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PLA/POSS Nanofibers: A Novel System for the Immobilization of Metal Nanoparticles

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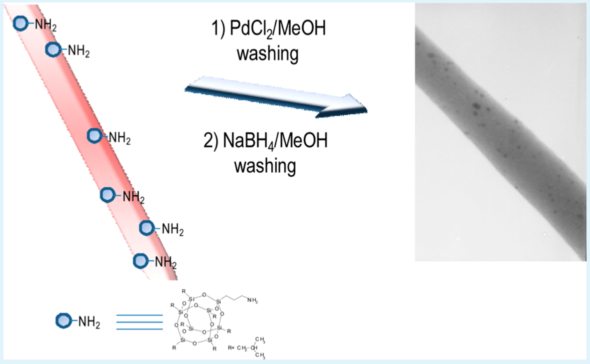
Supporting Information

ABSTRACT: In this work, a novel catalytic system is developed, consisting of palladium nanoclusters homogenously dispersed on the surface of nanostructured polymer nanofibers based on poly(L-lactic acid) (PLLA) and polyhedral oligomeric silsesquioxanes (POSS). Indeed, PLLA nanofibers containing amino-functionalized silsesquioxane molecules (POSS-NH_2), potentially capable of interacting with the metal precursor, are prepared by means of electrospinning. Conversely to the polymer matrix, which does not show any tendency to retain the metal precursor, the submicrometric dispersion of POSS-NH_2 in the PLLA nanofibers, as demonstrated by SEM-EDS analysis, turns out to promote the formation of metal nanoclusters. TEM measurements show a uniform distribution of Pd nanoparticles, characterized by an average dimension of ca. 4 nm, along the fibers. The prepared system proves a relevant catalytic activity toward the hydrogenation of stilbene under heterogeneous conditions. Moreover, as demonstrated by XPS measurements, the support is capable of retaining the catalyst during the hydrogenation reaction, thus preventing its leaching.



KEYWORDS: *electrospinning, POSS, heterogeneous catalysis*

INTRODUCTION

Recently, a growing research interest has been devoted to metal nanoparticles because of their attractive properties in chemistry, physics, biotechnology, and so on.[1] Among metal nanoparticles, those of palladium are particularly attractive, finding significant applications in optics,[2] electronics,[3] and catalysis.[4] In particular, the latter exploitation is of highest importance, since Pd often combines the characteristics of high reactivity and selectivity. As a general rule, high efficiency in catalysis often requires nanometric and uniform size as well as homogeneous distribution of the catalyst throughout a suitable substrate. Moreover, preventing nanoparticles from aggregation is one of the most important issues for preserving their properties. In general, polymers have proved to be effective supports in the preparation of heterogeneous catalytic systems.[5] In particular, the incapsulation of Pd nanoparticles in polymer-based materials, such as dendrimers,[6] star-shaped block polymers,[7] hyperbranched polymers[8] and cross-linked polymers[9] was achieved. Nevertheless, it is still very desirable to find a simple and reliable way to immobilize noble metal nanoparticles on the surface of polymers, in order to better control the metal loading and effective dispersion and make the catalytic system easily recoverable and recyclable. This is usually done by modifying the surfaces of polymers with suitable functional groups which can strongly anchor the nanoparticles.[10] Indeed, noble metal ions can be immobilized on the surface of polymers through chelating effect, thus escaping from aggregation. In the field of polymer materials, nanofibers prepared though the electrospinning technique represent an appealing metal supporting matrix for catalytic applications owing to their high aspect ratio and specific surface area.[11]

In this work, a novel catalytic system, based on poly(L-lactic acid) PLLA nanofibers containing an amino-polyhedral oligomeric silsesquioxane (POSS-NH_2) (Figure 1) uniformly dispersed into the polymer matrix, has been developed.

The above silsesquioxane has been chosen since its functional group, capable of interacting with the metallic precursor, likely through a coordinative mechanism, might be

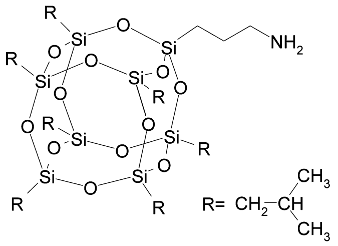


Figure 1. Aminopropylisobutyl-polyhedral oligomeric silsesquioxane (POSS-NH_2).

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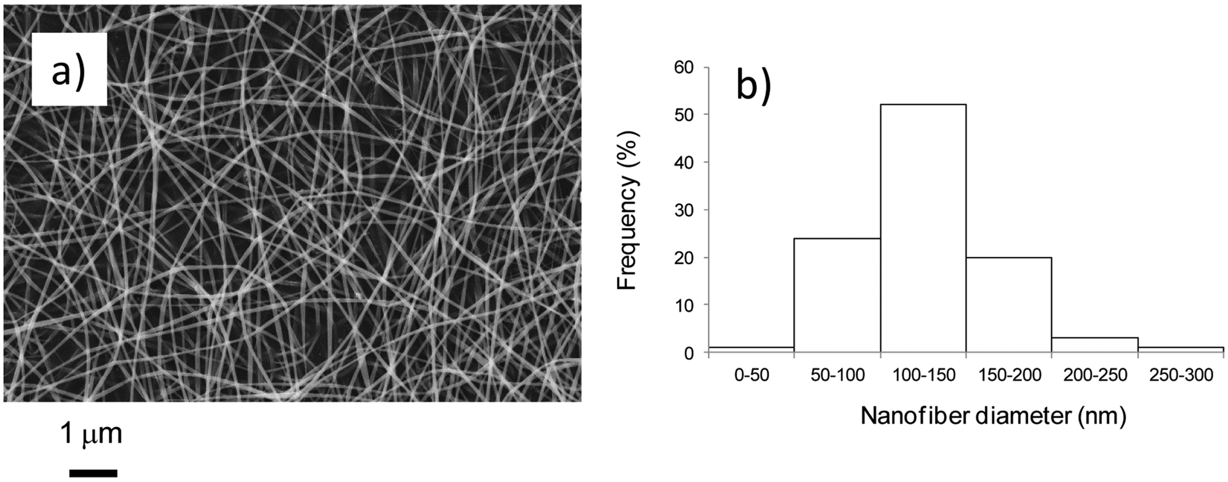

Figure 2. (a) SEM micrograph of PLLA/POSS-NH_2 nanofibers prepared by applying the optimal electrospinning conditions (PLLA concentration = 14 wt %, POSS-NH_2 concentration = 5 wt %, V = 15 kV, RH = 10%, Fr = 0.004 mL/min); (b) histograms of nanofiber populations as a function of nanofiber diameter.

potentially able to promote the metal nanoparticle deposition on the fiber surface. Indeed, POSS, which are organic–inorganic molecules[12] (approximately 1–3 nm in diameter), were successfully used as a linker for self-organization of Pd nanoparticles in methanol. In particular, a propylammonium POSS (octa(3-aminopropyl)octasilsesquioxane-octa-hydrochloride) allowed to obtain highly ordered spherical aggregates of Pd nanoparticles with a size of 4 nm,[13] and more recently, Letant et al.[14] have demonstrated the catalytic efficiency of the above system. These studies corroborated POSS capacity to efficiently interact with a metal precursor in a homogeneous system.

In this paper, for the first time an innovative exploitation of POSS in the field of development of heterogeneous catalytic systems is proposed, that is the use of a silsesquioxane as an additive for polymers characterized by a low affinity for metal precursors. Indeed, concerning the polymer/POSS nanofiber system, object of the present study, the silsesquioxane can (i) be dispersed at a nanometric level, thanks to the fast solvent evaporation occurring during the electrospinning process;[15] (ii) improve the nanofiber mechanical[16] and thermal properties;[17] (iii) interact with the metal precursor through its functional groups, which can be properly chosen, and consequently, it is potentially capable of promoting the catalyst deposition on the nanofiber surface. PLLA has been chosen as polymer matrix because of its biodegradability, which could meet the requirement of a low environmental impact catalytic system.

■ RESULTS AND DISCUSSION

This work has been preliminary focused on the assessment of the most suitable electrospinning parameters, which allow to obtain defect-free fibers; that is, fibers without beads. Indeed, as acetone/chloroform is a classical solvent mixture used to prepare electrospun PLA-based nanofibers,[18] some of the electrospinning parameters, such as voltage tension and polymer concentration were chosen on the basis of the literature data. Moreover, as it was demonstrated that the presence of POSS does not influence the viscosity of the polymeric solution but, reducing the surface tension, improves the system electrospinnability,[16] the same conditions were applied for the preparation of both PLLA and PLLA/POSS fibers. Among the various electrospinning parameters, the relative humidity (RH), namely the amount of water vapor that is contained in the gaseous mixture of air which is fluxed into the cylindrical electrospinning chamber, is generally not considered. Nevertheless, as we demonstrated the relevant influence of the above parameter on the electrospun fiber morphology,[11c,16] a detailed investigation was carried out by comparing the structures of fiber mats obtained by varying RH from ca. 10% to 50%. Figures 1S and 2S in the Supporting Information show SEM micrographs of the electrospun fiber mats prepared by using different RH values. By keeping all the electrospinning parameters constant and increasing the relative humidity, the morphology completely changes. On varying the RH from 10 to 50%, the homogeneity of both the fibers based on PLLA (see Figure 1S in the Supporting Information) and PLLA/POSS-NH_2 (see Figure 2S in the Supporting Information) decreases. This finding is in contrast with the trend reported in the case of other polymer matrices, such as PSMA[11c] and PVDF.[16] Indeed, as already commented,[19] the specific effect of the humidity on the fiber morphology depends on the polymer/solvent system used, and it is not possible to deduce a general rule.

Defect-free fibers (Figure 2a), characterized by an average diameter of ca. 150 nm (Figure 2b), obtained by applying the optimal electrospinning conditions, were subsequently dispersed in a methanol solution containing $PdCl_2$.

To verify the effect of POSS-NH_2 on the capacity of the polymer matrix to retain Pd, we contacted both neat PLLA and PLLA/POSS-NH_2 fibers with the same solution. The following reduction with $NaBH_4$ led to a significant change in the color of PLLA/POSS-NH_2 fibers, while those based on PLLA remained almost unchanged (see Figure 3S in the Supporting Information). Although this is only an indicative finding, it demonstrates the effectiveness of the metal precursor reduction and, qualitatively, the different Pd content in the fiber with POSS-NH_2 with respect to those based on PLLA.

Pd dispersion on fiber surface was studied by FE-SEM equipped with an EDS system. In the case of the PLLA nanofibers, Pd concentration is almost zero (see Figure 4Sa in the Supporting Information). This result proves, once again, the scarce capacity of the polymer matrix to retain the metal precursor and thus the efficiency of the washing treatment. On the contrary, PLLA/POSS-NH_2 nanofibers are characterized by

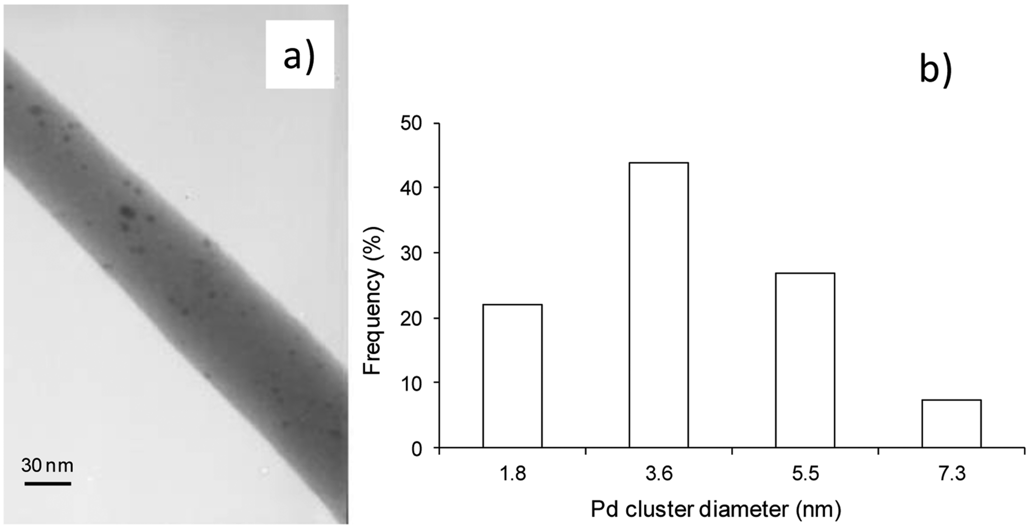

Figure 3. (a) TEM micrograph of PLLA/POSS-NH_2/Pd nanofiber, (b) histogram of the relative population as a function of Pt particle diameter.

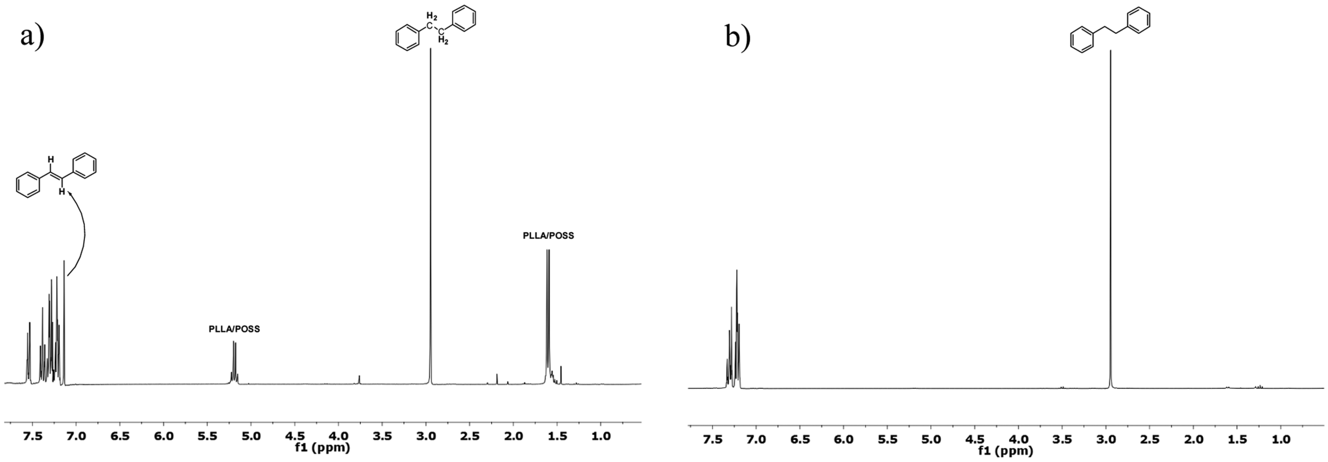

Figure 4. (a) Crude ^{1}H NMR of homogeneous reaction at 50% conversion, (b) crude ^{1}H NMR of heterogeneous reaction at 100% conversion.

a constant and homogeneous distribution of Pd and Si (see Figure 4Sb in the Supporting Information), as revealed by measuring the concentration of the above elements in several points of the nanofibers. The dispersion of the latter element, related to the presence of the silsesquioxane, demonstrates, as previously reported,[16] that electrospinning promotes a submicrometric distribution of POSS. Moreover, also these results confirm that POSS-NH_2 modifies the polymer matrix metal retain capability. Indeed, it is worthwhile to underline that SEM micrographs do not show any palladium aggregates characterized by a micrometer dimension, thus proving that metal dispersion is connected with the silsesquioxane distribution on the fiber surface. The Pd concentration calculated by the above measurements is ca. 1 wt %.

TEM measurements were carried out to better assess the dimension and dispersion of the metal particles deposited onto the fiber surface. Indeed, both features are important in determining the catalytic activity, as a high metallic dispersion (i.e., low dimensions of the metal particles) generally corresponds to a high number of metal sites on the catalyst surface. A TEM micrograph of a PLA/POSS fiber containing Pd clusters is reported in Figure 3. In the same figure, the histogram of Pd aggregate dimensions is given. The metallic dispersion (MD) was calculated as the ratio between the superficial ($N(s)_m$) and the total ($N(t)_m$) number of metallic atoms, whereas metal particle diameter was reported as both number diameter (dn) and volume/area diameter (dva $=6\sum(V_i)/\sum(A_i)$, where V_i and A_i are the volume and area of a single cluster). The calculation of dva was performed considering the particles spherical, using the following expression[8]

$$\text{dva} = 6\left[\frac{\sum(V_i)}{\sum(A_i)}\right] = 6\frac{v_M N(t)_m}{a_M N(s)_m} = \frac{6\left(\frac{v_M}{a_M}\right)}{\text{MD}}$$

where v_M and a_M are respectively 1.47×10^{-29} m^3 and 7.87×10^{-20} m^2.[8]

The aggregates, formed on the surface of the fiber, appear to be uniformly distributed with dn of 4 nm, dva of 6 nm, and MD of 18%. It is worth mentioning that the cluster dimensions, in terms of average diameter, are similar to those obtainable using inorganic supports for palladium catalysts (1.1−1.3 nm on C[20] and 3.5 nm on Al_2O_{31}[21]) as well as those reported for other polymeric supports (less than 4 nm on nylon,[22] between 2 and 4 nm on resins[23] and hyperbranched aramids[8a]).

The catalytic activity of PLLA/POSS-NH_2/Pd nanofibers was tested in the catalytic hydrogenation of stilbene. In a control experiment, stilbene (20 mg) and nanofibers (20 mg) were dissolved in tetrahydrofuran (2 mL) and the resulting homogeneous solution was placed under a H_2 atmosphere (1 atm) at room temperature for 1 h, time required by the reaction to reach ca. 50% conversion. The solvent was then evaporated and the crude analyzed by ^1H NMR. The resulting spectrum (Figure 4a) shows the peaks ascribable to stilbene and diphenylethane, as well as those of PLLA/POSS-NH_2.

In a second experiment, the catalytic hydrogenation was performed under heterogeneous conditions, using methanol as the solvent. This time the reaction was stopped upon completion (3 h), the solution was then filtered, concentrated in vacuo and analyzed by ^1H NMR (Figure 4b): comparison of spectra a and b in Figure 4 shows complete conversion of stilbene into diphenylethane as well as the complete absence of peaks belonging to PLLA/POSS-NH_2 (see Figure 5S in the Supporting Information). This latter experiment confirms that the Pd nanoparticles, deposited onto the surface of PLLA nanofibers, can be used as heterogeneous catalyst and that a simple filtration allows to remove the polymer from the reaction medium. In addition, in respect to this specific reaction, the activity of PLLA/POSS-NH_2/Pd nanofibers is comparable to the one of commercial Pd on activated charcoal.[24]

To verify the support capacity of retaining the catalyst during the hydrogenation reaction, we analyzed the product, after separation from the nanofibers, by means of X-ray photoelectron spectroscopy (XPS). The results, reported in Figure 6S in the Supporting Information, in the energy range typical for Pd 3d peaks, clearly show that no Pd was released during the hydrogenation process.

CONCLUSIONS

In conclusion, this work opens the way to innovative exploitations of POSS in the field of heterogeneous catalysis. It has indeed been demonstrated that these hybrid molecules, already widely used as drug and enzyme supports, can be successfully employed as a polymer additive in the formulation of novel heterogeneous catalytic systems, where the silsesquioxane nanometric dispersion and its peculiar functionalities promote the formation of metal nanoclusters on the polymer surface. In particular, having chosen as polymer support a system consisting of nanostructured nanofibers based on PLLA and amino-functionalized POSS, it has been verified that, unlike the neat polymer matrix, the formation of Pd nanoclusters homogenously dispersed on the nanofiber surface. It is of utmost relevance the high reactivity of the prepared system and its capacity of retaining the catalyst, thus preventing its leaching in the reaction medium.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details. SEM micrographs of PLLA and PLLA/POSS-NH_2 nanofibers prepared by applying different RH. Photos of PLLA/POSS-NH_2 and PLLA nanofibers after impregnation with $PdCl_2$, washing and reduction with $NaBH_4$. FE-SEM EDS analysis of PLLA and PLLA/POSS-NH_2 nanofibers after impregnation with $PdCl_2$, washing and reduction with $NaBH_4$. XPS characterization of PLLA/POSS-NH_2/Pd nanofibers before and after the catalytic experiments, together with the results on the reaction product. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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