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Aerosol-assisted atmospheric pressure cold plasma deposition of organic-inorganic nanocomposite coatings

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Abstract

Low pressure plasma technologies have been widely and successfully utilized for the production of a large variety of organic-inorganic nanocomposite thin films consisting of metal or metal oxide nanoparticles embedded in a polymer matrix. Recently, the deposition of this class of coatings has been also accomplished by atmospheric pressure cold plasmas using aerosol-assisted processes in which a dispersion containing preformed inorganic nanoparticles and the liquid precursor of the polymeric component is atomized and injected in aerosol form in the atmospheric plasma. This short review is aimed at presenting this approach which is expected to enlarge the range of structures and properties of organic-inorganic nanocomposite coatings deposited by cold plasma technologies.

Keywords organic-inorganic nanocomposite, thin film, atmospheric pressure cold plasmas, aerosol, nanoparticle

1 Introduction

Organic-inorganic nanocomposites (NCs), consisting of polymers and inorganic nanoparticles (NPs) with size generally smaller than 100 nm, have attracted considerable attention over the past decades in the field of materials chemistry. The final properties of these multiphase hybrid materials depend on the NPs type, size and shape, on the polymer nature and on the spatial organization of the two phases. More importantly, the close coexistence at the nanoscale level of dissimilar and, very often, incompatible components produces a wealth of novel structural features, physical properties, and complex functions that make such materials attractive for applications in various fields including optoelectronics, chemical or biological sensing, biomaterials, textiles, energy storage and catalysis [1]. This has promoted the huge development of a large variety of strategies for the preparation of organic-inorganic NCs, and nowadays research efforts are still directed towards the design and implementation of new synthetic approaches and methodologies with the aim of enlarging the range of structures and properties that can be reached by these materials, as well as affording large-scale production.

Low pressure (LP) plasma technologies are widely and successfully utilized for the production of organic-inorganic NC coatings consisting of a plasma-polymer matrix embedding metal or metal oxide inclusions [2–4]. Up to now the most frequently reported approaches exploit the plasma-enhanced chemical vapor deposition (PE-CVD) of organic and metal-organic compounds and/or various sputter-deposition techniques. The main features of these processes are the in situ formation of the NPs and the fact that the synthesis of both the polymer matrix and the inorganic particles very often occurs in a single step.

In the last two decades, the interest of both the academic and industrial communities have been expanded to the employment of atmospheric pressure (AP) cold plasmas technologies in thin film deposition. The main motivation in exploring such field has lied in the perspective of plasma reactors and processes easier to handle than low pressure ones, essential requirement for enabling their simpler integration into continuous production lines.

However, over the years, both the technological expectations and the fundamental interest have been accompanied by the growing awareness of the specific features of AP plasmas that differentiate them from low pressure ones and can even restrict their successful utilization in thin film deposition [5–7]. For instance, due to the atmospheric pressure operation and hence the high collision frequency, the kinetic energy of ions impinging the surfaces is always very low (<1 eV) because ions lose most of their kinetic energy in elastic collisions in the sheaths [6]. As far as thin film deposition is concerned, the lack of an effective ion bombardment of the surfaces makes the production of dense and crystalline films very challenging at room temperature and precludes the utilization of AP plasmas in sputtering-based processes for in situ production of metal or metal oxide NPs to be incorporated in NC coatings.

Nevertheless, there are still many exciting and often scarcely explored areas in NC thin film deposition, where the AP cold plasmas can be used. In fact research efforts are today directed to exploit AP cold plasmas considering their intrinsic specificities, rather than as limits, as the opportunity of indentifying new promising and even unique processes. This is expected to lead the plasma chemistry community to further enlarge the variety of coatings in terms of chemical composition and morphology, as well as not to consider the perfect replication at AP of the thin films successfully deposited by LP plasmas, as the only possible goal of the research in this field.

Recent studies have reported, for instance, that the deposition of organic-inorganic NC coatings by atmospheric pressure cold plasmas can be accomplished utilizing aerosol-assisted processes, in which a dispersion containing both inorganic NPs and a liquid organic precursor is atomized and introduced into the atmospheric plasma [8–12]. The deposited coatings consist of NPs and the organic component formed by plasma-polymerization of the precursor. This strategy is inspired by the literature on the preparation of NC thin films by different aerosol-assisted processes, such as the aerosol-assisted chemical vapor deposition in which an aerosol is utilized to transport preformed nanoparticles to a heated substrate [13–15]. Moreover, since preformed NPs are utilized, this approach has not to fulfill the requirements for the synthesis of the NPs in the plasma; as a consequence, the type and complexity of NPs (or, more generically, nanoobjects) included in the coatings could potentially be enlarged, allowing the production of novel multicomponent materials.

This short review is aimed at presenting this strategy, with the main purpose of giving a general sense of what has been accomplished so far and where the field is going. First, an overview is given of the currently available low pressure plasma-based processes and aerosol-assisted techniques for the deposition of organic-inorganic NC coatings. Then, the recent publications on the production of this class of coatings by aerosol-assisted atmospheric cold plasma deposition are presented. Finally, our recent study of the growth and structure of hydrocarbon polymer/ZnO NPs NC coatings in atmospheric pressure dielectric barrier discharges (DBDs) is briefly reported as an illustrative example for this deposition strategy.

2 Low pressure plasmas processes for organic-inorganic nanocomposite coatings

Low pressure plasma technology is nowadays widely utilized for the production of organic-inorganic NC materials in the form of thin films consisting of a plasma polymer matrix and inorganic inclusions (sizes ranging from a few nm to about 100 nm). Typical examples of successfully developed films consist of metallic (e.g., Ag, Au, Pt, Ti) or metal oxide (e.g., SiO₂, TiO₂, ZnO) NPs embedded in a large variety of polymeric matrixes (e.g., hydrocarbon, fluorocarbon, organosilicon plasma-polymers). An overview on the numerous approaches reported in the literature is provided in ref. 3 and 4; these approaches usually exploit the PE-CVD of organic and/or metal organic compounds and various sputter-

deposition techniques utilizing for instance DC glow discharges, capacitively-coupled RF discharges, DC/RF magnetron plasma sources. For the sake of brevity, considering the chemical sources and strategies utilized to obtain the organic and inorganic components of the coating, the deposition processes can be schematically divided into three main classes:

- *Class 1* corresponds to the simplest approach and uses a single chemical source and a single strategy for the growth of both the organic and inorganic components. This is the case, for instance, of the PE-CVD from a metal-organic precursor (referred to as metal-organic plasma-enhanced chemical vapor deposition, PE-MOCVD) which contains all the desired elements for the growth of the multicomponent material [16]. A very recent and notable example reports the deposition of nanometer-sized ZnO inclusions in a highly oxygenated organic matrix using zinc acetylacetonate as single source precursor [17]. Broadly, the optimization of these processes has proven challenging because the deposition conditions for the formation of both the inorganic particles and the organic matrix must coincide, often leaving only a narrow operational window.
- *Class 2* utilizes two independent chemical sources but a single strategy for the contemporaneous deposition of both the organic and inorganic components. For example, NC coatings can be deposited by co-sputtering of two independent magnetron sources with a polymer and a metal target [18–19].
- *Class 3* corresponds to the combination of two different strategies which utilize independent chemical sources for the contemporaneous deposition of both the organic and inorganic components. The most representative process of this route utilizes the pioneering process developed by Kay et al. [20] consisting of simultaneous plasma-polymerization (i.e., PE-CVD) of an organic precursor of the polymeric matrix and sputtering-deposition of the inorganic NPs using a RF diode-parallel plate electrode arrangement. To date this process is the most used and versatile because it offers several advantages such as: (i) the combination of a large variety of inorganic NPs and polymer matrices by selecting appropriate target materials and organic precursors, (ii) the rather homogeneous dispersion of NPs in the organic matrix, (iii) the easy control of the metal NPs content (i.e., metal filling factor) in the film from a few percent up to 100%, (iv) the modification of the properties of the polymer matrix over a broad range from essentially the same organic precursor by changing the experimental parameters during plasma-polymerization [2–4, 20–24]. For instance, Dilonardo et al. [23–24] reported the deposition of NC films made of platinum nanoclusters embedded in a hydrocarbon matrix (CH_x/Pt) by simultaneous PE-CVD of ethylene and sputtering of a Pt target (plasma reactor shown in Fig. 1a [23]), demonstrating that the Pt content in the coatings can be finely controlled by tuning the RF power delivered to the plasma, and varying or pulsing the ethylene flow rate. Fig. 1b [23] shows the atomic percentages of the CH_x/Pt films evaluated by X-ray photoelectron spectroscopy (XPS) as a function of the RF power; the Pt content increases with the power for the highest bias potential on the target and

consequently the higher sputtering rate. Moreover, as it can be appreciated from the transmission electron microscopy (TEM) images reported in Fig. 1c [23], the NC films show clusters of nanoparticles (up to several tens of nanometers in diameter) embedded in a light contrast low density matrix, apparently amorphous. The selected area diffraction (SAD) patterns (insets of Fig. 1c) confirm the crystalline nature of the nanoparticles and their random orientation within the film; for a Pt content of 60%, nanoparticles are larger (up to 7 nm) and form more populated clusters with respect to the film at Pt content of 1% [23].

Another widely utilized approach proposes the magnetron sputtering of a metal-containing target and the simultaneous plasma-polymerization of an organic precursor [25]. This approach is particularly suitable when, for instance, metal oxides need to be sputtered. In fact, since the sputtering yield of oxides is generally low, the enhancement of the gas ionization rate by a magnetic field allows achieving more efficient sputtering conditions.

Alternative processes, ascribable to *class 3* but not entirely based on plasma technology, propose for instance either the simultaneous deposition of the metal by vacuum evaporation and the plasma-polymerization of an organic precursor [26] or the simultaneous sputtering of a metal target and the vacuum thermal decomposition (often incorrectly named “evaporation”) of a polymer [27].

The common threads among the above described classes of processes are the in situ formation of the NPs and the fact that the synthesis of both the polymeric matrix and the inorganic particles occurs concurrently in a single step.

A notable exception, that can be classified as a variation of *Class 3*, is provided by the more recent approaches that utilize gas aggregation cluster sources (GAS) for the generation of metal NPs uniform in size by vacuum metal evaporation [28] or magnetron sputtering [29]. Specifically, in these processes the inner volume of the aggregation cluster sources is separated from the main deposition chamber in which for instance the plasma-polymerization of an organic precursor occurs. Due to the pressure difference between the GAS and the deposition chamber, the GAS injects NPs through an orifice smaller than a few mm in diameter into the plasma zone, leading to their incorporation in the growing polymer matrix. It is worth highlighting that, even if in this approach the synthesis of the NPs and the matrix does not occur simultaneously in a single step and in the same chamber, sequential tandem operation of both the GAS and the deposition chamber is required, also when a multilayer NC coating (e.g., consisting of alternating layers of metallic clusters and polymeric matrix) is deposited by a layer-by-layer method, in which the plasma-polymerization and the injection of metal clusters from the GAS do not occur simultaneously [30].

To the best of our knowledge, the deposition of NC coatings from preformed NPs using LP plasmas was reported only by Ross and Gleason[31]. Actually, this study pointed out for the first time the possibility of incorporating in a plasma-deposited coating different types of particles, e.g., commercially available or newly synthesized particles. The novel

deposition strategy utilized an aerosol for delivering the NPs to the reactor chamber during the PE-CVD of the matrix and, for sake of clarity, it will be presented in the next section of this review.

At the end of this overview on the utilization of low pressure plasmas for the production of organic-inorganic NC thin films, it is worth mentioning some of the functional properties of the deposited coatings that have been investigated for several applications:

- Optical properties. If the NPs are small compared to the wavelength of light, scattering is avoided, and the composites are transparent even at high nanoparticle filling factors; thus, the refraction index can be tuned over a wide range by changing the filling factor and type of filler [19]. Furthermore, for instance, in case of Au containing NCs, a strong absorption maximum occurs generally in the visible region or in the near infrared region of the optical spectrum due to collective resonant oscillations of the conduction electrons in Au NPs (i.e. a particle plasmon resonance) [2–4, 32]. This can lead to applications of the NCs coatings for the production of colored glass, sensors, integrated optical components, photonic devices, etc. [2–4].
- Electrical properties. Nanocomposites containing a metallic filler in a dielectric matrix exhibit interesting electronic properties. The conductivity varies from insulating to metallic as a function of the metal concentration and increases many orders of magnitude near the percolation threshold [33].
- Antibacterial properties. Organic-inorganic NC coatings containing Ag NPs exhibit, for instance, very good antibacterial effect, attributed to the controlled release of silver ions in contact with water. It was demonstrated that the Ag release properties of the coatings can be controlled by changing the coating thickness, the Ag content, as well as the composition of NPs and of the polymer matrix [34, 35].
- Catalytic properties. The application of NCs containing highly dispersed NPs of metals, such as platinum, for heterogeneous catalysis has been demonstrated so far. High performance electrocatalytic CH_x/Pt thin films were deposited by LP plasmas [23, 24, 36]. In these coatings the hydrocarbon matrix provides the mechanical support and electronic continuity, ensuring a uniform metal dispersion, avoiding Pt nanoparticle agglomeration.
- Wettability properties. Biederman and coworkers [37] demonstrated that the two-step process, combining the deposition of metal NP films by GAS, with subsequent polymer coating by plasma-polymerization or RF magnetron sputtering of a polymeric target, permits to adjust independently the chemical composition and the roughness of the resulting surfaces, allowing in turn the tuning of the surface wettability. With this approach it is possible either to increase (in the case of the overlayer having hydrophobic character) or decrease (in the case of hydrophilic overlayer) the static water contact angle (WCA) by approximately 50% as compared to the samples

without NPs. Even superhydrophobic (i.e., WCA higher than 150°) surfaces can be produced by overcoating the NPs films with a fluoropolymer [30].

3 Aerosol-assisted processes for the deposition of NC coatings

Aerosol-assisted processes have been widely utilized for the preparation of nanostructured and nanocomposite functional materials. In their simplest form they involve the atomization of a liquid into fine droplets (average size ranging from a few hundreds of nm to some μm) [13]. The atomization of the liquid can be carried out using various types of aerosol generators such as ultrasonic, pneumatic and electrostatic generators [14].

Among the variety of processes reported in the scientific literature, as far as the production of NC coatings is concerned, first the aerosol-assisted chemical vapor deposition (AACVD) has to be considered [14, 15]. This method is a liquid-phase variation of the conventional chemical vapor deposition (CVD) in which a liquid precursor in aerosol form is transported by a carrier gas to a reactor (either hot-wall or cold-wall reactor) where a heated substrate is located. The aerosol droplets undergo evaporation, decomposition, chemical reactions, on or in the vicinity of the heated substrate surface, leading to the deposition of a thin film. The principles, applications and recent progress of AACVD processes are reviewed in ref. 14 and 15.

The AACVD has traditionally been used when a CVD precursor is involatile or thermally unstable [14, 15]. The starting liquid to be atomized can be either a pure liquid (i.e., a single-source precursor) or a mixture of several liquid precursors, otherwise it can be prepared by dissolving solid or liquid precursors in a suitable solvent. Preformed nanometer-sized materials such as NPs can be also used as unconventional precursors; in this case the injection of the NPs into the reactor is accomplished by atomizing a dispersion of the NPs in a solvent. This implies that the crucial prerequisite for the utilization of this strategy is the good dispersibility of the NPs in a suitable solvent [14, 15]. This approach can be used to prepare NPs-containing coatings by simultaneously codepositing the NPs and the matrix deriving from a conventional CVD precursor through two possible methods:

- (i) *The injection in the CVD reactor of the aerosol of a dispersion of NPs which also contains the CVD precursor [38–41].* In these processes, after atomization, the aerosol droplets are directed towards the heated deposition zone, where the solvent is rapidly evaporated, and the CVD precursor undergoes decomposition and chemical reaction, near or on the heated substrate, to form the matrix of the NC coating embedding the NPs. For instance, Palgarve et al. [38] deposited thin films consisting of gold NPs incorporated in a tungsten or titanium oxide (i.e., WO_3 or TiO_2) matrix from a gold colloid in toluene in which tungsten phenoxide, $(\text{W}(\text{OPh})_6)$ or titanium isopropoxide $(\text{Ti}(\text{O}^i\text{Pr})_4)$ were also dissolved. It was demonstrated that the composition of the coatings (i.e., the content of NPs) and their final optical properties can be reliably changed by varying the mass ratio between the

NPs and the conventional precursor in the starting dispersion. Another notable example reports the incorporation of inorganic fullerene-like tungsten disulfide (IF-WS₂) NPs into a Cr₂O₃ matrix by an AACVD process starting from the alcoholic suspension of the NPs in which chromium nitrate nonahydrate was also dissolved [40, 41]. Interestingly, it was shown that if the aerosol droplets are large enough to contain several nanoparticles (droplet and NPs diameters in the range 1-10 μm and 80-220 nm, respectively), agglomeration of NPs can occur when the droplets shrink in the reactor chamber due to solvent evaporation. This can lead to the formation of NPs aggregates with a Cr₂O₃ shell and to their subsequent incorporation in the Cr₂O₃ matrix of the coating. This evidence suggests that using finer aerosol droplets or lowering the NPs concentration in the dispersion may be helpful to reduce the possible agglomeration.

- (ii) *The contemporaneous injection in the CVD reactor of the aerosol of a NPs dispersion and the vapor of a CVD precursor.* For instance Saeli et al. [42] proposed a single-step hybrid CVD process (i.e., hybrid atmospheric pressure CVD and aerosol-assisted CVD) to deposit NC films of gold NPs in vanadium dioxide. The VO₂ matrix was obtained by conventional CVD from vapors of vanadyl acetylacetonate transported in the deposition chamber by a carrier gas, while gold NPs were preformed in methanol and admitted in the reaction chamber using an aerosol.

The flexibility offered by aerosol-assisted deposition processes, respect to those in which NPs are generated in situ, mainly resides in the possibility of using many preformed NPs in combinations with any compatible conventional precursor. In fact, since the NPs synthesis is distinct from the deposition step, the deposition parameters do not need to be tailored to accommodate NPs formation. In addition, it is expected that preformed nanoobjects of complex compositions and shapes may be used, such as alloy NPs, core-shell NPs, nanorods, nanotubes. This makes AACVD a highly attractive approach in the design and synthesis of a wide range of novel multicomponent materials [14].

It is important to highlight that, as mentioned in the previous section, one of the first examples on this approach deals with the aerosol-assisted plasma-enhanced deposition of NC films in low pressure plasmas by Gleason and coworkers [31]. This work explored the use of an ultrasonic atomizer to distribute multimolecular and polymeric particles during PE-CVD of an organosilicon matrix from tetraethoxysilane (TEOS) and oxygen. Aqueous suspensions of dextran (i.e., a hydrophilic polysaccharides) NPs, ethylene glycol suspensions of dextran NPs, and aqueous suspensions of polystyrene nanospheres were used for the deposition. Particle deposition was explored in the context of solvent properties as well as reactor conditions, by examining their effect on the droplets evaporation rate and lifetime. The rate of solvent drying was experimentally controlled by changing both the reactor pressure and the solvent composition; the change of the drying rate was demonstrated to affect the dispersion of the particles in the coatings. To date this is the

only published study on the use of an aerosol for the deposition of NC coatings from preformed NPs using a low pressure plasma. The reason for the scarce utilization of this approach could lie in the fact that the handling of aerosols at low pressure is very difficult and problematic in particular if the deposition processes need to be carried out at room temperature (e.g., for the risk of contamination of the vacuum chamber with liquids).

It seems important to highlight that the first published examples on the deposition of nanocomposite coatings by AACVD referred to the production of inorganic NCs in which for instance inorganic NPs were embedded in a host metal oxide matrix. However, very recently it was demonstrated that the adequate choice of the starting dispersion and of the deposition conditions, such as the temperature, allows avoiding the pyrolytic decomposition of the organic fraction and affords the deposition of a NC coating consisting of inorganic NPs embedded in a polymeric matrix. Noticeably, Crick et al. [43, 44] incorporated preformed NPs into a polydimethylsiloxane (PDMS) polymer using a cold-walled AACVD technique. They atomized a chloroform suspension of a thermosetting silicone elastomer, containing a curing agent, and NPs adequately functionalized with a surfactant. While the NPs were functionalized to be readily dispersible in chloroform, the curing agent was added to promote crosslinking and hardening of the polymer, and therefore to generate a heat resistant organic matrix. Also in this study, it was observed that, since the chloroform in the aerosol droplets inevitably starts to evaporate between the atomizer and the CVD reactor, NPs tend to agglomerate due to the droplet shrinking; upon contact with the heated substrate, the solvent rapidly and definitely evaporates leaving a spherical agglomeration of the NPs [44]. The elastomer then cures around the agglomerates forming PDMS bulbs that protrude from the surface and are responsible of the microstructure of the coatings clearly evident in the scanning electron microscopy (SEM) image of Fig. 2a [43]. This material combines the low surface energy of the silicone polymer and the properties of the NPs for photocatalysis, magnetic applications or high surface area catalysis [44]. Actually, the surface texture of the coating coupled with the low surface energy of the polymeric component renders these NC coatings superhydrophobic; in particular, in the case of TiO₂ NPs, the NC films were able to exhibit both superhydrophobicity and photocatalytic properties, even after extensive periods of UV irradiation (Fig. 2a) [43].

Besides AACVD processes, the simple spray-deposition (also referred to as spray-casting) of a dispersion of both preformed NPs and an organic polymer in an adequate solvent has been also successfully utilized to produce organic-inorganic NC coatings with a hierarchical nanotextured surface morphology. Typically, spray-deposition is followed by air-drying under ambient condition or by mild heat treatment to remove any solvent residual and cure the coating. For instance with this method, a perfluoroacrylic polymer/ZnO NP nanocomposite film was obtained by Steele et al.[45] from suspensions of fluoroalkyl methacrylic copolymer and ZnO NPs in water, using acetone as cosolvent. The

substrate were coated with a single spray application and then air-dried for 12 h. Acetone was demonstrated to be the proper cosolvent, with a boiling point much lower than water, to ensure the evaporation of a substantial portion of the solvent within the spray mist before impacting the substrate, and hence to promote the formation of uniform coatings upon air-drying. As shown in Fig. 2b the surface morphology of this coating reveals the formation of a solid polymer microfoam-like structure coated with ZnO nanoparticles; a hierarchical multiscale surface roughness was obtained (i.e., microscale-to-nanoscale roughness) which allowed obtaining both superhydrophobic and even superoleophobic surfaces.

Noticeably, a possible alternative to this approach is the production of organic-inorganic NCs films by spray-deposition of a NPs dispersion containing the organic precursors of the polymeric component, followed by photoinduced [46] or thermal polymerization [46–48] of the precursors. For example, very recently, Sparks et al. [46] reported a simple and versatile method for the fabrication of an organic-inorganic nanocomposite coating via spray-casting of a dispersion of silica nanoparticles, UV-curable resin (i.e. thiol-ene resin) and a photoinitiator in a low boiling point organic solvent, followed by photopolymerization to afford the organic matrix formation.

4 Aerosol-assisted atmospheric pressure cold plasma deposition of organic/inorganic NC coatings

Thin film deposition by AP cold plasmas is accomplished either by using the precursor gas or vapor, as in the classical PE-CVD, or by injecting a liquid precursor, as in the aerosol-assisted plasma deposition (AAPD). It is important to remark that, due to the lack of an effective ion bombardment, sputter-deposition processes cannot be carried out by AP cold plasmas, with consequent limitations in the deposition of organic-inorganic NC coatings. However, as it can be easily realized in the light of the scientific literature mentioned in the previous section, the aerosol-assisted plasma deposition at atmospheric pressure can be considered an effective strategy towards the production of multicomponent nanocomposite coatings.

In AAPD processes the aerosol is usually generated by pneumatic or ultrasonic atomizers; while the first approach requires an atomizing gas, as for instance the dilution gas of the discharge feed mixture, the second technology allows the direct atomization of the liquid introduced into an ultrasonic nozzle which can be either integrated in the discharge cell or located outside (i.e., upstream) the discharge area.

First, Badyal and co-workers [49–50] developed in 2003 a polymerization process at AP in which a He dielectric barrier discharge was combined with the aerosol of a liquid precursor injected through an ultrasonic nozzle integrated in the ground electrode of the discharge cell. Utilizing acrylic acid as precursor, they demonstrated the possibility of obtaining a high retention of the precursor carboxylic acid group in the coatings [50]. Afterwards, several groups reported the employment of aerosols for the deposition of functional coatings [53–57].

One of the primary motivations in exploring such processes has lied in the fundamental challenge of comparing the AAPD with the classical PE-CVD process, with the aim of highlighting specific and even unique properties of the coatings deposited with these two strategies [53, 54]. Briefly, the injection in the atmospheric plasma of a liquid precursor, in the form of finely dispersed drops of liquid, is thought to protect the precursor structure from the action of the energetic species in the plasma, minimizing the fragmentation with respect to the classical PE-CVD process in which the precursor molecules in the vapor phase are directly exposed to the plasma. It is also supposed that, in the AAPD, most precursor in the liquid phase is shielded from the plasma, also when the droplets wet out the substrate surface [53, 54].

However, without doubt, the main motivation in utilizing aerosol-assisted processes resides in the fact that they offer the unique possibility of injecting in the atmospheric plasma involatile [55, 58, 59], thermolabile molecules and in particular solutions or dispersions [56–58, 60]. In the past few years, it was shown that an atmospheric cold plasma fed with a dilution gas (e.g., helium, argon, nitrogen, air) and the aerosol of a dispersion containing preformed NPs and a liquid organic precursor allows the deposition of NC coatings in which the NPs are embedded in the organic matrix formed by the plasma-polymerization of the precursor [8–12]. To date, only few studies on this strategy have been published and the most relevant examples are listed below:

- The first paper was published in 2009 by Bardon et al. [8] and deals with the deposition of organosilicon coatings containing aluminium-cerium oxide (AlCeO_3) NPs for corrosion protection. The deposition was accomplished by injecting in a parallel plate DBD reactor a dispersion of NPs in a liquid organosilicon precursor (i.e., hexamethyldisiloxane, HMDSO). Ethanol was added in small amounts (3%) to the dispersions as a non-covalent compatibilizer for improving NPs dispersibility in HMDSO, and hence the homogeneity and properties of the coating.
- Dembele et al. [11] reported the utilization of dispersions of TiO_2 NPs in tetramethoxysilane (TMOS) to deposit organosilicon polymer/ TiO_2 NCs coatings with a plasma jet characterized by a point-to-plane type corona configuration. Also in this case different alcohols (i.e., methanol, pentanol and octanol) were added to the dispersions, even at high concentration (i.e. 50%), to improve their stability, and therefore to enhance the homogeneity and thickness of the plasma-deposited coating. The effect of the alcohol was assessed with respect to the properties of the deposits. It was observed that coatings obtained from TMOS/ TiO_2 dispersions, with and without the addition of methanol, were broadly similar. In contrast the coatings deposited with octanol and pentanol addition were significantly thicker and also more homogeneous; this would indicate that these alcohols were incorporated into the plasma-polymerised siloxane as confirmed by the FTIR (Fourier-transform infrared) spectra of the coatings. The differences with alcohol type were ascribed to the different boiling points of methanol, pentanol and octanol

(65°C, 136°C, 196 °C, respectively) in comparison with the plasma temperature measured at the jet orifice (77 °C). Since methanol has a boiling point lower than the plasma temperature, it is expected to evaporate during the coating deposition and not to be incorporated in the coatings.

- Michel et al.[9] investigated the deposition of plasma-polymerized polyaniline (PANI) coatings including Pt nanoparticles functionalized with mercaptoaniline. Pt nanoparticles were first synthesized and subsequently functionalized with mercaptoaniline that acts as covalent compatibilizer to obtain a good dispersion of the NPs in ethanol; then aniline was added to obtain the final dispersion injected in aerosol form in a DBD discharge. The formation of a dense three-dimensional porous network characterized by PANI-Pt fibers with a diameter in the range 50-70 nm was observed. These fibers did not form in the case of the pure plasma-polymerized PANI coating obtained when NPs were not admitted. This point suggested that NPs can act as nucleation sites, where PANI can easily grow.
- Uygun et al.[12] deposited different organic-inorganic NC coatings from dispersions of the polymer precursor (i.e., pyrrole, thiophene and furan), TiO₂ NPs, and LiClO₄ in acetonitrile. The chemical, morphological, thermal and electrical characteristics of the plasma-deposited polypyrrole/TiO₂, polythiophene/TiO₂ and polyfuran/TiO₂ nanocomposites were examined. It was shown that the coatings were doped with ClO₄⁻ anions, which allowed an increase of composite conductivity.

It is however also worth highlighting that in 2013 Beier et al. [61] reported the utilization of a combined PE-CVD and AAPD process in which for the first time the metal nanoparticles are synthesized in situ in the atmospheric pressure plasma. Specifically, in this process vapors of HMDSO and the aerosol of a silver nitrate (AgNO₃) solution in water and isopropanol were transported by an air flow to a cold plasma jet to obtain a NC coating consisting of Ag NPs embedded in a SiO_x matrix.

We have investigated the deposition of hydrocarbon polymer/ ZnO NPs NC thin films in an atmospheric pressure DBD. Specifically, the DBD is fed with helium and the aerosol of a dispersion of oleate-capped ZnO NPs in a hydrocarbon solvent such as n-octane and/or 1,7-octadiene [62]. First, commercial ZnO NPs (average particle size of 36 nm) are appropriately compatibilized by surface-functionalization with oleate using a wet chemistry procedure, to obtain a stable dispersion in hydrocarbon solvents. Nanocomposite thin films are deposited in the DBD reactor shown in Fig. 3 [59, 62, 63]. The plasma is generated in He between two parallel plate electrodes both covered with an Al₂O₃ plate, by applying a sinusoidal AC high voltage (26 kHz, 2 kV_{rms}) in pulsed mode (20 ms period, 13 ms plasma on-time, 65% duty cycle). A pneumatic atomizer fed with He allowed the atomization of the dispersion at a mass flow rate of about 0.23 g·min⁻¹.

As assessed by attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy, the deposited nanocomposite coating combines the chemical features of both the oleate-capped ZnO NPs and the polyethylene-like organic component, originated from the plasma-polymerization of the hydrocarbon precursor. In fact the ATR-FTIR spectrum of the thin film deposited from a 3 wt % dispersion of oleate-capped ZnO NPs in octane, reported in Fig. 4, is characterized by the absorption signals due to ZnO (420 cm^{-1}), OH stretching (3400 cm^{-1}), COO asymmetric and symmetric stretching ($1300\text{-}1600\text{ cm}^{-1}$), ascribed to the oleate-capped ZnO NPs, as well as due to CH₂ and CH₃ stretching and bending signals ($2800\text{-}3000\text{ cm}^{-1}$ and $1300\text{-}1600\text{ cm}^{-1}$, respectively). CH₂ and CH₃ absorptions are in good agreement with the corresponding bands observed in the case of the polyethylene-like coating deposited from a pure n-octane aerosol. Interestingly, the ZnO NPs loading in the coating is about 70% (evaluated by anodic stripping voltammetry of zinc, after dissolution of the NC coating in HNO₃ and HClO₄), while XPS analyses indicate that the surface composition of the NC coating is dominated by the hydrocarbon polymer layer which covers the NPs (C = 10 at.%, Zn = 3 at.%, O = 10 at. %).

Additionally, SEM analyses (Fig. 5a) indicate that the coating contains quasi-spherical NPs agglomerates which promote the formation of a hierarchical surface roughness: while the NPs agglomerates provide the micrometer-scale roughness, the NPs on top of the agglomerates provide the nano-roughness. The hydrocarbon polymer covers the agglomerates (Fig. 5b) to different extents and contributes to their immobilization in the coating (Fig. 5c). The presence of NPs agglomerates supports the hypothesis that a certain n-octane evaporation occurs at the aerosol droplets surface, and therefore the NPs tend to form locally closely-packed structures.

This NC coating is superhydrophobic, in fact it exhibits advancing and receding water contact angles (WCA) higher than 160° and very low hysteresis (i.e., the difference between advancing and receding WCAs). It is worth noting that a polyethylene-like coating without NPs, deposited from pure n-octane aerosol under the same experimental conditions, shows advancing and receding WCA values equal to 106° and 95° , respectively. The wetting behavior of the NC coating can be ascribed to the presence of a hydrocarbon polymer component with a low surface energy and of NPs agglomerates which generate the hierarchical multiscale texture.

Several important aspects have to be considered and deserve a deeper investigation for the rationalization of this aerosol-assisted deposition process, as for instance:

- The evaporation of the hydrocarbon solvent between the aerosol generator and DBD reactor that can induce NPs agglomeration [40, 41, 44].
- The plasma/liquid droplet interaction in the gas phase, which can cause for instance droplet charging, vaporization of the liquid, formation of activated precursor molecules in the gas phase [6].

- The relative importance of two possible pathways responsible of coating formation (and in particular of the growth of the organic component): first, the gas phase formation of hydrocarbon fragments and oligomers that can lead to thin film growth either on the substrate or on the agglomerates surface in the gas phase (i.e. formation of an organic shell); second, the action of the plasma on the liquid layer of dispersion that can eventually form on the substrate for the direct impact and spread out of the aerosol droplets.
- The plasma charging of NPs and in particular of NPs agglomerates in the aerosol and subsequent electro-deposition or electro-collection. This can play an important role in the deposition process considering the dimensions of the agglomerates observed in the coating (between 200 nm and 2 μm) and the plasma excitation frequency (26 kHz). As reported by Borra et al. [64, 65] in DBDs an effective charging is expected for intermediate and coarse particles (from 0.1 to more than 1 μm) due to drift of ions on the field lines intersecting the surface of the particles; this can lead to a quite high electro-collection efficiency in DBDs working in the 1-60 kHz frequency range.

4 Conclusion

Nowadays atmospheric pressure cold plasma technology has attracted increasing attention in thin film deposition and intense research efforts are directed to identify new promising processes. Very recently the deposition of organic-inorganic NC coatings by AP cold plasmas has been accomplished utilizing an aerosol-assisted process in which a dispersion containing inorganic NPs and a liquid organic precursor is atomized and injected in aerosol form in the atmospheric plasma. Even if this methodology is not yet mature enough, as demonstrated by the small number of studies published to date, it seems to be very convenient for the fabrication of multicomponent coatings. The most appealing advantage is the fact that, due to the aerosol utilization, in principle any type of preformed NPs can be injected in the plasma and incorporated in the coating, provided that a good dispersion of the NPs in a suitable solvent is obtained. Interestingly, this strategy towards the production of organic-inorganic NC coatings seems very different from the numerous low pressure plasma-based processes in which very often the formation of both the polymer matrix and the inorganic particles occurs in situ and in a single step. Also for this reason, the aerosol-assisted atmospheric pressure plasma deposition is expected to lead, rather than to the replication of the same coatings successfully obtained with LP plasmas, to enlarge the range of structures and properties of organic-inorganic NCs deposited by cold plasma technologies.

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References

- [1] Sanchez C, Julián B, Belleville P, Popall M (2005) *J Mater Chem* 15:3559-3592
- [2] Faupel F, Zaporojtchenko V, Strunskus T, Elbahri M (2010) *Adv Eng Mater* 12:1177-1190
- [3] Biederman H (2011) *Surf Coat Technol* 205:S10-S14
- [4] Biederman H, Kylián O, Drábik M, Choukourov A, Polonskyi O, Solař P (2012) *Surf Coat Technol* 211:127-137
- [5] Fanelli F (2010) *Surf Coat Technol* 205:1536-1543
- [6] Massines F, Sarra-Bournet C, Fanelli F, Naudé N, Gherardi N (2012) *Plasma Process Polym* 9:1041–1073
- [7] Fanelli F, Benedikt J (2012) *Plasma Process Polym* 9:1040
- [8] Bardon J, Bour J, Del Frari D, Arnoult C, Ruch D (2009) *Plasma Process Polym* 6:S655-S659
- [9] Michel M, Bour J, Petersen J, Arnoult C, Ettingshausen F, Roth C, Ruch D (2010) *Fuel Cells* 10:932-937
- [10] Dowling DP, Twomey B, Byrne G (2010) *J Nanosci Nanotechnol* 10:2746-2752
- [11] Dembele A, Rahman M, Reid I, Twomey B, Don MacElroy JM, Dowling DP (2011) *J Nanosci Nanotechnol* 11:1-8
- [12] Uygun A, Oksuz L, Yavuz AG, Guleç A, Sen S (2011) *Curr Appl Phys* 11:250-254
- [13] Boissiere C, Grosso D, Chaumonnot A, Nicole L, Sanchez C (2010) *Adv Mater* 23:599-623
- [14] Hou X, Choy K-L (2006) *Chem Vap Deposition* 12:583-596
- [15] Marchand P, Hassan IA, Parkin IP, Carmalt CJ (2013) *Dalton Trans* 42:9406-9422
- [16] Tkachuk BV, Marusii NY, Laurs EP (1973) *Vysokomol Soedin A* 15:2046-2051
- [17] Duque L, Förch R (2011) *Plasma Process Polym* 8:444-451
- [18] Biederman H, Holland L (1983) *Nucl Instr Meth* 212:497-503
- [19] Schürmann U, Takele H, Zaporojtchenko V, Faupel F (2006) *Thin Solid Films* 515:801-804
- [20] Kay E, Dilks A (1979) *J Vac Sci Technol* 16:428-430
- [21] Fracassi F, d’Agostino R, Palumbo F, Bellucci F, Monetta T (1995), *Thin Solid Films* 264:40-45
- [22] Fracassi F, d’Agostino R, Palumbo F, Bellucci F, Monetta T (1996) *Thin Solid Films* 272:60-63
- [23] Dilonardo E, Milella A, Palumbo F, Capitani G, d’Agostino R, Fracassi F (2010) *Plasma Process Polym* 7:51-58
- [24] Dilonardo E, Milella A, Cosma P, d’Agostino R, Palumbo F (2011) *Plasma Process Polym* 8:452-458
- [25] Hanuš J, Drábik M, Hlidek P, Biederman H, Radnoczi G, Slavínská D (2009) *Vacuum* 83:454-456
- [26] Beale HA (1981) *Ind Eng Chem Prod Res Dev* 23:135-139

- [27] Choukourov A, Gordeev I, Arzhakov D, Artemenko A, Kylián O, Kousal J, Polonskyi O, Pešička J, Slavínská D, Biederman H (2011) *Surf Coat Technol* 205:2830-2837
- [28] Lamber R, Wetjen S, Jaeger NI (1995) *Physical Review B* 51:10968-10971
- [29] Polonskyi O, Solař P, Kylián O, Drábik M, Artemenko A, Kousal J, Hanuš J, Pešička J, Matolínová I, Kolíbalová E, Slavínská D, Biederman H (2012) *Thin Solid Films* 520:4155-4162
- [30] Kylián O, Petr M, Serov A, Solař P, Polonskyi O, Hanuš J, Choukourov A, Biederman H (2014) *Vacuum* 100:57-60
- [31] Ross D, Gleason KK (2006) *Chem Vap Deposition* 12:225-230
- [32] Martinů L, Biederman H (1986) *Vacuum* 36:477-478
- [33] Kay E (1986) *Phys D At Mol Clusters* 3:251-262
- [34] Sardella E, Favia P, Gristina R, Nardulli M, d'Agostino R (2006) *Plasma Process Polym* 3:456-469
- [35] Zanna S, Saulou C, Mercier-Bonin M, Despax B, Raynaud P, Seyeux A, Marcus P (2010) *Appl Surf Sci* 256:6499-6505
- [36] Dilonardo E, Milella A, Palumbo F, Thery J, Martin S, Barucca G, Mengucci P, d'Agostino R, Fracassi F (2010) *J Mater Chem* 20:10224-10227
- [37] Kylián O, Polonskyi O, Kratochvíl J, Artemenko A, Choukourov A, Drábik M, Solař P, Slavínská D, Biederman H (2012) *Plasma Process Polym* 9:180-187
- [38] Palgrave RG, Parkin IP (2006) *J Am Chem Soc* 128:1587-1597
- [39] Qureshi U, Blackman C, Hyett G, Parkin IP (2007) *Eur J Inorg Chem* 10:1415-1421
- [40] Hou X, Choy K-L (2008) *Thin Solid Films* 516:8620-8624
- [41] Hou X, Choy K-L, Brun N, Serín V (2013) *J Nanomater* 2013:219039
- [42] Saeli M, Binions R, Piccirillo C, Hyett G, Parkin IP (2009) *Polyhedron* 28:2233-2239
- [43] Crick CR, Bear JC, Kafizas A, Parkin IP (2012) *Adv Mater* 24:3505-3508
- [44] Crick CR, Bear JC, Southern P, Parkin IP (2013) *J Mater Chem A* 1:4336-4344
- [45] Steele A, Bayer I, Loth E (2009) *Nano Lett* 9:501-505
- [46] Sparks BJ, Hoff EFT, Xiong L, Goetz JT, Patton DL (2013) *ACS Appl Mater Interfaces* 5:1811-1817
- [47] Tiwari MK, Bayer IS, Jursich GM, Schutzius TM, Megaridis CM (2010) *ACS Appl Mater Interfaces* 2:1114-1119
- [48] Raza A, Si Y, Wang X, Ren T, Ding B, Yuc J, Al-Deyab SS (2012) *RSC Advances* 2:12804-12811
- [49] Ward LJ, Schofield WCE, Badyal JPS, Goodwin AJ, Merlin PJ (2003) *Langmuir* 19:2110-2114
- [50] Ward LJ, Schofield WCE, Badyal JPS (2003) *Chem Mater* 15:1466-1469
- [51] O'Neill L, O'Hare LA, Leadley SR, Goodwin AJ (2005) *Chem Vap Deposition* 11:477-479

- [52] Heyse P, Dams R, Paulussen S, Houthoofd K, Janssen K, Jacobs PA, Sels BF (2007) *Plasma Process Polym* 4:145-157
- [53] Herbert PA, O'Neill L, Jaroszynska-Wolinska J (2009) *Chem Mater* 21:4401-4407
- [54] Herbert PA, O'Neill L, Jaroszynska-Wolinska J, Stallard CP, Ramamoorthy A, Dowling DP (2011) *Plasma Process Polym* 8:230-238
- [55] Beck AJ, Short RD, Matthews A (2008) *Surf Coat Technol* 203:822-825
- [56] Heyse P, Van Hoeck A, Roeffaers MJB, Raffin JP, Steinbuchel A, Stoveken T, Lammertyn J, Verboven P, Jacobs PA, Hofkens J, Paulussen S, Sels BF (2011) *Plasma Process Polym* 8:965-974
- [57] Tynan J, Ward P, Byrne G, Dowling DP (2009) *Plasma Process Polym* 6:S51-S56
- [58] Da Ponte G, Sardella E, Fanelli F, Van Hoeck A, d'Agostino R, Paulussen S, Favia P (2011) *Surf Coat Technol* 205:S525-S528
- [59] Da Ponte G, Sardella E, Fanelli F, d'Agostino R, Gristina R, Favia P (2012) *Plasma Process Polym* 9:1176-1183
- [60] Boscher ND, Duday D, Heier P, Heinze K, Hilt F, Choquet P (2013) *Plasma Process Polym* 10:336-344
- [61] Beier O, Pfuch A, Horn K, Weisser J, Schnabelrauch M, Schimanski A (2013) *Plasma Process Polym* 10:77-87
- [62] Fanelli F, Mastrangelo AM, Fracassi F (2013) submitted
- [63] Fanelli F, Lovascio S, d'Agostino R, Fracassi F (2012) *Plasma Process Polym* 9:1132-1143
- [64] Borra JP (2006) *J Phys D Appl Phys* 39:R19-R54
- [65] Borra JP (2008) *Plasma Phys Control Fusion* 50:124036

Figures captions

Fig. 1 (a) Schematic of the plasma reactor utilized for the low pressure plasma deposition of CH_x/Pt coatings by simultaneous plasma-polymerization of ethylene and sputtering from a Pt target; (b) XPS atomic percentages vs. RF input power; (c) TEM images and SAD patterns (inset) of films containing 60% and 1% of Pt. Reprinted with permission from ref. 23 (Dilonardo E, Milella A, Palumbo F, Capitani G, d'Agostino R, Fracassi F (2010) *Plasma Process Polym* 7:51-58). Copyright 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

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Fig. 3 Schematic diagram of the atmospheric pressure DBD reactor utilized for the deposition of hydrocarbon polymer/ ZnO NPs coatings.

Fig. 4 ATR-FTIR spectrum of a NC coating deposited in a DBD fed with He and the aerosol of a 3 wt % oleate-capped ZnO NPs dispersion in n-octane.

Fig. 5 SEM images of a NC coating deposited in a DBD fed with He and the aerosol of a 3% w/w oleate-capped ZnO NPs dispersion in n-octane: (a) low-magnification image, (b) high-magnification image evidencing the organic layer on the NPs agglomerate, (c) cross-sectional image.

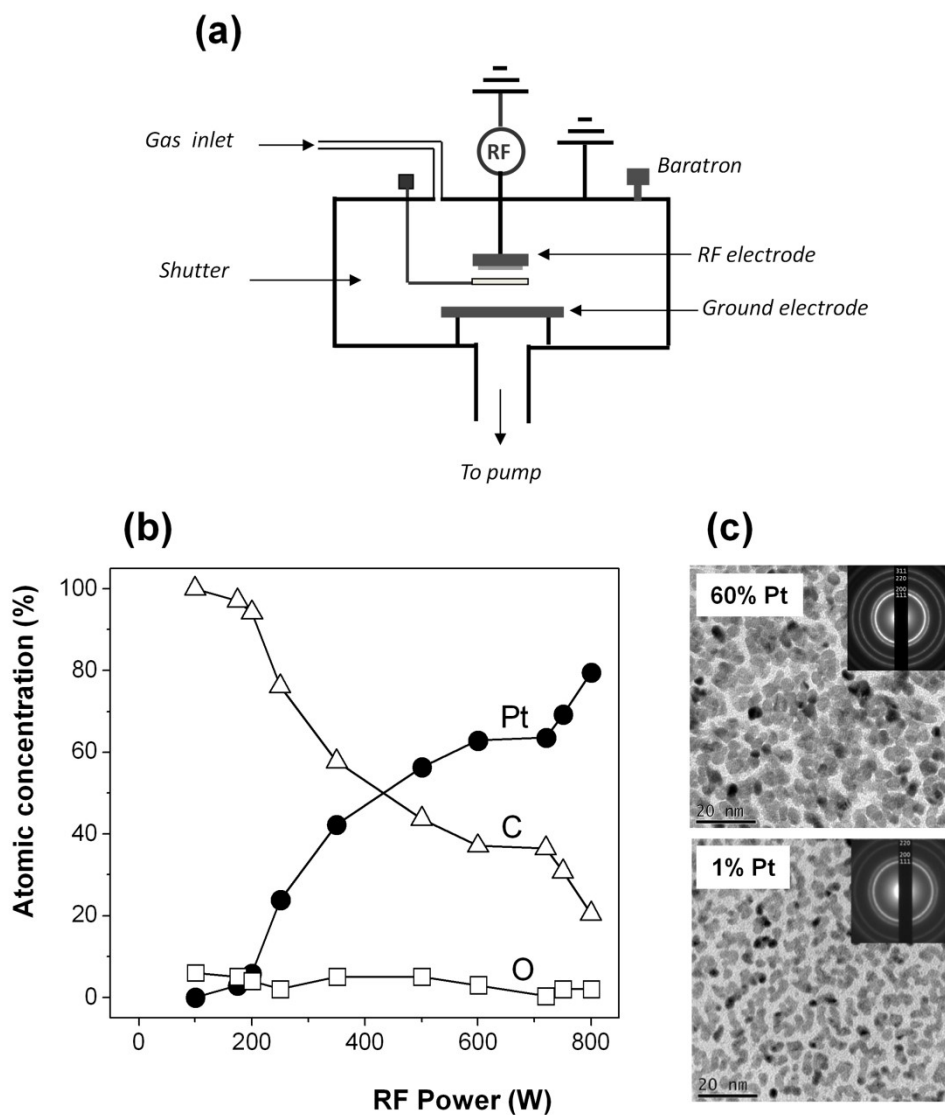


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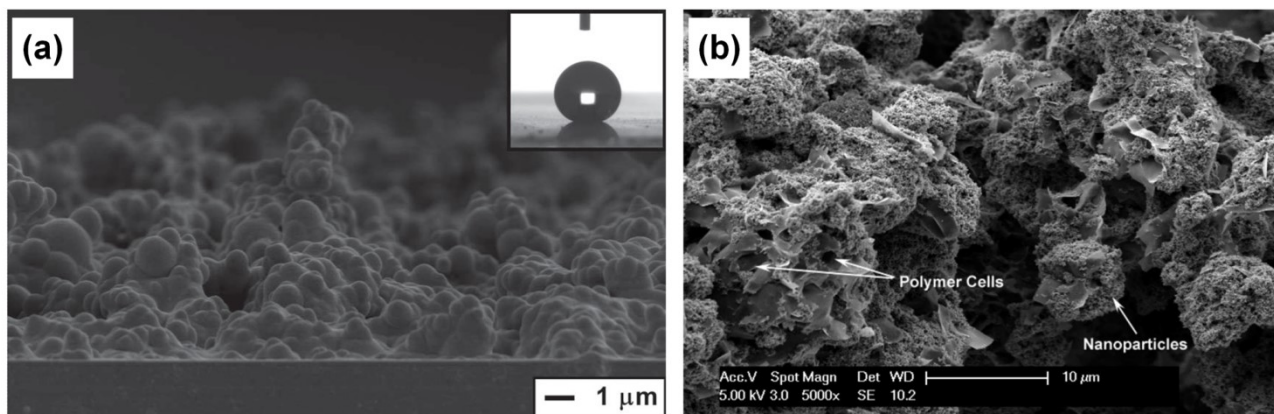


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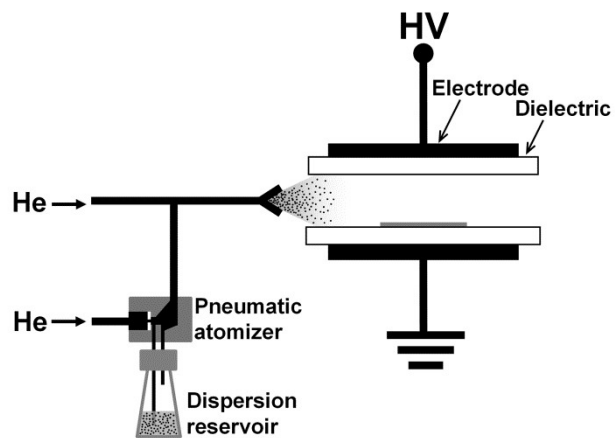


Fig. 3 Schematic diagram of the atmospheric pressure DBD reactor utilized for the deposition of hydrocarbon polymer/ZnO NPs coatings.

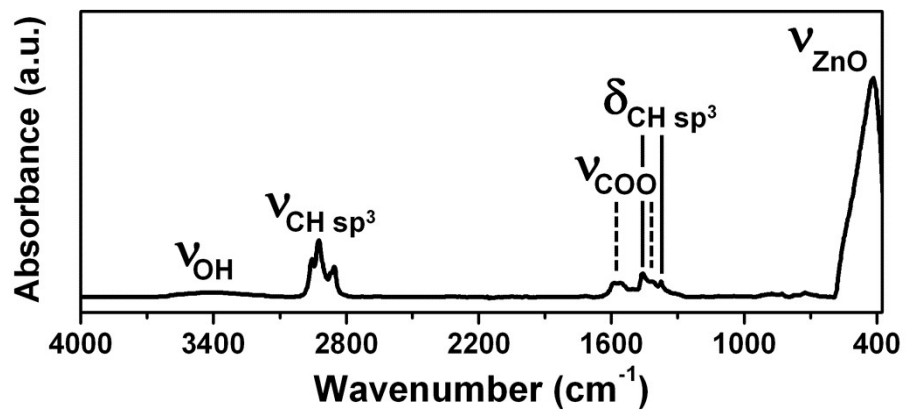


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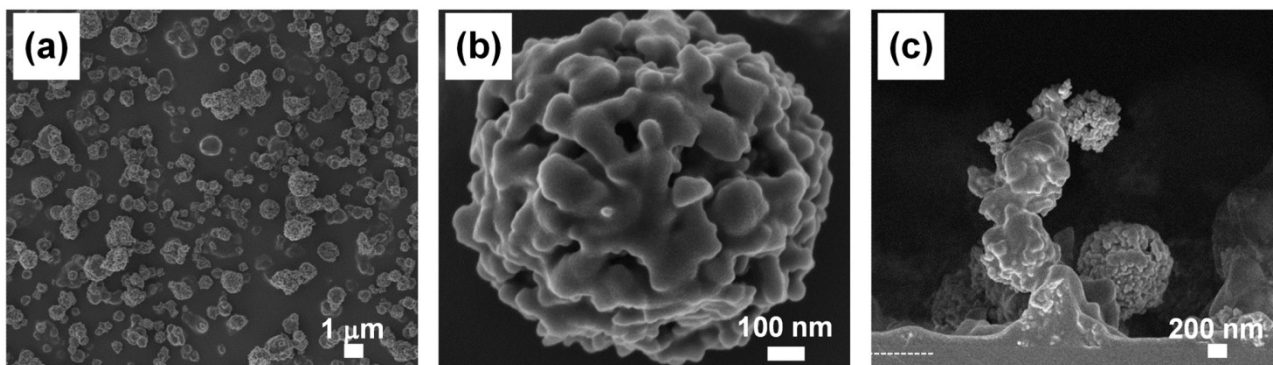


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