Research paper

Design of growing points for silver nanoparticles on polypropylene membranes

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ABSTRACT

The nucleation process of a nanoparticle requires an environment that stabilizes the initial seed and favors the growth action. In this paper, we present a specific design of growing points for silver nanoparticles based on the well-known affinity of the silver to the chlorine atoms and to aromatic groups by cation-π interactions. [2-(vinylphenyl)ethyl]chloromethylphenylsilane was proposed as growing point of nanoparticles, which has been synthetized and grafted on a polypropylene membrane. Nanoparticles were synthesized by chemically reducing an $AgNO_3$ solution with $NaBH_4$ and the so synthesized nanoparticles were also fully characterized. Using DFT-QTAIM calculations a model of the initial seed and a growth mechanism were proposed.

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1. Introduction

In recent years, the study and preparation of inorganic crystalline particles in the nanometric scale has attracted considerable attention from both fundamental and applied research [1]. Metal nanoparticles of silver, gold and copper have been the focus of great interest because of their unique optical properties determined by the collective oscillations of electron density, termed plasmons [2,3]. Several methods to obtain nanoparticles have been recently reported, using several templates and experimental conditions [4]. One of them is the impregnation of the metal ion, which consists in the reduction of any metal ion to metal zero valence at room temperature, atmospheric pressure and using water as solvent [5]. Also, the use of a polymer material as template to grow nanomaterials has become popular due to the versatility of polymeric matrixes [6]. It is possible to modify the activity of polymers by electroless plating in fabrication of advanced nanomaterials [7]. Polymeric membranes can be also used as support of metal particles due to their porous structure, produces a good dispersion of the particles over the membrane surface and allows the reactants to flow through it. Membranes can be modified by grafting reaction with several molecules to modulate the physical and chemical

properties [8]. In this work, we modified a polypropylene membrane to be used as template for the nanoparticle growing.

The nucleation process of a nanoparticle requires a suitable environment to stabilize the initial seed and to favor the growth action. The metal nucleation in the impregnation method is dominated by weak or non-covalent interactions between metal ions and the solvent, solution or Supporting material [9]. Usually soft electron donors such as amine, pyridine, pyrazole or thiol functional group are used to create a stabilizing growing environment [10]. In this work, we explore an alternative approach to stabilize nanoparticles in non-polar environment, creating specific growing points (GP) for silver nanoparticles based on the affinity between the silver cations and the aromatic rings, and on the ion-dipole interaction with the Si-Cl bonds. The Ag^+-π interactions has been widely studied, both experimentally [11] and theoretically [12]. The Ag^+-benzene interaction presents a binding energy around 1.34 and 2.63 kcal/mol, [13] and shows a cooperative effect in the presence of several aromatic ring as observed in the argentivorous molecules, which have aromatic side-arms as 'petals that caught the Ag^+ ions in the way insectivorous plants catch insects' [14]. In this way, the GP proposed in this work acts as silver cations trap site, with the advantage of the large flexibility that a silicon atom can provide as pivot point. Then, after a silver cation has been captured within a GP, it is possible that other silver atoms congregate around it, by argentophilic interactions, [15] after chemical reduction to produce clusters or nanoparticles.

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In this work, the GP was obtained by a modification of polypropylene membrane with [2-(vinylphenyl)ethyl]chlorome thylphenylsilane (ECMPS), which was synthesized by the first time. The nanoparticles were grown, in the modified membrane, by chemical reduction of a solution of AgNO$_3$ by NaBH$_4$. ECMPS exhibits three possible sites of interaction with Ag$^+$ ions, a Si-Cl bond and two phenyl rings, which behave as trap of silver cations and growing point for nanoparticles.

2. Experimental Methods

2.1. Synthesis of methylphenylsilane (MPS)

Methylphenylsilane was synthesized by a reported procedure, [16] by the reaction between dichloromethylphenylsilane and lithium aluminum hydride in the presence of anhydrous ether. Into a three-necked flask with constant stirring, a solution of dichloromethylphenylsilane (0.0372 mol of 12 ml of anhydrous ether) was added to LiAlH$_4$ (0.0372 mol) and refluxed for 4 h. Then, a solution of hydroquinone (9.08 × 10^{-4} mol in 8 ml of distilled water) was added to remove unreacted LiAlH$_4$. Finally, methylphenylsilane was extracted with ether from the reaction solution.

2.2. Synthesis of monomer of [2-(vinylphenyl)ethyl] chloromethylphenylsilane (ECMPS)

In a round flask, equipped with a stirrer and under N$_2$ atmosphere, divinylbenzene (DVB, 8.42 × 10^{-3} mol), dichloromethylphenylsilane (DCMPS, 4.27 × 10^{-3} mol) and 2,2-azobisisobutyronitrile (AIBN, 1.58 × 10^{-4} mol) were mixed, then MPS (2.67 × 10^{-3} mol) was added. The mixture was then left under constant stirring for 12 h.

2.3. Polymerization of ECMPS onto the polypropylene membrane to obtain modified membrane PP-ECMPS

A solution prepared with 5 mol of ECMPVS, 1.1 mol of DVB (as crosslinker), 0.093 mol of 2,2-dimethoxy-2-phenylacetophenone (DMPA) and 1 ml of dimethylformamide (DMF), was impregnated onto the surface of the polypropylene membrane (from 3 M Company with porosity of 84.6%, pore diameter of 0.45 μm and thickness of 114 μm), which was placed between two films and subjected to 300 nm UV–vis radiation for 13 h. Then the membrane was washed with THF and rinsed with methanol. Finally, the material was placed under high vacuum for 60 min.

2.4. Synthesis of silver particles onto PP-ECMPS

The silver metal particles were synthesized by the impregnation-reduction method, using AgNO$_3$ as precursor and NaBH$_4$ as the reducing agent. PP-ECMFVS was submerged into a 5 mM AgNO$_3$ solution, varying the immersion time (from 10 to 30 min). Then, the membrane was rinsed with ethanol to remove not retained Ag$^+$ ions. Subsequently, the membrane was placed into a NaBH$_4$ solution (0.1% by weight) for 20 min, then it was washed with deionized water and dried under high vacuum for 2 h.

2.5. Computational methods

The computational study was performed at M05-2X/LANL2DZ [17] theoretical level as implemented in Gaussian 09 program [18]. Full optimization of every structure was performed and the stable stationary point was confirmed by a frequency calculation. For each structure, a wave function was obtained to calculate local and integrated properties of electron density with AIMAll [19].
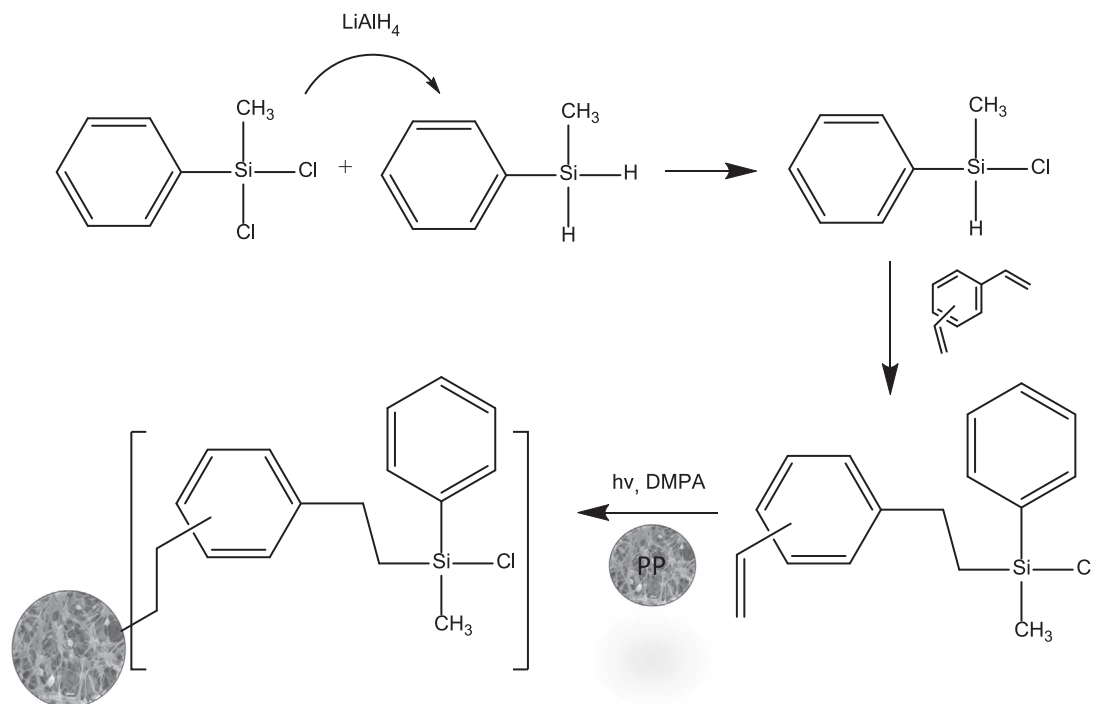

Fig. 1. Synthetic route to obtain ECMPS grafted onto the polypropylene membrane.

3. Results

Fig. 1 presents the synthetic route to obtain ECMPS and grafting it into the polypropylene membrane (PP). The reduction of commercial dichloromethylphenylsilane by lithium aluminium hydride gave methylphenylsilane. Redistribution product between dichloromethylphenylsilane and methylphenylsilane, followed by a radical reaction with divinylbenzene produces ECMPS, using AIBN as catalyst [20]. As far as we know there are not previous reports of the synthesis of ECMPS.

The ECMPS monomer was grafted onto PP by photopolymerization catalyzed by 2,2-Dimethoxy-2-phenylacetophenone (DMPA) and UV light (300 nm), using DMF as solvent. Synthesis of silver particles was performed by impregnation of PP with a $AgNO_3$ solution, followed by a reduction using $NaBH_4$ as reducing agent.

Here, we briefly describe the characterization of the membrane after each step of the synthesis and the grafting reaction. The IR spectrum of methylphenylchlorosilane shows a Si-H band in 2137 cm^{-1}. In addition, other signals are also observed at 3009 cm^{-1} ((Ph)-H), 2968 cm^{-1} (CH_3), 1632–1594 cm^{-1} (Ph-Si) and 1263 cm^{-1} (Si-CH_3). The RMN ^1H spectrum presents the signals of expected groups: 0.4 ppm (Si-CH_3), 4.35 ppm (Si-H) and 7.3–7.6 ppm ((Ph)-H). ECMPS has IR signals in 1629 cm^{-1} (Ph-Si), 1260 cm^{-1} (Si-CH_3), 544, 479 and 432 cm^{-1} (Si-Cl). The RMN ^1H presents six characteristic signal: 0.45 ppm (Si-CH_3), 2.6 ppm (dt, Si-CH_2), 4.35 ppm (dt, CH_2-Ph), 5.25 and 5.75 ppm (d, vinyl protons), 6.8 and 7.3 ppm (m, aromatic protons). The evidence of ECMPS being grafted onto the PPM was the weight increase and the FT-IR-ATR bands of the modified membrane at: 3020 (Ph-C-Si), 2953–2840 (CH_3-CH_2-), 1685–1602 cm^{-1} (Ph-Si), 1263 cm^{-1} (Si-CH_3), 580, 480 and 438 cm^{-1} (Si-Cl). Also in the scanning electronic microscopy (SEM) images, it is possible to observe a porous reduction by thickening of the fibers. BET multipoint analysis indicates that the unmodified membrane has 11.97 m^2/g of surface
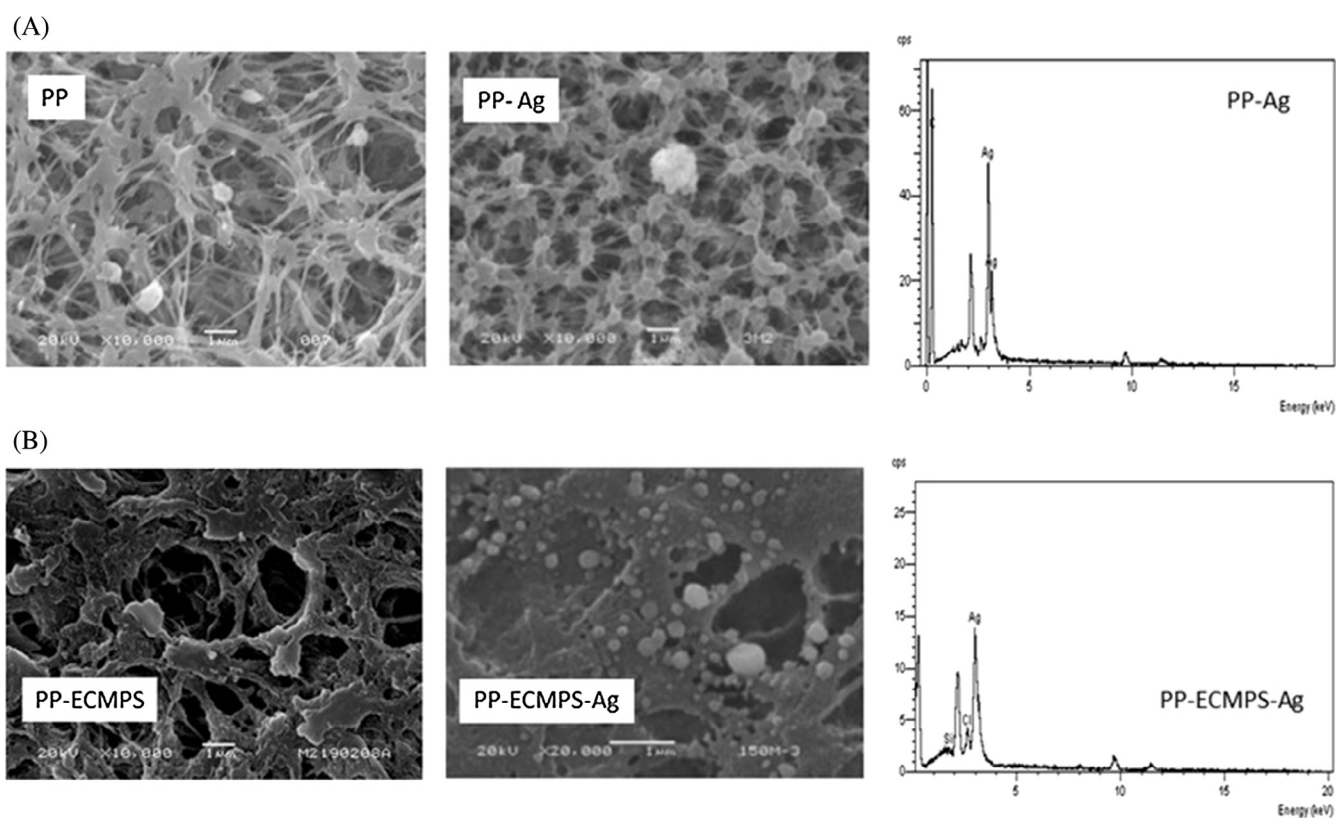

Fig. 2. SEM images and EDS analysis of (A) unmodified membrane supporting agglomerates of silver clusters, (B) modified membrane supporting silver nanoparticles.
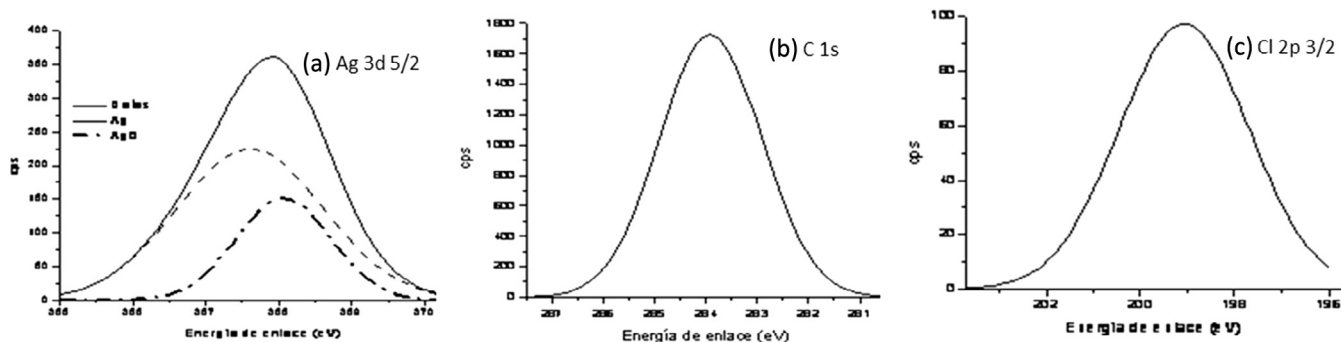

Fig. 3. XPS analysis of modified membrane supporting silver nanoparticles.

area whereas modified membrane has 52.66 m^2/g. Although it is well known that Si-Cl bond undergoes hydrolysis, [21] our results shows ECMPS remains unchanged after the impregnation and reduction processes with water as solvent. To hydrolyze the Si-Cl bond on the modified membrane it is necessary to raise the temperature to boiling point of water as shown in IR spectra in Supporting information, where it is possible to observe the Si-OH signal at 1016 cm^{-1}. It seems that the Si-Cl bond is stabilized within the membrane.

The best conditions for the synthesis of nanoparticles include the immersion of the membranes in a solution of AgNO$_3$ (5mM)
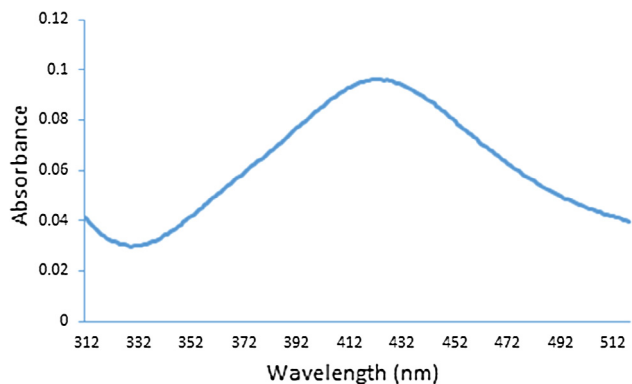

Fig. 4. Surface plasmon resonance of silver nanoparticles.

for 30 min, then the impregnated membranes were introduced into an aqueous solution of NaBH$_4$ (0.1 M) for 20 min. Finally, the samples were rinsed with methanol and dried at high vacuum for 2 h. The characterization of nanoparticles was performed by microscopy, X-ray photoelectronic spectroscopy (XPS) and UV–vis spectroscopy. SEM images of unmodified PP membrane show just few agglomerates of silver particles, indicating that it is important to functionalize the membrane (Fig. 2A), while modified membrane (PP-ECMPS) presents silver particles with defined shape of nanometric size (Fig. 2B). In both cases, energy dispersion analysis (EDS), which provides information of elemental composition, displays signals for silver, chlorine and silicon.

The modified membrane was analyzed by UV diffuse reflection and showing an absorption band at 432 nm, which corresponds to silver particles smaller than 100 nm of size (Fig. 3). Silver particles were extracted by sonication during 6 h and UV–visible absorption spectra were obtained, which shows a peak at 418 nm, which is characteristic of the surface plasmon resonance of absorption of Ag nanoparticles [22].

The XPS analysis indicates that the silver is supported on the modified membrane, and shows a peak at 368.08 eV corresponding to Ag 3d silver 5/2, a second peak at 283.91 eV assigned to carbon C 1 s, and a last peak in 199.07 eV attributed to chlorine Cl 2p 3/2, (Fig. 4).

To understand the growing process of nanoparticles on grafted PP-ECMPS, we suggest a mechanism below described. When the modified membrane is within the solution of AgNO$_3$, some Ag$^+$ ions are trapped by functional groups of ECMPS, which donate electron
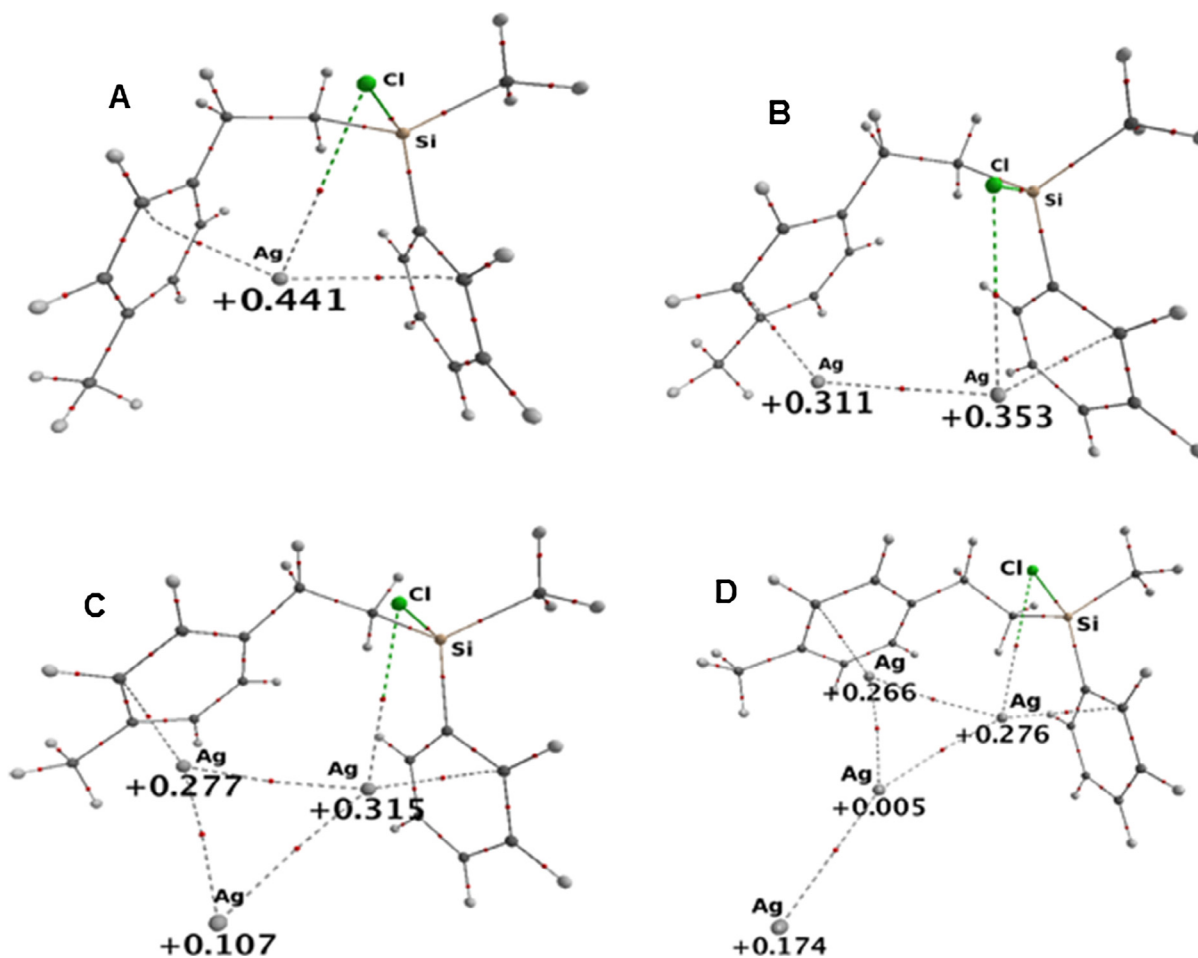

Fig. 5. Molecular graph and atomic charges of silver atoms of (A) GP-Ag$^+$, (B) GP-Ag$^+$-Ag^0, C) GP-Ag$^+$-(Ag^0)$_2$ and D) Ag$^+$-(Ag^0)$_3$.

density to the cations thus changing their redox potential and forming the GP. Once the reducing agent is added to the impregnated membrane, free Ag^+ ions in solution are reduced and linked around not reduced Ag^+ ions at the GP, assembling a silver cluster. It is possible that several clusters, linked to ECMPS, merge until a nanoparticle is formed.

To give theoretical support to the proposed mechanism, we carried out a computational study at M05-2X/LANL2DZ [17] theoretical level with Gaussian 09 program, [23] using [2-(4-methylphenyl)ethyl]chloromethylphenylsilane as a model of GP. The first step of the mechanism is the impregnation of Ag^+ into the grafted ECMPS, therefore we studied the interaction between the cation and GP model, which presents an interaction energy of 63.54 kcal/mol, which is 61.71 kcal/mol more stable than Ag^0-ECMPS interaction and 26.26 kcal/mol more stable than that experimentally observed for Ag^+-benzene, due to the cooperative effect of the interactions with the two aromatic rings and the chlorine atom [24]. The presence of interactions was determined by the topology of the electron density, [25] which was calculated with AIMAll program [26]. From the molecular graph [27] of Ag^+-model complex (Fig. 5A), it is possible to observe that the silver cation binds to the chlorine atom and to both phenyl rings by a π-cation-π interaction. The Ag-Cl distance is 3.098 Å whereas the distance between the cation and the phenyl rings are 2.480 Å and 2.475 Å, respectively. Once an Ag^+ is linked to ECMPS, the growing of a nanoparticle starts with an addition of Ag^0 atoms to form an Ag^+-$(Ag^0)_n$ clusters during the reduction process. We calculated the redox potential [28] of silver cation coordinated to ECMPS, which is -2.51 V whereas the potential for Ag^+ in solution is -1.9 V, [29] supporting the growing model. Fig. 5B, C and D shows Ag^+-Ag^0, Ag^+-$(Ag^0)_2$ and Ag^+-$(Ag^0)_3$ systems respectively. The first complex shows a π-Ag-Ag-π interaction with an Ag-Ag distance of 2.7546 Å, whereas the second one presents an Ag_3 three-member ring, where the Ag-Ag distances are 2.786 Å and 2.720 Å. These distances fully agree with those found for argentophilic bonding.[15] The positive charge of the cation is delocalized to the organic structure and the silver atoms as shown in Fig. 5. Once the Ag^+-$(Ag^0)_2$ is formed, the rest of the growing occurs outside the GP as shown in Fig. 5D. The Ag^+-$(Ag^0)_n$ clusters were grown until n = 10, finding several configurations for each n and several growing paths, which are presented in Supporting information. We are currently conducting more experiments to support this mechanism.

4. Conclusions

In this paper, we report the design and development of an environment suitable to stabilize the initial seed thus favoring the growth action based on well-known affinity of the silver to the chlorine atoms and to aromatic groups by cation- π interactions. [2-(vinylphenyl)ethyl]chloromethylphenylsilane was synthesized (for the first time) and grafted onto a polypropylene membrane with a photochemical reaction. In this material the nanoparticles were synthesized by chemical reduction of an $AgNO_3$ solution by $NaBH_4$. The nanoparticles were fully characterized by several techniques. The growing difference between the unmodified and modified membranes confirm that the grafted monomer provided an adequate environment to obtain nanoparticles. A growing mechanism was proposed by computational methods. The initial step in such mechanism involves the formation of a Growing-Point-Ag^+ complex, followed by the aggregation of silver to produce Ag^+-$(Ag^0)_n$ clusters. The formation of the nanoparticles is directed by the change of the redox potential modulated by the functional groups of the grafted monomer.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.cplett.2018.01.013.

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