Preparation of multifunctional organic-inorganic nanocomposite thin films by aerosol-assisted atmospheric cold plasma deposition

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The research field of organic/inorganic nanocomposite (NC) materials is one of the most promising areas in materials chemistry. The combined unique properties offered by both organic and inorganic components on a nanoscale level make such materials attractive for a large number of applications. Intense efforts have been made to develop novel multifunctional nanocomposite coatings that simultaneously offer various functionalities such as superhydrophobic properties, electrical conductivity, catalytic activity, anticorrosion resistance, self-cleaning and antibacterial properties.

Recently, aerosol-assisted atmospheric pressure cold plasma processes have been proposed as an attractive route towards the preparation of NC thin films (Fanelli and Fracassi 2014). These processes have demonstrated to be particularly convenient when, for instance, the dispersion of preformed nanoparticles (NPs) in a liquid organic precursor is injected directly in the atmospheric plasma. This allows the deposition in a single step and at room temperature of hybrid organic/inorganic nanocomposite coatings consisting of NPs embedded in the organic matrix formed by the plasma polymerization of the precursor.

This contribution is focused on the study of the growth, structure and properties of hydrocarbon polymer/ZnO NPs nanocomposite coatings deposited in a dielectric barrier discharge (DBD) fed with He and the aerosol of dispersions of oleate-capped ZnO NPs in hydrocarbon precursors, such as n-octane and 1,7-octadiene (Fanelli *et al.* 2014, Fanelli *et al.* 2015). The characterization of the coatings is performed using X-ray photoelectron spectroscopy (XPS), attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR), anodic stripping voltammetry (ASV), scanning electron microscopy (SEM), transmission scanning electron, microscopy (TSEM), and contact angle (CA) goniometry.

As assessed by XPS and ATR-FTIR spectroscopy, the deposited nanocomposite thin films combine the chemical features of both the oleate-capped ZnO NPs and the polyethylene-like organic component originated from the plasma polymerization of n-octane and 1,7-octadiene. Additionally, SEM and TSEM confirm the synthesis of hierarchical micro/nanostructured coatings containing quasi-spherical NPs agglomerates (Fanelli *et al.* 2014). The polyethylene-like polymer covers the NPs agglomerates and contributes to their immobilization in the three-dimensional network of the coating. The increase of the NPs concentration in the dispersion (0.5-5 wt %) has a significant effect on the chemical and morphological structure of the thin films and, in fact, results in the increase the ZnO NPs content, leading to superhydrophobic surfaces (advancing and receding water contact angles higher than 150°) with low hysteresis due to the hierarchical multiscale roughness of the coating (Fanelli *et al.* 2014).

Interestingly, the deposited coatings show superhydrophobic and superoleophilic properties simultaneously, in fact water and hexadecane contact angles are greater than 150° and lower than 5°, respectively. Therefore the coatings present wettability selectivity, and they can be exploited in the preparation of filtration materials able to separate oil from water (Xue *et al.* 2014). Encouraging preliminary results have been obtained for the separation of hexadecane/water mixtures when the nanocomposite thin films are deposited on a polymeric mesh. While hexadecane passes easily through the plasma-treated mesh, water can not pass; therefore, an effective separation of the two liquids is obtained.

In addition, these plasma-deposited NC coatings exhibit also the peculiar photocatalytic properties of ZnO. To enlighten the photocatalytic activity of the ZnO-containing nanocomposite coating, the degradation of a dye molecule (i.e., methylene blue) in water is demonstrated (Fanelli *et al.* 2015).

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