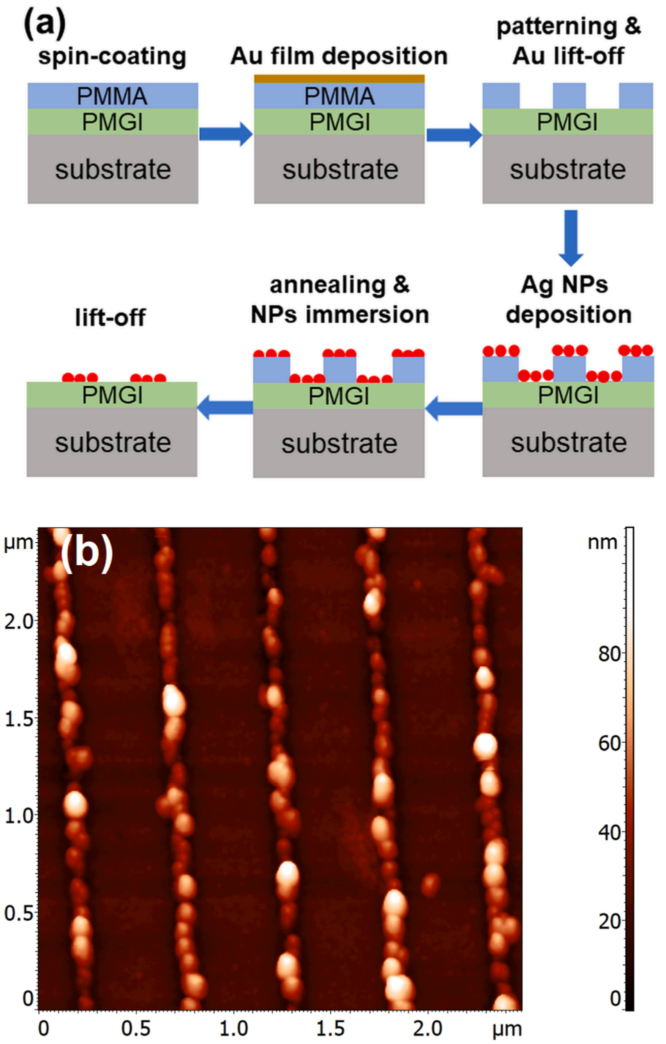

Fig. 7. (a) Schematic picture of the procedure for formation of cluster arrays (see text for details) and (b) AFM image of Ag NPs stripes obtained using this procedure.

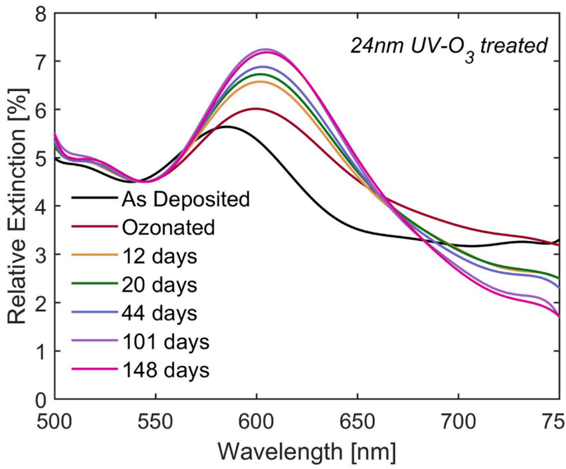

Fig. 8. Relative extinction spectra of 24 nm in diameter Cu NPs treated with UV-ozone for 20 min and stored in ambient atmospheric conditions at room temperature.

3.3. Polymer-NP composite films with tunable electrical properties

Embedding metal NPs into polymer film leads to change of electrical properties; increase of metal volume factor causes a gradual rise of conductance followed by a stepwise change when the percolation of NPs is reached, i.e. the conductive paths are formed through the polymer matrix [67]. Thus, by controlling the NP filling factor one can effectively tune the conductivity of the composite film. This approach was used to fabricate elastomeric electrodes by implantation of gold NPs into thin PMMA and PDMS films to the concentrations above the percolation threshold [68]. These films showed stable changes in resistance under repeating mechanical stretching, which is a big advantage compared to traditional electrodes made by thin metal film deposited on polymers in which the repeating strain leads to the film cracking and conductivity degradation. Another application area of thin polymer films with conductive NPs is formation of elastic actuators. 100 nm-thick polymer electrodes formed by gold cluster implantation showed sensitivity to voltages as small as 0.1 V and responded to frequency of 1 Hz [69].

Change of conductance of polymer films with metal NPs can be used for sensing. It can, for instance, be the detection of mechanical stress. One of the examples is the strain gauge fabricated by deposition of gas-aggregated Cr NP arrays on polyethylene terephthalate (PET). This device was found to be sensitive to very small relative strain change of 0.3% providing gauge factor of 20 (compared to 2 typical for metal film sensors) [70]. Later work on Pd NPs deposited on PET has shown that controlling the NP coverage was a key factor in tuning the sensitivity and extremely high gauge factors (up to 1000) can be reached [71]. Recent detailed review on the progress of strain sensors utilizing gas aggregated NPs can be found elsewhere [72].

Change of resistance of cluster-assembled films on interaction with gas species can also be used for chemical sensing. In this case, the polymer overcoating can serve as a sieve allowing the light gas molecules penetrate to the metal cluster assembly, which is the transducer, while protecting it from other damaging environmental factors. Such strategy was adopted when using arrays of percolating Pt NPs covered by poly(2-hydroxyethylmethacrylate) [73]. These sensors have shown good performance in measuring the humidity and ethanol. Currently, highly sensitive detection of hydrogen is of increasing demand due to broad consumer-level use of it. A few years ago, a sensor configuration involving gas-phase aggregated Pd NPs overcoated by PMMA was suggested [74]. It showed high capabilities in detection of H_2 while the PMMA layer protected the NPs from degrading gases like CO and CH_4. Recently, the configuration was improved by introducing a metal-organic framework (MOF) layer (see Fig. 9) altering the nature of the interaction with hydrogen and leading to significant sensing performance improvement [75].

4. Conclusions and outlook

Using the knowledge on physics of nanoparticle-polymer interaction and combining the existing technologies of gas cluster aggregation with the methods of polymer synthesis provide several possibilities for the production of polymer composite films, namely, by soft-landing of NPs on polymers followed by thermal annealing facilitating the immersion, by adjusting NP kinetic energy to provide direct implantation into polymers and by co-deposition of NPs and plasma polymers. Every approach has its advantages and disadvantages and can be chosen depending on the required structure and properties of the composite. These capabilities stimulate research on the polymers with gas aggregated NPs for the development of materials with advanced optical and electrical properties, electronic components, small electro-mechanical devices, platforms for sensing and biocompatible coatings.

Despite such wide applications in research, the industrial use of cluster sources is still sparse. One of the main limiting factors is a low production rate, which is on the level of tens of micrograms per hour for the majority of conventional GAC sources. However, recent efforts put

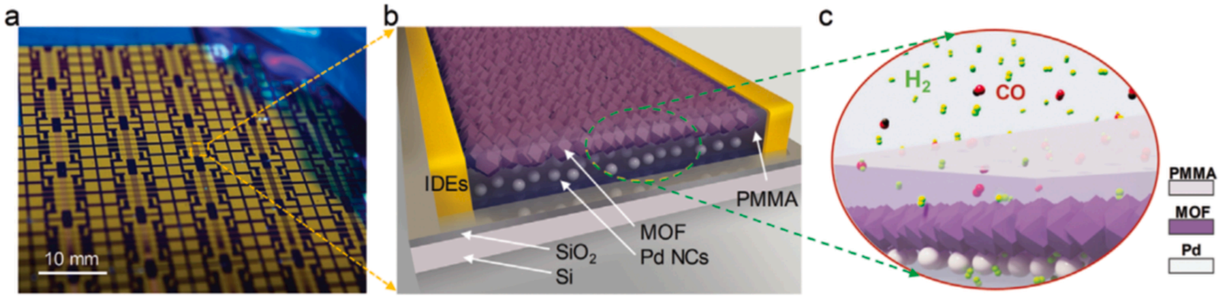

Fig. 9. Concept of hydrogen sensor based on the layered structure consisting of array of deposited Pd nanoclusters (NCs), MOF and PMMA overcoating between interdigital electrodes (IDEs). Reprinted with permission from Xie et al. [75].

on the optimization of the source geometry, nanoparticle aggregation conditions as well as the development of new types of sources showed significant progress reaching the capability to deposit 10–20 mg of clusters per hour [8,76]. This is already a sufficient level for some industrial use of precious metals for catalytic applications. Another very related issue is a need to improve efficiency of the cluster beam technology, i.e. to reduce costs, prolong operation times and increase reliability. To promote the production of multi-component materials, a better synergy of the gas-phase cluster aggregation technologies with *in situ* polymer synthesis methods such as plasma polymerization and in-flight coating is needed. Thus, the current mature state of the cluster beam method just requires next step of thorough engineering and technological development to be promoted to the industrial level.

CRediT authorship contribution statement

The manuscript is prepared by one author, i.e. everything is done by the same person.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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