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Covalent Surface Grafting of Branched Polyethylenes on Silica Nanoparticles by Surface-Initiated Ethylene "Living" Polymerization with Immobilized Pd−Diimine Catalysts

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ABSTRACT: We report in this article a new versatile surface-initiated ethylene "living" coordination polymerization technique for "grafting from" surface functionalization of silica nanoparticles with narrow-distributed branched polyethylene brushes of controllable length. The key to the success of this technique is the use of the acetonitrile Pd−diimine complex, $[(ArN{=}C(Me){-}(Me)C{=}NAr)Pd(CH_3)(N{\equiv}CMe)]^+SbF_6^-$ (Ar = 2,6-(iPr)$_2$ C$_6$H$_3$) (**1**), which possesses unique immobilization and polymerization chemistry. In this technique, complex **1** was immobilized covalently onto acryloyl-functionalized silica particle surface by reacting with the surface-tethered acryloyl groups, giving rise to Pd−diimine chelate complexes covalently tethered on silica surface through an ester linkage. The tethered Pd−diimine chelate complexes catalyzed successfully surface-initiated ethylene "living" polymerization at 5 °C and ethylene pressure of 400 psi, leading to narrow-distributed branched polyethylene chains covalently tethered on silica surface through the ester linkage. The branched polyethylene brushes, after cleaved off from the silica particles, were found to possess narrow molecular weight distribution (polydispersity index of about 1.18) and have a linear increase of their number-average molecular weight and relative mass content with the polymerization time. The covalent grafting of polymer brushes was confirmed by using characterization techniques including nuclear magnetic resonance (NMR), thermogravimetric analysis (TGA), and transmission electron microscopy (TEM). To the best of our knowledge, this represents the first report on the use of surface-initiated ethylene "living" coordination polymerization technique for surface functionalization of inorganic particles with polyethylene brushes.

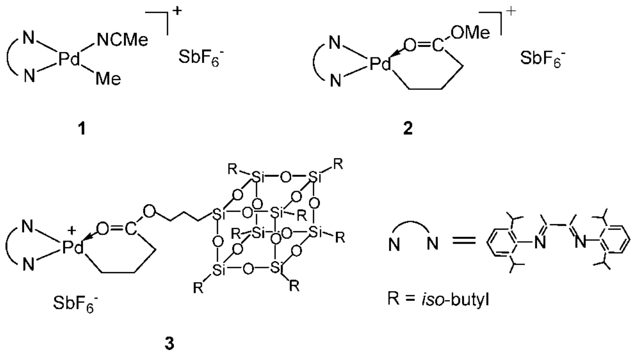
Introduction

Surface-initiated "living"/controlled polymerization techniques have recently been extensively developed for "grafting from" surface functionalization of various inorganic or metal particles with polymer brushes.[1−3] The presence of covalently surface-grafted polymer shell imparts the modified particles with some highly desired enhanced properties, such as processability, dispersion, and stability in selected solvents and interfacial compatibility with polymer matrix.[1−3] Most "living"/controlled polymerization techniques developed to date, including, most notably, the various types of controlled radical polymerization techniques[4−6] as well as anionic[7] and ring-opening metathesis polymerization techniques,[8] have been successfully employed for surface grafting of different types of polymers, including polyacrylates, polyacrylamides, polystyrene, and polycycloolefins. A variety of inorganic or metal particles, including silica particles, gold nanoparticles, quantum dots, carbon nanotubes, and magnetic nanoparticles, have been used as substrates to surface-initiate controlled polymerizations. The covalent immobilization of corresponding initiating species on the substrate surface to form self-assembled monolayer (SAM) is critical in these techniques to subsequent surface-initiated "living"/controlled polymerizations.

The "living" coordination polymerization technique specific to olefin monomers like ethylene has gained tremendous advancements in the past decade. A number of well-behaved transition-metal catalyst systems have been successfully developed for "living" polymerization of olefins, wherein the catalysts not only provide initiating sites for chain growth but also catalyze the coordinative insertion of olefin monomers.[9] However, this unique "living" polymerization technique has rarely been developed for surface grafting of polyolefins, which are commercially important polymers of many desired properties. The difficulty in finding versatile transition-metal catalysts, which not only can be covalently surface-immobilized but also can subsequently surface-initiate olefin "living" polymerization after immobilization to give rise to covalently surface-tethered polyolefin chains, is the primary reason that diminishes the possible application of this unique "living" polymerization technique for covalent surface grafting of polyolefins.

Pd−diimine catalysts discovered by Brookhart et al. (such as the acetonitrile adduct, **1**, and the chelate complex, **2**, shown in Scheme 1) are a novel series of late-transition-metal catalysts of high versatility in catalyzing "living" polymerization of ethylene and α-olefin under prescribed conditions.[10] We have recently discovered a unique immobilization chemistry for covalently supporting the acetonitrile Pd−diimine complex (**1**) onto homogeneous polyhedral oligomeric silsesquioxane (POSS) model support to obtain homogeneous POSS-supported Pd−diimine complex (**3**).[11] This immobilization chemistry utilizes the characteristic reaction of **1** with the acrylate functionality of acryloisobutyl-POSS to form a six-membered chelate structure,

Scheme 1. Pd−Diimine Complexes



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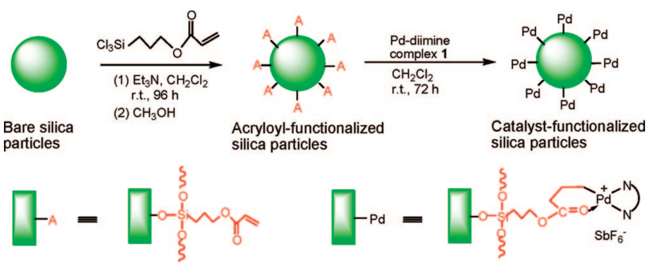
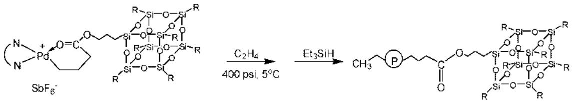
Scheme 2. Silica Surface Modification and Catalyst Immobilization Procedure



which occurs through the 2,1-insertion of the acrylate double bond into Pd−Me bond of **1** followed by rearrangement. The acrylate functionality serves as the specific anchoring site for the cationic Pd complex **1** in this immobilization strategy.[11] More importantly, this homogeneous model POSS-supported catalyst is featured with its unprecedented abilities to successfully catalyze ethylene “living” polymerization at 5 °C and 400 psi and to give rise to narrow-distributed branched polyethylene (PE) chains with each of them end-tethered onto the POSS model support through the ester linkage (eq 1).[11]



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(1)

The underlying polymerization chemistry, which leads to the covalent tethering of PE chain onto the POSS support, occurs via chain initiation by dissociation of the Pd−carbonyl coordination under high ethylene pressure followed by subsequent ethylene insertion into the Pd−CH_2 bond.[11] This chemistry is typical with Pd−diimine acrylate chelate complexes and has been utilized for synthesis of several narrow-distributed telechelic polyethylenes via ethylene “living” polymerization using functionalized Pd−diimine chelate complexes bearing different functionality through the ester linkage.[10,13,14]

Homogeneous POSS-supported catalysts are often used as mechanistic model systems for studying the chemistry of heterogeneous silica-supported catalysts.[15] In this work, we utilize this established immobilization chemistry to covalently tether the Pd−diimine complex (**1**) onto acryloyl-functionalized silica particles. We demonstrate that such silica-supported Pd−diimine chelate catalyst can successfully surface-initiate ethylene “living” polymerization at 5 °C and ethylene pressure of 400 psi to give rise to silica particles covalently grafted with narrow-distributed branched polyethylene (PE) brushes of controllable length. This is the first report on the use of surface-initiated ethylene “living” polymerization for the surface functionalization of inorganic particles, and it demonstrates another unique feature of the Pd−diimine catalysts. This versatile “living” coordination polymerization technique can thus be used for surface modification of other various substrates.

Results and Discussion

Commercially obtained bare silica particles, which were aggregates of nanoparticles of diameter of about 10 nm, were used in this work. The bare silica particles were first modified to generate surface-tethered acryloyl groups, which were used as the anchoring sites for the subsequent covalent immobilization of the Pd−diimine complex **1**. Scheme 2 shows the silica surface modification and catalyst immobilization procedure employed in this work. After drying in vacuo at 210 °C for 2 h, the bare silica particles were then dispersed in anhydrous CH_2Cl_2 under ultrasonication followed by the addition of 3-acryloxypropyltrichlorosilane and triethylamine. The reaction between the silica surface silanol groups and the Si−Cl groups of 3-acryloxypropyltrichlorosilane gave rise to acryloyl-functionalized silica particles containing a SAM of acryloyl functionality. As each Si−Cl group of the trichlorosilane monomer can potentially react with the silica silanol groups, the tethering of the acryloyl functionality can be established through maximally three −Si−O− linkages as shown in Scheme 2. The functionalized particles were then treated with CH_3OH to consume the remaining unreacted Si−Cl groups, which lead to the formation of −Si−OCH_3 groups. After further washing and drying, the acryloyl-functionalized silica particles were subsequently treated with acetonitrile Pd−diimine complex **1** in CH_2Cl_2. The surface reaction of the tethered acryloyl groups with complex **1** led to the formation of catalyst-functionalized silica particles (or silica-supported Pd−diimine catalysts). The product was isolated by centrifugation followed by extensive washing with anhydrous CH_2Cl_2 to remove unreacted **1**. On the basis of our prior study of the homogeneous POSS model supported catalyst,[11] the covalently immobilized cationic Pd centers should be chelate complexes bonded onto the silica particles through the ester linkage (Scheme 2). However, despite the extensive washing applied, the presence of a residual amount of physically adsorbed Pd−diimine complex **1** on the silica surface in the product could not be ruled out.

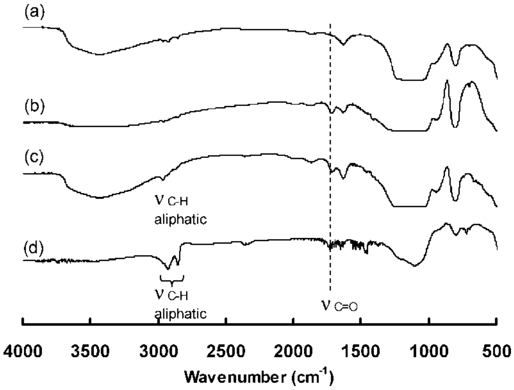


Figure 1. Fourier transformed infrared spectrum of (a) bare silica particles, (b) acryloyl-functionalized silica particles, (c) catalyst-functionalized silica particles, and (d) polyethylene-functionalized silica particles (PE-silica-1h) obtained after 1 h of ethylene “living” polymerization at 5 °C and 400 psi.

Because of the insolubility of the products formed in each of the above functionalization steps, their structural characterization was restricted to Fourier transformed infrared (FTIR) spectroscopy. Figure 1a−c illustrates and compares the FTIR spectra of the bare silica, acryloyl-functionalized silica, and catalyst-functionalized silica particles. The Si−O stretch due to bulk silica at around 1050 cm^{-1} remains a prominent feature in all the spectra. An absorbance band at 1712 cm^{-1}, characteristic of C═O stretch of ester group, is clearly observed in the spectra of both acryloyl- and catalyst-functionalized silica particles, while it is absent in that of bare silica. This absorbance should be primarily attributed to the ester group of the grafted acryloyl functionalities. The absorbance of the coordinating C═O group on the covalently grafted chelate Pd−diimine complexes should be typically at about 1640 cm^{-1} on the basis of literature reports on POSS-supported and other homogeneous Pd−diimine chelate complexes.[11,12] However, it is not clearly observable as from the Figure 1c due to the weak concentration of the grafted catalyst and/or significant overlap of the absorbance peaks. In the spectrum of the catalyst-functionalized silica particles, weak absorbances at around 2946 cm^{-1}, characteristic of alkyl C−H stretching vibration modes, are also found, corresponding to the added alkyl groups from the tethered

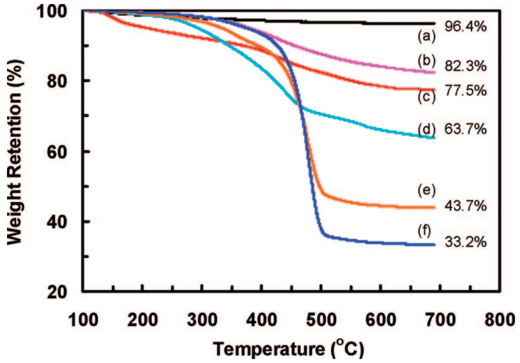


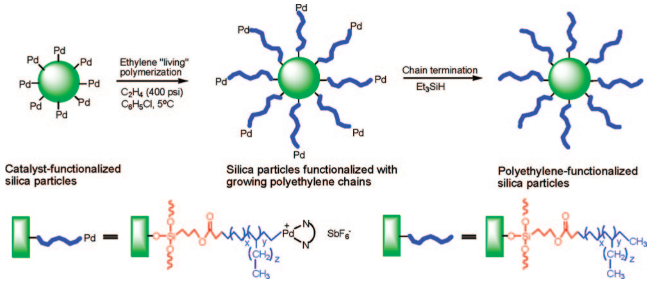
Figure 2. Thermogravimetric analysis (TGA) curves of (a) bare silica particles, (b) acryloyl-functionalized silica particles, (c) catalyst-functionalized silica particles, (d) polyethylene-functionalized silica particles (PE-silica-1h) obtained after 1 h of ethylene "living" polymerization at 5 °C and 400 psi, (e) polyethylene-functionalized silica particles (PE-silica-3h) obtained after 3 h of ethylene "living" polymerization at 5 °C and 400 psi, and (f) polyethylene-functionalized silica particles (PE-silica-5h) obtained after 5 h of ethylene "living" polymerization at 5 °C and 400 psi. TGA was performed in a N_2 atmosphere at a heating rate of 20 °C/min.

catalyst. But these absorbances are not clearly observable in the spectrum of the acryloyl-functionalized silica probably due to a lower number of alkyl groups.

Thermogravimetric analysis (TGA) was carried out on the three types of silica particles in a N_2 atmosphere at a heating rate of 20 °C/min. Figure 2 compares their TGA curves. TGA data show that the weight loss at 700 °C is 3.6% for bare silica, 17.7% for acryloyl-functionalized silica, and 22.5% for catalyst-functionalized silica. The weight loss for the bare particles might be due to the associated water loss. Taking the mass loss at 700 °C as the reference, the increase in the weight loss in the acryloyl-functionalized silica particles would be 14.1% relative to the bare silica particles. By assuming all the acryloyl moieties were lost at 700 °C, the grafting density of the acryloyl functionality is estimated to be ca. 3.0 molecule/nm^2 with the average surface area of 160 m^2/g for the bare silica particles. This result is consistent with literature reports[4b,e] and is comparable to the generally accepted surface hydroxyl content of silica of 5 OH/nm^2.[4b] This grafting density also indicates monolayer or near-monolayer coverage of the particle surfaces. Not knowing the char composition of the mounted Pd−diimine catalyst in TGA analysis, we used inductively coupled plasma mass spectrometry (ICP-MS) to analyze the Pd loading amount on the catalyst-functionalized silica particles. From ICP-MS analysis, the loading amount of Pd is 0.048 mmol/g, which corresponds to ca. 0.23 Pd/nm^2. Using the thermal ellipsoid molecular structure data of a very similar Pd−diimine chelate complex reported in our prior study,[14a] we estimate that each immobilized Pd−diimine complex occupies a surface area of ~1.2 nm^2, which gives the maximum Pd loading density of 0.83 Pd/nm^2. The current Pd loading density found here indicates that the tethered acryloyl functionalities were in excess with only 8% used for immobilization of the Pd−diimine complex.

Surface-initiated ethylene polymerizations were carried out using the catalyst-functionalized silica particles. Aiming at achieving "living" polymerization behavior, a polymerization condition of 5 °C and ethylene pressure of 400 psi with chlorobenzene as solvent was chosen. This polymerization condition has been typically used for ethylene "living" polymerization with various homogeneous cationic Pd−diimine catalysts (such as **1**−**3**) due to significantly reduced chain transfer/termination reactions at this condition.[10,11,13,14] Following the polymerization chemistry established with Pd−diimine chelate complexes,[10−12,14] chain initiation with the immobilized Pd−diimine chelate complexes on silica particles should occur through dissociation of the Pd−carbonyl coordination followed with subsequent ethylene insertion into the resulting Pd−CH_2 bond. Subsequent chain growth by continuous ethylene insertion into the Pd−alkyl bond should yield the growing polyethylene chains covalently tethered onto the silica particles through the ester linkage (Scheme 3). In the polymerization, the Pd metal centers, which stay at the distal end of the growing chains, leave the silica surface, and so the ever-thickening layer of already-formed polymer will not impede insertion of fresh monomer. This is thus a typical surface-initiated "living" polymerization. The length of the polyethylene brushes should be "linearly" dependent on the polymerization time for "living" polymerization, as the ethylene monomer pressure was maintained constant during polymerization.

Scheme 3. Surface-Initiated Ethylene "Living" Polymerization with Catalyst-Functionalized Silica Particles for Covalent Surface Grafting of Polyethylene Brushes on Silica Particles



Herein, three polymerization runs with different polymerization times, 1, 3, and 5 h, were carried out with the catalyst-functionalized silica particles to investigate the dependence of the chain length and mass content of polymer brushes on polymerization time, which would allow us to examine the presumed "living" characteristics of this surface-initiated polymerization. After the polymerization, the solution was quenched with Et_3SiH, which cleaved the Pd−polymer bond and yielded polymer brushes of a saturated free end (Scheme 3).[10,11] The solid polymerization products, obtained by precipitating the solution quenched with Et_3SiH in methanol, often contained fine black Pd powders from deactivated Pd−diimine complexes. To remove the Pd powers, the raw solid polymerization products were redispersed in THF and treated with a small amount of HCl/H_2O_2 mixture. THF is a good solvent for polyethylenes from Pd−diimine catalysts as they are highly branched, which will be shown below. This treatment was found effective in removing black Pd residue and rendering clean products while without damaging the polymers.[11] The products further underwent a thorough THF washing and centrifugation procedure to remove the very small quantity of untethered free polymers (generally less than 5 wt % compared to the grafted polymers) in the products, which might result from a residual amount of noncovalently supported (e.g., physically adsorbed) Pd−diimine complex **1** on silica. The PE-functionalized silica particles were obtained by drying the products. These PE-functionalized particles are termed here as PE-silica-1h (1 h of polymerization), PE-silica-3h (3 h of polymerization), and PE-silica-5h (5 h of polymerization). They were characterized by FTIR, TGA, gel permeation chromatography (GPC), proton nuclear magnetic resonance (^{1}H NMR), and transmission electron microscopy (TEM), and the presence of covalently grafted PE brushes on these particles was confirmed.

A typical FTIR spectrum obtained on PE-silica-1h is shown in Figure 1d. A significant enhancement in the intensity of the alkyl C−H stretches at 2946 and 2846 cm^{-1} can be observed, indicative of the increased number of alkyl groups in the grafted particles as a result of the surface-tethered polyethylene brushes.

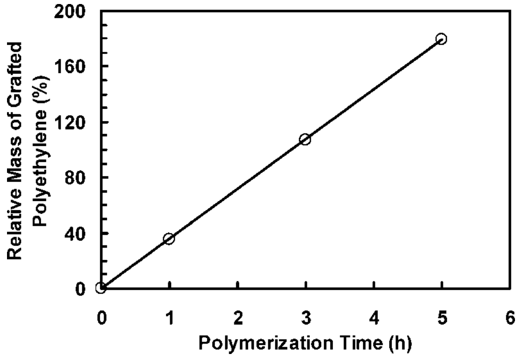


Figure 3. Mass percent of the grafted polyethylene relative to the mass of residual silica at 700 °C (corrected from acryloyl-functionalized silica particles) vs the polymerization time. Relative mass of grafted polyethylene = $[(1 - W_{PES})/W_{PES} - (1 - W_{AS})/W_{AS}] \times 100$, where W_{PES} and W_{AS} represent weight retention at 700 °C of PE-functionalized silica particles and acryloyl-functionalized silica particles, respectively.

In Figure 2d−f, the TGA curves of the three different PE-functionalized silica particles, obtained with a polymerization time of 1, 3, and 5 h, respectively, are also shown. The amount of the grafted PE increases with the increase of polymerization time. The weight of retention at 700 °C decreases from 63.7% (PE-silica-1h) to 43.7% (PE-silica-3h) to 33.2% (PE-silica-5h). Using the mass of the residual silica at 700 °C as reference, a quantitative analysis of the TGA data shows that the amount of grafted PE increases linearly with the polymerization time (Figure 3). This implies that the number of growing chains on the silica surface was constant and the surface-initiated polymerization was a "living" process with a linear increase of brush length with polymerization time.

To determine the molecular weight and molecular weight distribution of the grafted PE brushes and to further elucidate the "living" characteristics, the silica cores of the PE-functionalized silica particles were destroyed with hydrofluoric acid.[4b,e,5a,b] The cleaved polymers were collected and characterized by GPC and ^{1}H NMR. Figure 4a shows the GPC elution traces of the three cleaved polymers, which are monomodal with a consistent reduction of elution volume (i.e., increasing molecular weight) with the increase of polymerization time. For the purpose of comparison, we also carried out homogeneous ethylene polymerization with the homogeneous Pd−diimine chelate complex **2** at the same conditions, 5 °C and ethylene pressure of 400 psi, to obtain free untethered polymers. Figure 4b shows the GPC elution traces of the corresponding free untethered polymers obtained at the same polymerization times (1, 3, and 5 h). Figure 5 plots the number-average molecular weight ($M_{n,GPC}$) and polydispersity index (PDI), obtained relative to narrow polystyrene standards, vs polymerization time for the two sets of polymers.

Consistent with literature reports[10] on "living" polymerization with **2**, the resulting untethered free polyethylenes exhibit narrow molecular weight distribution (with PDI around 1.10) together with a linear increase of $M_{n,GPC}$ with polymerization time (Figure 5). The cleaved polymers showed monomodal GPC traces, and their $M_{n,GPC}$ data are very similar to those of the untethered analogues with an almost identical linear dependency on polymerization time. In both heterogeneous and homogeneous systems, the active Pd metal centers staying at the growing end of the polymer chain should have identical structures. The similar $M_{n,GPC}$ data observed in both systems suggest that ethylene turnover frequency (TOF) is similar in both polymerization systems, not significantly affected by the presence of heterogeneous silica support. Compared to the corresponding free untethered polymer analogues synthesized in the homogeneous system, the cleaved polymers, however, exhibit slightly broader, yet still quite narrow, molecular weight distribution with PDI typically around 1.18. Slight broadening in molecular weight distribution has often been observed in surface-initiated "living"/controlled radical polymerizations.[4e,h,6d] It is possibly due to diffusion problems present in heterogeneous polymerization systems. Along with the above relative mass content data (Figure 3), the results based on molecular weight analysis further imply that this surface-initiated polymerization with the heterogeneous silica-supported Pd−diimine catalysts is a "living" process, producing polyethylene brushes with controllable molecular weights and relatively narrow molecular weight distribution.

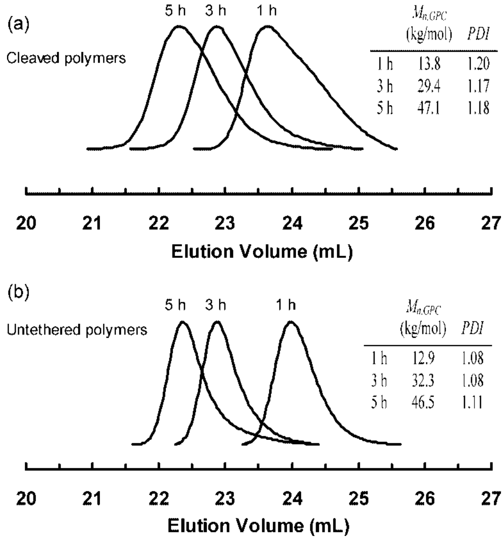


Figure 4. Gel permeation chromatography elution traces of (a) cleaved polyethylenes from PE-functionalized silica particles (PE-silica-1h, PE-silica-3h, and PE-silica-5h, respectively) obtained in ethylene "living" polymerization with catalyst-functionalized silica particles at 5 °C and 400 psi with a polymerization time of 1, 3, and 5 h, respectively, and (b) untethered polyethylenes obtained in ethylene "living" polymerization with homogeneous chelate catalyst **2** at 5 °C and 400 psi with a polymerization time of 1, 3, and 5 h, respectively.

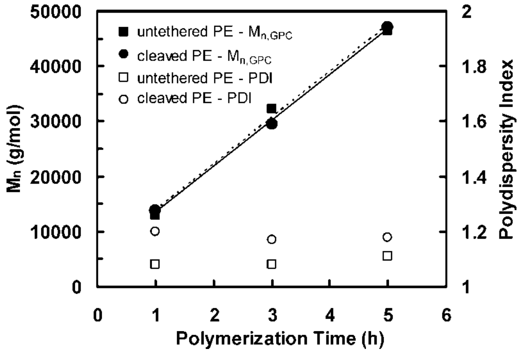


Figure 5. Plot of number-average molecular weight (M_n) and polydispersity index (PDI) as functions of polymerization time for the cleaved polymers and untethered free polymers.

The microstructure of the cleaved polymers was elucidated by using ^{1}H NMR spectroscopy. Representatively, Figure 6a shows the ^{1}H NMR spectrum of the cleaved polymer from PE-silica-3h. For comparison purpose, the spectrum of the corresponding untethered free polymer analogue from homogeneous polymerization with **2** (3 h of polymerization) is also shown in Figure 6b. Following the catalyst impregnation chemistry of **1** and the polymerization chemistry of chelate complexes as shown in Scheme 3, the cleaved polymer brush should possess the ester end group with structure shown in Figure 6a.[11,14] This ester

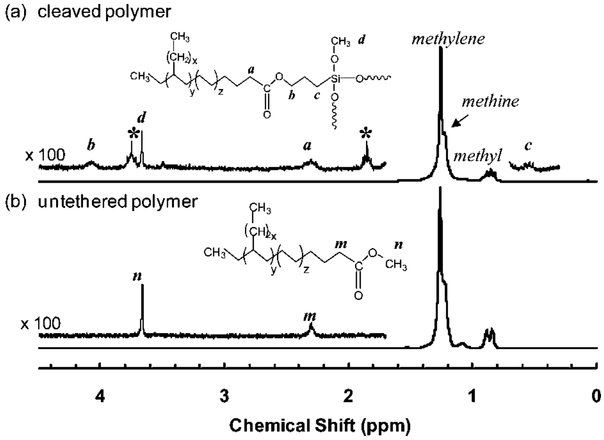
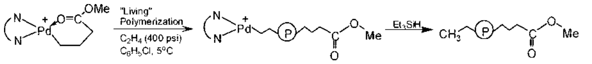


Figure 6. ^1H nuclear magnetic resonance spectra of (a) cleaved polyethylene from PE-silica-3h and (b) untethered free polyethylene synthesized with complex **2** at 5 °C and 400 psi with a polymerization time of 3 h. In (a), the signals marked with an asterisk (*) are from THF solvent residue in the polymer.

end group is the linkage through which both the Pd−diimine chelate complex and the resulting polymer bond to the silica surface. From Figure 6a, this characteristic ester end group is clearly present in the cleaved polymer from the signals *a*−*c*, thus confirming the covalent tethering of the polymer brushes on silica particle surface and verifying the polymerization chemistry depicted in Scheme 3 for this surface-initiated ethylene polymerization process. In addition, the presence of signal *d* at 3.64 ppm attributable to the methyl protons of the $-Si-OCH_3$ group indicates that some of Si−Cl groups of 3-acryloxypropyltrichlorosilane did not completely react with the silica surface silanol groups during the silica surface functionalization step; instead, they were quenched by the subsequently added CH_3OH. On the basis of integration results of the signals (*a*, *b*, *d*), we estimate that approximately each polymer chain contains one $-Si-OCH_3$ group. In Figure 6b, the untethered free polymer analogue resulting from homogeneous catalyst **2** contains a methyl ester group as expected (eq 2).[10]



(2)

With the fact that each polyethylene chain resulting from the chelate Pd−diimine metal centers contains an ester end group, the ^1H NMR spectra shown in Figure 6 allowed the estimation of polymer number-average molecular weight, $M_{n,NMR}$, based on end-group analysis.[11,14a] The estimated $M_{n,NMR}$ values are very close, being 26.8 and 29.2 kg/mol for the cleaved polymer and the untethered polymer analogue, respectively. This similarity is in consistency with the above GPC characterization results showing their very close $M_{n,GPC}$ values. However, because of the differences in the hydrodynamic volumes of these polymers and polystyrene standards, $M_{n,GPC}$ data determined above from GPC measurements are relative values and do not equal $M_{n,NMR}$ data, which reflect the true number-average molecular weight of the polymers.[11,14a] The TOF values, estimated from $M_{n,NMR}$ data are 319 and 348 h^{-1} for the cleaved polymer and the untethered polymer analogue, respectively, and they are very close to TOF value (325 h^{-1}) found with the homogeneous POSS-supported catalyst **3**.[11] These results further imply that the TOF of the covalently impregnated Pd−diimine chelate catalysts is not significantly affected by the presence of silica support in this heterogeneous surface-initiated polymerization system since the Pd metal centers progressively leave the silica surface with the growth of polymer brushes (Scheme 3).

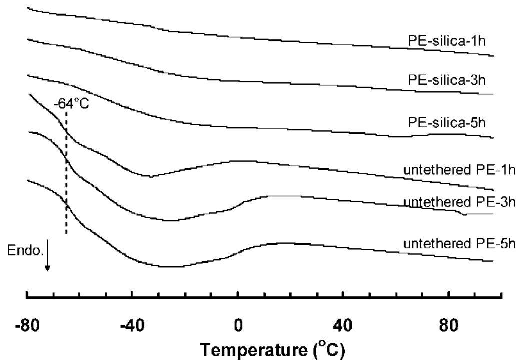


Figure 7. Differential scanning calorimetry thermograms of the polyethylene-functionalized silica particles and untethered free polyethylenes synthesized at 400 psi and 5 °C at different polymerization times.

Using the relative mass of grafted PE to silica residue for PE-silica-3h at 700 °C shown in Figure 3 and the $M_{n,NMR}$ data together with the average specific surface area of the silica particles (160 m^2/g), the polymer grafting density on silica surface of PE-silica-3h is estimated to be ca. 0.15 polymer chains/nm^2. This value is very close to the Pd loading density on silica surface (0.23 Pd/nm^2) determined above from ICP-MS measurement, thus suggesting that most Pd metal centers were chelate complexes covalently immobilized on silica surface through the ester linkage, and they successfully initiated the chain growth with each metal center leading to one surface-tethered polyethylene chain. The other small fraction of the mounted Pd is possibly attributed to Pd metal centers that were not activated successfully for polymerization, and/or physically adsorbed complex **1** on silica surface that led to untethered polymers easily removed during the washing step, and/or decomposed Pd complexes.

Both the cleaved polymers and the untethered free polymer analogues appear as sticky viscous oil-like liquids, characteristic of polyethylenes synthesized with Pd−diimine catalysts.[11,14] They are highly branched from their ^1H NMR spectra. Calculations based on the resonances of methylene, methine, and methyl protons of the ethylene sequence indicate that the polymers have a similar branching density of about 83 branches per 1000 carbons, consistent with the literature data found with polymers synthesized through ethylene polymerization with homogeneous Pd−diimine catalysts at the same condition.[11,14] Such a highly branched chain structure is a result of the chain walking mechanism of the Pd−diimine catalysts, and it imparts the polymers with high solubility in solvents like toluene and THF even at room temperature.[16,17] On the basis of our prior studies, the polymers, however, should still possess a linear chain topology with a linear backbone grafted with mainly short branches given the polymerization condition of 400 psi and 5 °C.[17]

Differential scanning calorimetry (DSC) characterizations of the PE-functionalized silica particles were performed. Figure 7 shows the DSC thermograms of the PE-functionalized silica particles along with those of the three untethered free polymer analogues for comparison. The three untethered polymers exhibit similar thermal transitions with a glass transition centered at about −64 °C and a weak endotherm in a broad temperature range from −50 to 10 °C, which is possibly a melting endotherm attributable to the branched polyethylene sequences.[11,14a] The peak temperature of the endotherm increases slightly with the increase of polymer molecular weight of the untethered free polyethylenes. Differently, though having significant polymer contents, the PE-functionalized silica particles do not show well-defined thermal transitions, with only a weak decrease of heat

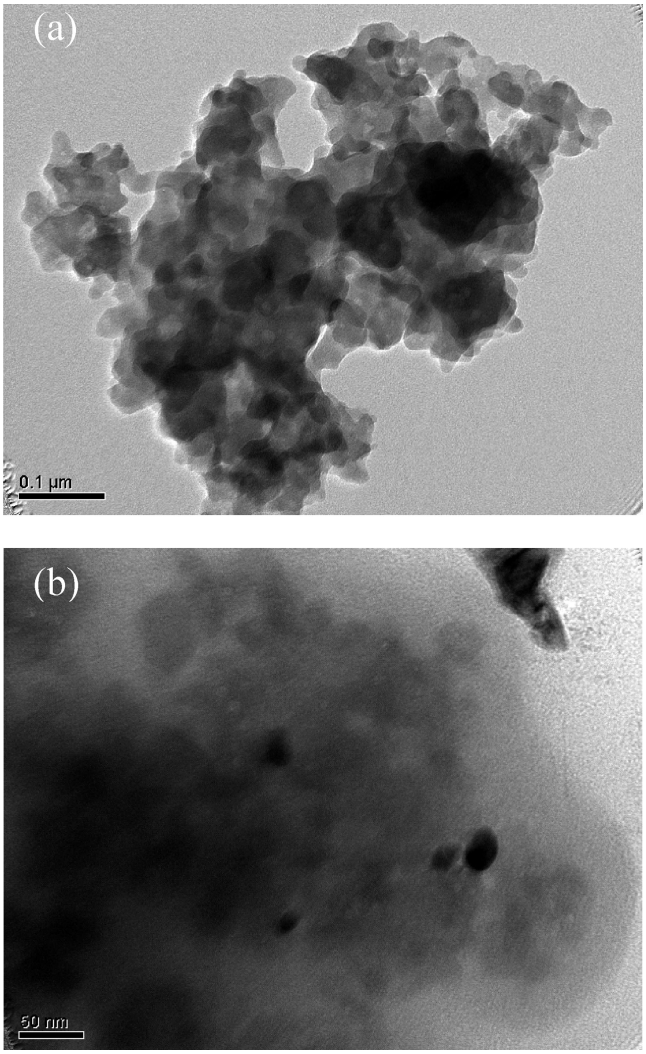


Figure 8. TEM images of (a) bare silica particles and (b) polyethylene-functionalized silica particles, PE-silica-1h.

capacity found in a broad temperature range from −64 to −5 °C. This difference in the thermal properties indicates that the inorganic silica particles restrict the chain relaxation process of the tethered polymer brushes that are constrained at one end.[8a,18]

Figure 8 shows the TEM images of bare silica particles and a representative PE-functionalized silica sample, PE-silica-1h. These TEM samples were prepared by depositing a drop of freshly sonicated THF solution containing dilute dispersed silica particles on a copper grid covered with a perforated carbon film followed by evaporation of THF. The bare silica particles are observed as large aggregates with a size of several hundred nanometers, and no isolated bare silica nanoparticles can be found (Figure 8a). The silica particles bearing branched PE brushes, PE-silica-1h, are gel-like hybrids with aggregates of silica particles dispersed in hazy sticky branched polyethylene gel (Figure 8b). The sticky nature of the surface-tethered branched PE brushes having low glass transition temperature leads to the easy aggregation of these functionalized silica particles after evaporation of the solvent during the TEM sample preparation procedure. Individual isolated silica nanoparticles are not observable in the TEM image due to this reason. This is different from silica nanoparticles bearing nonsticky polymer brushes of high glass-transition temperatures, wherein individual silica nanoparticles having a clear polymer shell can be easily identified under TEM without aggregation.[4c,g,5a,8c] Similar TEM images were also found with the other PE-functionalized silica particles, PE-silica-3h and PE-silica-5h. The TEM analyses further confirms the presence of the covalently tethered PE brushes on the functionalized silica particles.

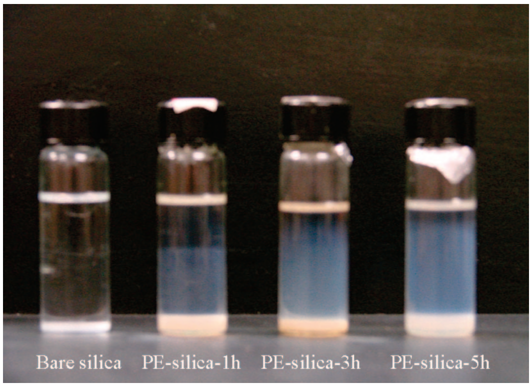


Figure 9. Dispersions of bare silica, PE-silica-1h, PE-silica-3h, and PE-silica-5h particles in toluene after standing for 4 days following sonication for 5 min.

Owing to the presence of the surface-tethered polymer brushes, the three polymer-grafted silica particles show enhanced solubility in solvents like THF and toluene, which are good solvents for the branched PE brushes. Figure 9 compares the dispersions of the bare silica particles and the three polymer-grafted silica particles in toluene after standing for 4 days following sonication for 5 min. The bare silica particles precipitated completely after standing for about half an hour. Differently, the precipitation rate of the polymer-grafted silica particles was significantly reduced. Stable dispersion could still be seen with the three polymer-grafted silica particles after 4 days of standing though slow precipitation was present. Moreover, as from Figure 9, the rate of precipitation decreases in the order from PE-silica-1h to PE-silica-5h due to the increasing length of the tethered branched PE brushes.

Conclusions

We have demonstrated in this work a new versatile surface-initiated ethylene "living" polymerization technique for the covalent surface grafting of branched polyethylene brushes on silica particles. In this technique, the acetonitrile Pd−diimine complex **1** is immobilized onto acryloyl-functionalized silica particles by reacting with the surface-tethered acryloyl groups, leading to catalyst-functionalized silica particles containing covalently surface-immobilized Pd−diimine chelate complexes. Surface-initiated polymerization occurs successfully with the catalyst-functionalized silica particles at 5 °C and an ethylene pressure of 400 psi, giving rise to the surface-initiated growth of branched polyethylene brushes. On the basis of the TGA study on polymer mass contents and GPC characterization of the cleaved polymer brushes, the polymerization was found to be "living" with linear increases of both the $M_{n,GPC}$ and relative mass content of PE brushes with the polymerization time. We found the $M_{n,GPC}$ and PDI data of the cleaved PE brushes were very close to those of untethered free polymers synthesized by well-established ethylene "living" polymerization with homogeneous complex **2** at the same conditions. ^{1}H NMR end-group analysis of the cleaved PE chains and TEM characterization of the PE-functionalized silica particles further confirmed the covalent tethering of the polymer brushes on the silica particle surface.

Experimental Section

Materials. All manipulations of air- and/or moisture-sensitive compounds were performed in a N_2-filled glovebox or using Schlenk techniques. 3-Acryloxypropyltrichlorosilane was obtained from Gelest Inc. and was used as received. Bare silica particles, which were aggregates of nanoparticles (nanoparticle size of about 10 nm as from supplier), were purchased from Aldrich, and they were reported to have an average surface area of 160 m^2/g. The received silica particles were washed with a large amount of methanol and then dried in vacuo at 40 °C overnight before use. The Pd−diimine complexes, $[(ArN{=}C(Me){-}(Me)C{=}NAr)Pd(CH_3)(N{\equiv}CMe)]^+SbF_6^-$ (**1**) and $[(ArN{=}C(Me){-}(Me)C{=}NAr)Pd(CH_2)_3C(O)OMe)]^+SbF_6^-$(**2**) (Ar = 2,6-($i$Pr)$_2$ C_6H_3), were synthesized according to the literature procedure.[12] Ultrahigh-purity N_2 and polymer-grade ethylene (both obtained from Praxair) were purified by passing through 3 Å/5 Å molecular sieve and Oxiclear columns to remove moisture and oxygen, respectively, before use. Chlorobenzene (99%, Aldrich) was refluxed over CaH_2 (powder, 90−95%, Aldrich) for 2 days and distilled before use. Other chemicals, including anhydrous dichloromethane (99.8%), tetrahydrofuran (THF) (>99%), triethylsilane (97%), toluene (ACS reagent, ≥99.5%), methanol (ACS reagent, ≥99.8%), HCl acid (reagent grade, 37%), HF acid (ACS reagent, 48%), HNO_3 acid (ACS reagent, 70%), and H_2O_2 solution (50 wt %), were obtained from Aldrich and were all used as received.

General Procedure for Preparation of Acryloyl-Functionalized Silica Particles. Bare silica particles (4.0 g), which were dried at 210 °C for 2 h in vacuo, were dispersed under ultrasonication in anhydrous CH_2Cl_2 (40 mL) in a Schlenk flask under a N_2 atmosphere. 3-Acryloxypropyltrichlorosilane (8.0 g, 32.3 mmol) and triethylamine (5.0 mL, 35.8 mmol) were subsequently added. The suspension was stirred at room temperature under a N_2 atmosphere for 96 h. Methanol (5 mL) was then added dropwise under stirring to react with the excess 3-acryloxypropyltrichlorosilane. The reaction mixture was centrifuged. The recovered particulates were washed with methanol and acetone (three times for each with 20 mL for each wash) followed with centrifugation. The product (3.4 g) was obtained after drying overnight in vacuo at room temperature.

General Procedure for Preparation of Catalyst-Functionalized Silica Particles. The acryloyl-functionalized silica particles (1.0 g), the acetonitrile Pd−diimine complex (**1**, 0.56 g, 0.69 mmol), and dichloromethane (40 mL) were added into a Schlenk flask under N_2 protection. The suspension was stirred at room temperature under a N_2 atmosphere for 72 h. The reaction mixture was centrifuged, and the solid product was subsequently washed with anhydrous CH_2Cl_2 (20 mL) under stirring followed with centrifugation. The washing and centrifugation procedure was repeated for at least five cycles until the supernatant liquid after centrifugation turned to colorless. The catalyst-functionalized silica particles (0.8 g) were obtained after drying overnight in vacuo at room temperature.

To determine the amount of the Pd−diimine complex immobilized on the silica particles, 30 mg of catalyst-functionalized silica particles was dispersed in HNO_3 (68 wt %, 10 mL) and HF (35 wt %, 10 mL) in a Teflon beaker and stirred overnight. The solution was then heated on a hot plate for 20 min (*caution*: this procedure should be done in a fume hood as HF acid is highly corrosive). The residue solution was cooled and then diluted to 100 mL using distilled water. Inductively coupled plasma mass spectrometry (ICP-MS) characterization showed that the solution had a Pd concentration of 1.536 mg/L, which corresponded to a Pd loading amount of 0.048 mmol per 1 g of catalyst-functionalized silica.

General Procedure for Ethylene "Living" Polymerization with Catalyst-Functionalized Silica Particles at 5 °C and 400 psi. Ethylene "living" polymerizations with the silica-supported Pd−diimine catalyst were carried out at 5 °C and under an ethylene pressure of 400 psi in a 500 mL Autoclave Engineers Zipperclave reactor equipped with a MagneDrive agitator and a removable heating/cooling jacket. The reactor temperature was maintained by passing a water/ethylene glycol mixture through the jacket using a refrigerating/heating circulator set at the desired temperature. The reactor was cleaned carefully using toluene and then acetone, heated overnight at 80 °C under vacuum, and cooled down under positive N_2 pressure. In a typical run, anhydrous chlorobenzene (90 mL) was injected into the autoclave under N_2 protection, and the reactor was then cooled down to 5 °C under agitation. After establishing thermal equilibrium at 5 °C, the catalyst-functionalized silica particles (0.3 g) suspended in 10 mL of dichloromethane was injected into the reactor under N_2 protection. The polymerization was then started by quickly pressurizing the reactor to an ethylene pressure of 400 psi. During the polymerization, ethylene pressure was maintained at 400 psi by continuously feeding ethylene into the reactor, and the reactor temperature was controlled at 5 °C by using the circulator. After the prescribed polymerization time (1, 3, and 5 h), ethylene pressure was released.

The polymerization solution was then transferred out from the reactor to a glass beaker and was quenched by adding Et_3SiH (0.5 mL) under stirring. The solution was kept stirred for about 1 h and was then precipitated in a large amount of methanol to obtain the polyethylene-grafted silica particles. The products were then dried with a stream of air. In order to remove black Pd powder residues resulting from the deactivated Pd−diimine catalysts, the dried products were redispersed in THF (ca. 50 mL), and HCl acid (37%, 10 mL) and H_2O_2 solution (50 wt %, 2 mL) were subsequently added under stirring. After stirring for 1 h, the solution was precipitated in a large amount of methanol, and the precipitated particles were washed with excess methanol. To remove the small amount of untethered free polymer, the products, after drying using an air stream, were further dispersed in THF (20 mL) followed by centrifugation. The supernatant was decanted, and this wash−centrifugation cycle was repeated two more times. The precipitated products were subsequently washed with excess methanol. The clean polyethylene-grafted silica particles (ca. 0.4−0.6 g) were obtained after drying overnight in vacuo at 60 °C.

General Procedure for Cleaving Grafted Polyethylenes from Silica Particles. A slightly modified literature procedure was used in this work to cleave the grafted polymers from the silica particles.[5a,b] In a typical experiment, PE-functionalized silica particles (∼100 mg) were dispersed in THF (2 mL) in a 5 mL plastic vial. HF acid (1 mL, 48% in aq) was subsequently added. The solution was shaken rigorously and was then allowed to stand still at room temperature for 3 days. The cleaved polymer was obtained by precipitating the solution in methanol. The precipitate was redissolved in THF again followed by precipitation in methanol again for purification purpose. Finally, the cleaved polymer (about 10 mg) was washed with methanol and then dried overnight in vacuo at 50 °C.

General Procedure for Ethylene "Living" Polymerization with Complex 2 at 5 °C and 400 psi. A polymerization procedure similar to the above ethylene "living" polymerization with catalyst-functionalized silica particles was used. In a typical run, anhydrous chlorobenzene (250 mL) was injected into the autoclave under N_2 protection. The reactor was then cooled down to 5 °C under agitation. A dichloromethane solution of complex **2** (10 mL, containing 0.2 mmol of **2**) was subsequently injected into the reactor under N_2 protection. The reactor was then quickly pressurized to an ethylene pressure of 400 psi to start the polymerization. During the polymerization, ethylene pressure was maintained at 400 psi, and the reactor temperature was controlled at 5 °C by using the circulator. After the prescribed polymerization time (1, 3, and 5 h), ethylene pressure was released, and the polymer solution was collected from the reactor. The polymer solution was quenched by adding Et_3SiH (ca. 0.5 mL) and was continuously stirred for about 1 h. The polymers were then obtained by precipitation in a large amount of methanol. The polymer sample was then redissolved in THF, filtered using a 0.2 μm syringe filter to remove Pd particles, and then precipitated in methanol. Finally, the polymer sample was dried overnight in vacuo at 50 °C.

Characterizations and Measurements. ^1H nuclear magnetic resonance (NMR) spectra were obtained on a Varian Gemini 2000 200 MHz spectrometer at ambient temperature. $CDCl_3$ was used as the solvent. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q50 thermogravimetric analyzer. Measurements were carried out under N_2 atmosphere with a continuous N_2 flow of 60 mL/min. A N_2 flow at 40 mL/min was used as the balance purging gas. In a typical run, the sample (∼10 mg) was heated from 100 to 700 °C at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) analysis was performed on a TA Instruments Q100 DSC equipped with a refrigerated cooling system (RCS) under a N_2 atmosphere. The instrument was operated in the standard DSC mode and was calibrated with an indium standard. A N_2 purging flow of 50 mL/min was used. Samples (~10 mg) were heated from room temperature up to 90 °C at 10 °C/min and cooled to −90 °C at 10 °C/min, and the data were then collected on the second heating ramp from −90 to 90 °C at 10 °C/min. Gel permeation chromatography (GPC) measurements were performed on a Waters Alliance 2965 separation module equipped with a Waters 2410 differential refractive index detector, one Polymer Laboratory guard column (PL 1110-1120), and three Polymer Laboratory 30 cm mixed columns (PLgel 10 μm MIXED-B 300 × 7.5 mm, linear range of molecular weight: 500−10 000 000 g/mol). The system operated at 30 °C, and THF was used as the eluent at a flow rate of 1.0 mL/min. Polystyrene standards (PL EasiVials) covering molecular weights from 580 to 6 035 000 g/mol were used for the column calibration. ICP-MS measurement was performed on a Varian instrument. FTIR was obtained on a Spectrum GX spectrometer (Perkin-Elmer). All samples were prepared as pellets using spectroscopic grade KBr in a press at 10 000 psi. TEM analysis was performed using a Philips CM12 operating at 120 keV. The particles were dispersed in THF in an ultrasonic bath for 5 min, and then a drop of the dispersed solution was deposited on a copper grid covered with a perforated carbon film followed with the evaporation of THF.

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