

Dendrimer-Mediated Immobilization of Catalytic Nanoparticles on Flat, Solid Supports

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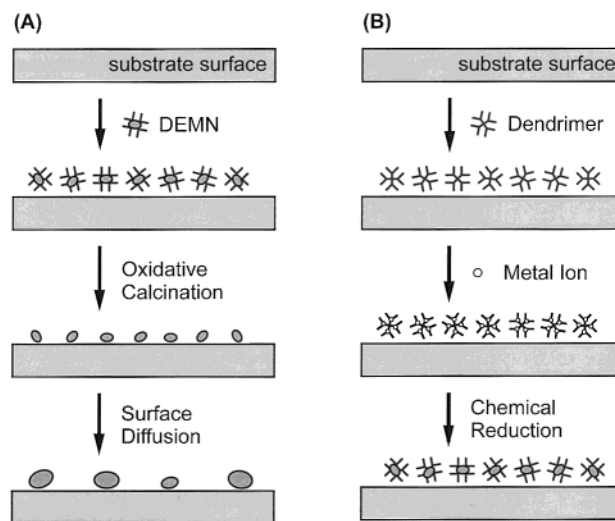
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Sixth-generation poly(amidoamine) (PAMAM) dendrimers have been used to explore methods for immobilizing Pd nanoparticles on atomically flat surfaces. Two methods are investigated. In the first method, dendrimer-encapsulated metal nanoparticles (DEMNs) are prepared using a PAMAM dendrimer with hydroxyl terminal groups. These particles are then deposited on a mica surface. Tapping-mode AFM images reveal a monodispersed size distribution of DEMNs that has an average composition of 40 Pd atoms per dendrimer. When thermal combustion in an O₂ stream is used to remove the dendrimer host at 630 °C, Pd particles aggregate via surface diffusion, resulting in an increase in particle diameter. In the second method, the step edges of a HOPG surface are first oxidized in an oxygen atmosphere. A PAMAM dendrimer with amine terminal groups is then allowed to adsorb selectively on the step edges, followed by immobilization of Pd particles via surface chemical reactions. The Pd particles prepared by this method are shown to be catalytically active for electroless copper deposition.

Introduction

Immobilization of nanoparticles on solid supports is an important step in fabrication of practical heterogeneous catalysts. Many methods have been devised to construct model catalytic nanoparticles supported on solid surfaces, including thermal evaporation,¹ laser ablation,² spin-coating,³ electron-beam lithography,^{4,5} molecular precursor adsorption,⁶ and electrochemical deposition.^{7,8} These approaches for fabricating nanomaterials and studying their catalytic properties seem to signal a shift of emphasis away from traditional studies of single-crystal model systems.⁹ The need for this shift can be appreciated from two different perspectives. First, researchers have already learned a great deal about the catalytic behavior of single-crystal surfaces, and now they are ready to apply this repertoire of knowledge to more complicated nanoparticle systems. Second, supported nanoparticles obviously resemble more closely the catalysts used in real-world applications, and they often show catalytic properties that are normally not observed on single-crystal surfaces. One such a property is size-dependent catalysis,^{2,10,11} which requires fabrication of supported nanoparticles of uniform size.

Scheme 1



In this study, we have explored two methods for dendrimer-mediated immobilization of nanoparticles on a flat solid support (Scheme 1). These methods are conceptually different from most methods reported previously in which the dendrimers act primarily as adhesion promoters.^{12,13} In method A, dendrimer-encapsulated metal nanoparticles (DEMNs) are prepared in solution, as we have previously reported,^{14–17} and then these composite particles are chemisorbed onto the substrate surface. Removal of the protective dendrimer sometimes is desirable, but if the substrate surface does not interact

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strongly with the nanoparticles, they will aggregate via surface diffusion, as shown in Scheme 1. In method B, dendrimers are first chemisorbed onto the substrate, and then the DEMNs are prepared directly on the surface. The potential advantages of our methods are (a) the metal particles are inherently small and monodispersed because the size of the particles is controlled by the number of metal precursor ions coordinated to one dendrimer molecule and (b) the location of immobilization may be controlled through specific chemical interactions between dendrimers and functional groups on the solid support.

Experimental Section

Chemicals. All solutions were prepared either with water (18 M Ω ·cm Milli-Q, Millipore) or with pure ethanol (Aaper Alcohol, Shelbyville, KY) as solvents. Sixth-generation poly-(amidoamine) (PAMAM) dendrimers (Dendritech, Midland, MI) with -OH or -NH₂ terminal groups (G6-OH or G6-NH₂) were dried under vacuum to remove the methanol solvent prior to use. The following chemicals were used as received: K₂Pd(II)-Cl₄, BH₃·NHMe₂, KNaC₄H₄O₆(tartrate)·4H₂O (Strem Chemical, Newburyport, MA), Bu₄NBF₄ (SACHEM, Austin, TX), HCHO (37% formaldehyde), CuSO₄·5H₂O, NaBH₄, and NaOH (EM Science).

Preparation of Dendrimer-Encapsulated Pd Nanoparticles.^{14–17} To an aqueous solution of G6-OH (4 mL, 0.125 mM) was added K₂PdCl₄ (2 mL, 10 mM). After 20 min, NaBH₄ (0.4 mL, 1.0 M) was added with vigorous stirring. Dialysis (250–7U cellulose tubing of 12 kD MW cutoff, Sigma) of the dark reaction product against water (4 × 4000 mL) over a period of 2 days yielded a stock solution (about 7 mL, 70 μ M) of DEMNs (G6-OH(Pd₄₀)) containing an average of 40 Pd atoms per dendrimer. Here, we have assumed that the average DEMN stoichiometry is equal to the ratio of the precursor Pd salt and G6-OH dendrimer. A more detailed summary on the synthesis and characterization of DEMNs has been reported previously.¹⁷ A control was prepared similarly but with pure water substituting for the K₂PdCl₄ solution.

Sample Preparation and Imaging. Mica (green muscovite, Asheville-Schoonmaker, Newport News, VA) and HOPG (ZYA or ZYB grade, Advanced Ceramics, Lakewood, OH) were cut into ~1 cm × 0.5 cm pieces and cleaved before each new experiment by peeling with Scotch tape (3M Company, St. Paul, MN). To minimize contamination, all-glass sample holders were used for various operations such as soaking, drying under a stream of filtered (U-02917-00 filter, Cole-Parmer) N₂, or calcination (model 55035, Lindberg furnace) in a stream of O₂. AFM images were obtained using a NanoScope III microscope (Digital Instruments, Santa Barbara, CA) equipped with a tapping tip (260–400 kHz, NanoSensors, Germany) operating at a free oscillating amplitude of about 4.0 V.

Attachment of Dendrimers on HOPG via Electrochemical Oxidation.¹⁸ Freshly cleaved HOPG was anodized with one linear potential sweep from 0 to 1.4 V (vs a freshly anodized Ag/AgCl wire) in an ethanolic electrolyte solution containing 8 μ M G6-NH₂ and 0.1 M Bu₄NBF₄. The sample was rinsed with ethanol, dried, and immediately imaged.

Electroless Deposition of Cu on HOPG Step Edges. A freshly cleaved HOPG sample was thermally oxidized in a stream of O₂ for 15 min at 630 °C. The substrate was then soaked sequentially in 4 nM G6-NH₂ (ethanol as solvent) for 11 min, 0.1 mM K₂PdCl₄ (aqueous, freshly prepared) for 1 min, and finally 1 mM Me₂NH-BH₃ (ethanol as solvent) for 10 min.^{19,20} Immediately after each soaking step, the sample was rinsed with solute-free solvent and dried under a stream of N₂. The Cu electroless deposition solution was prepared by mixing 10 mL of solution A with 0.1 mL of solution B.²¹ Solution A contained 10 mM CuSO₄, 0.1 M tartrate, and 0.1 M NaOH. Solution B was a 37% (w/w %) or 12 M HCHO aqueous solution. The time required

to deposit a fixed amount of Cu (Cu line height around 20 nm, as measured by AFM) was not very reproducible but typically ranged from 10 to 30 min.²⁰

Results and Discussion

G6-OH(Pd₄₀) on Mica Surfaces. Clean mica surfaces are useful for AFM studies because large, single-crystal terraces of over 1 μ m can be easily observed (Figure 1A). Both G6-OH and G6-OH(Pd₄₀) (Figure 1B) readily adsorb onto mica from an aqueous solution. Soaking is the most convenient method for inducing adsorption, but spin-coating also yields good results, especially at low surface coverages.²² Adhesion of individual dendrimers to the mica surface is sufficiently strong that they are not pushed around by the imaging tip. There are two likely sources of strong interaction energies between the dendrimers and the mica surface. First, electrostatic attraction between positively charged dendrimers (at neutral pH) and the negatively charged mica surface is expected.^{23,24} Second, surface functional groups on the dendrimer may also interact with the mica surface through hydrogen bonding. This type of interaction may be quite strong because many hydrogen bonds can form per dendrimer molecule.²⁵ Strong dendrimer–mica interactions cause a spherically symmetric dendrimer to adopt an oblate shape on the surface.²⁶ This has two consequences. First, the full width at baseline, as measured from AFM images (25 nm), is considerably larger than the diameter of a G6-OH dendrimer in solution (~6.7 nm).²⁷ Of course, convolution of true surface topology with a finite-radius tip will also lead to a larger than expected width.²⁸ Second, consistent with a flattened shape, the measured height (0.6 nm) is much smaller than the dendrimer diameter in solution and is in agreement with a previous report for G6-NH₂ on mica.²² Compared with G6-OH, G6-OH(Pd₄₀) has a slightly larger height (0.9 nm) when adsorbed onto mica using a similar set of adsorption conditions. This result implies that incorporation of Pd clusters within dendrimers renders them either more rigid or more expanded, and thus the geometry of a surface-adsorbed dendrimer is somewhat more spherical when it contains a metal nanoparticle. It should be pointed out that height measurements obtained by tapping-mode AFM are subject to the influence of many ill-defined mechanical as well as environmental parameters (such as humidity);^{29–33} thus, the absolute height values described here are not entirely accurate. However, the relative height difference between

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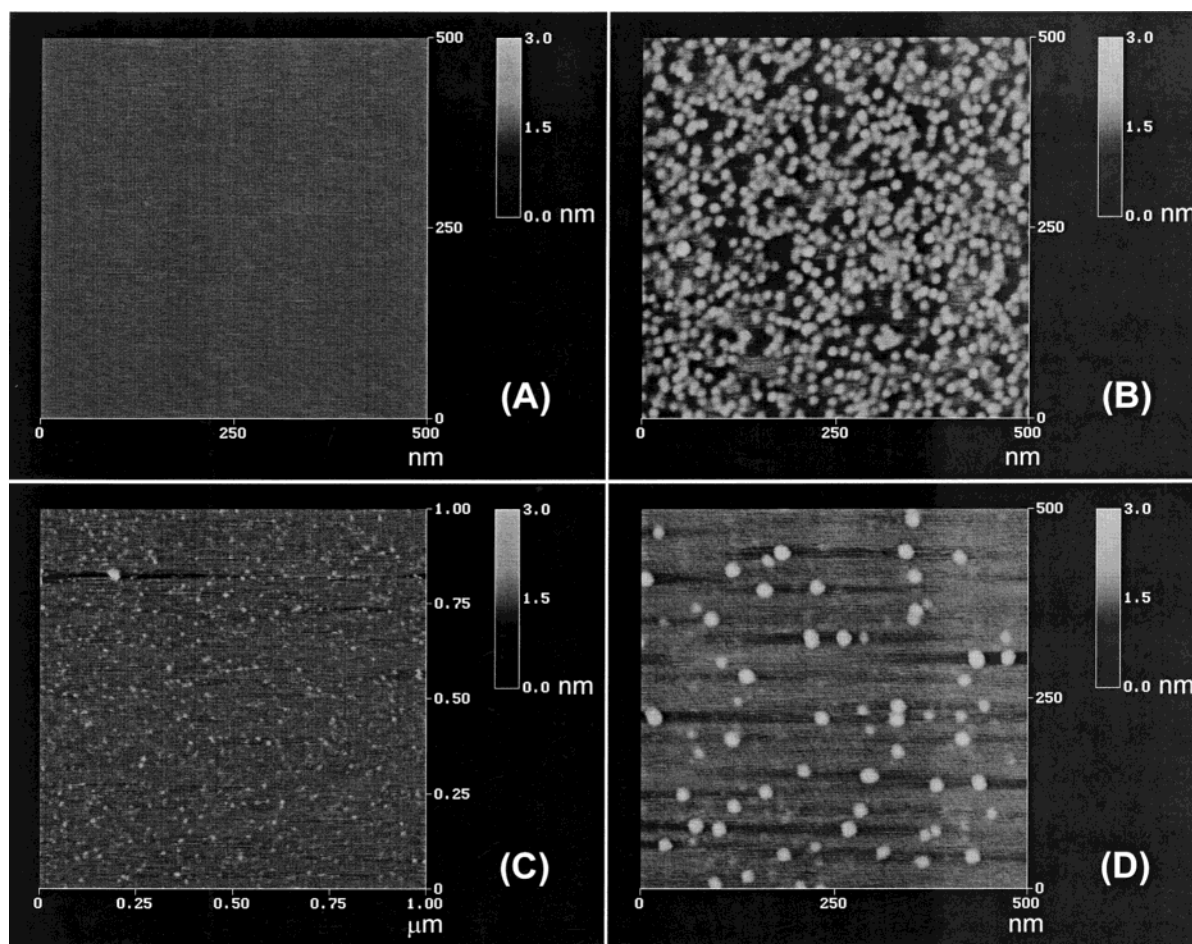


Figure 1. AFM images of dendrimer-encapsulated Pd nanoparticles on mica substrates: (A) a freshly cleaved mica surface; (B) the surface formed after soaking the substrate shown in part A in an aqueous 700 nM G6-OH(Pd₄₀) solution for 2 min; (C) a mica control substrate modified by soaking in aqueous 700 nM G6-OH for 2 min and then heating for 10 min at 630 °C in flowing O₂; (D) the substrate in part B after heating for 10 min at 630 °C in flowing O₂.

G6-OH and G6-OH(Pd₄₀) may be real, since tip–dendrimer interactions are expected to remain relatively constant during imaging.

We hypothesized that the catalytic activity of immobilized DEMNs would be enhanced if the dendrimer host could be selectively removed without causing any structural change in the guest Pd cluster. Catalytic enhancement would result from a higher mass transport rate because reactants would not have to penetrate the protective dendrimer matrix. Additionally, we suspect that some fraction of a DEMN surface is passivated by the dendrimer, and thus removal of the dendrimer should increase the active surface area somewhat. We expected that PAMAM dendrimers could be selectively removed via combustion in an oxygen rich environment.³⁴ The surface shown in Figure 1C was prepared from a dendrimer solution identical to that shown in Figure 1B except the K₂PdCl₄ salt was omitted. The topograph shows that oxidative calcination removes most of the organic material from the surface, although some solid residue (average height: ~0.5 nm) remains even after heating at 630 °C in flowing O₂ for 10 min. We do not fully understand this observation but speculate that the residue might be an inorganic chemical, such as NaBH₄, which is used during the preparation of this control sample and not completely removed by dialysis. Under identical calcination conditions, G6-OH(Pd₄₀) particles grow in size (Figure 1D): their

average height (2.4 nm) is almost 3 times larger than that measured before calcination. The particle spacing is also increased significantly (compare with Figure 1B), suggesting that Pd clusters interact only weakly with mica and that when heated they agglomerate with each other via surface diffusion.

G4-NH₂ and Composites with Pd on HOPG Surfaces. The previous section described an example of how method A (Scheme 1) could be used to immobilize metal catalysts on surfaces. In this section we will demonstrate that method B (Scheme 1) is equally effective. We selected highly oriented pyrolytic graphite (HOPG) for this example, because its crystal step edges have chemical properties distinctively different from those of its terrace planes.³⁵ In addition, our purpose in carrying out these types of experiments is partly motivated by the importance of carbon-supported electrocatalysts in the development of fuel cells.^{36,37} In general, it is highly desirable to load a carbon support with very small, uniformly distributed catalytic particles so that the total cost of the catalyst is reduced but the performance stays constant.

Freshly cleaved HOPG surfaces exhibit straight step edges (Figure 2A), which are relatively nonspecific toward

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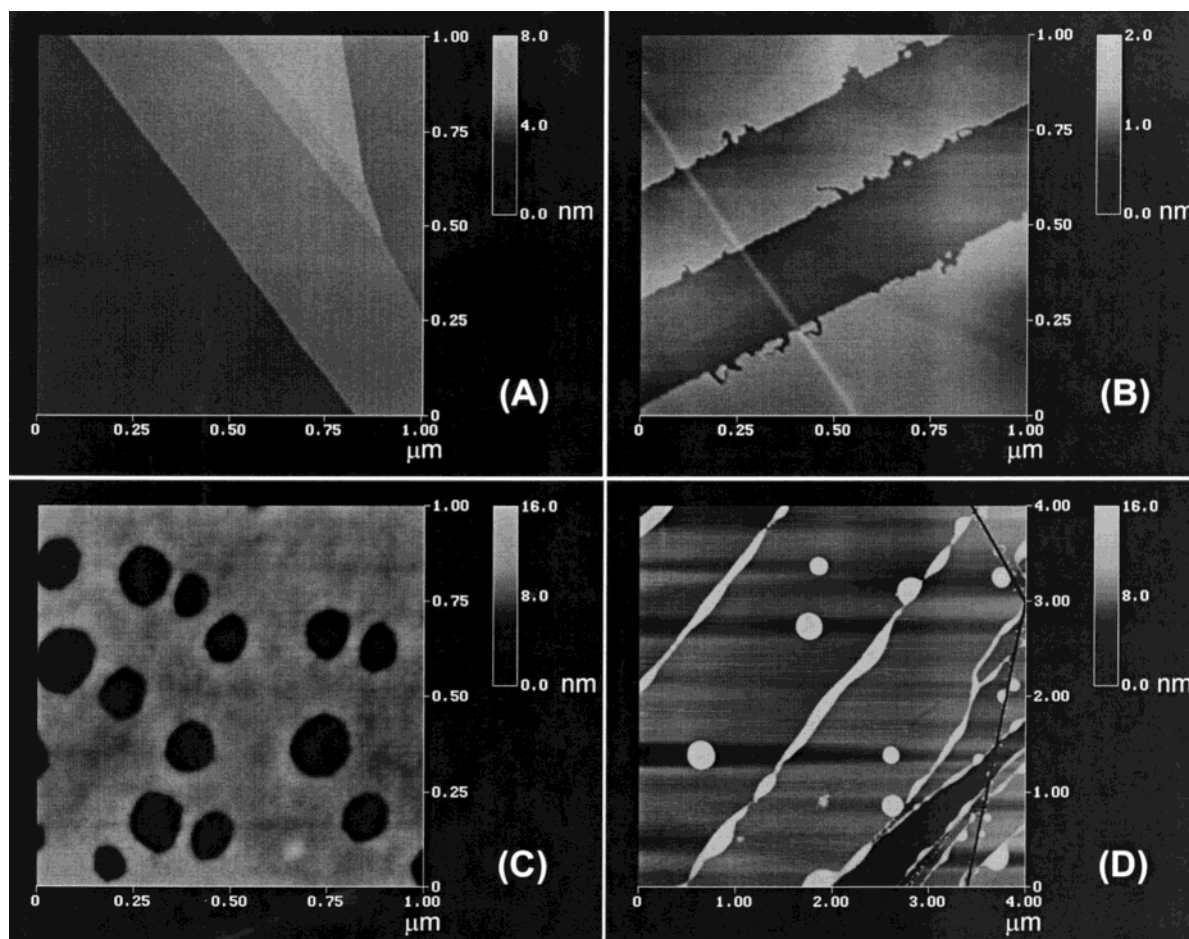


Figure 2. AFM images of modified HOPG surfaces: (A) freshly cleaved HOPG; (B) HOPG thermally oxidized at 630 °C in a flowing stream of O₂ for 15 min; (C) HOPG after electrochemical oxidation in the presence of G6-NH₂ dendrimer (see text for experimental details); (D) HOPG thermally oxidized as in part B and then soaked in a 4 μM aqueous G6-NH₂ solution for 7 min.

G6-NH₂ adsorption. To enhance adsorption specificity, we tried to activate step edges using two methods. Heating in concentrated, boiling nitric acid,³⁸ or heating in flowing O₂ at high temperature (630 °C for 15 min, Figure 2B),^{39,40} causes the step edges to roughen. This is an indication that the edges are oxidized and presumably decorated with COOH groups.³⁵ Unfortunately, attempts to obtain convincing evidence for covalent linking of COOH groups present on the activated edges to G6-NH₂ (no Pd metal) by converting the edges to acid chlorides were not successful because after surface reactions the entire HOPG surface was covered with ill-defined, large aggregates. Covalent attachment of G6-NH₂ onto HOPG step edges via anodic oxidation¹⁸ also leads to negative results. This electrochemical treatment in the presence of G6-NH₂ results in perforation of the original well-defined atomically flat terraces with pits as deep as 6 nm (Figure 2C). From the AFM image alone, it is not possible to discern the presence of surface-confined dendrimers.

Interestingly, G6-NH₂ can be easily immobilized onto thermally oxidized HOPG step edges by simply soaking the substrate in an ethanolic or aqueous solution of dendrimer (Figure 2D). We believe that multidentate acid–base interactions are responsible for this strong dendrimer adhesion.⁴¹ Sonication in water or ethanol for at least 1 min and even a 10 min treatment with 0.1 M

HCl did not dislodge these surface-confined dendrimers. Adsorption from a high-concentration (micromolar in dendrimer) aqueous solution results in severe dendrimer aggregation although aggregates seem to prefer step edges (Figure 2D). These aggregates have an average height of about 20 nm and width of about 200 nm.

Aggregation can be avoided by adsorbing the dendrimers from ethanolic solutions containing <10 nM G6-NH₂. Under these conditions, much smaller and reproducible features are observed by AFM (Figure 3A), which, on the basis of their nearly monodispersed size, are almost surely individual dendrimers. However, their height and full width at baseline (2.8 and 42 nm, respectively) are much larger than those of the G6-OH dendrimers observed on the mica surface (0.6 and 25 nm, respectively). One explanation for this difference is that G6-NH₂ interacts only very weakly with the HOPG terrace surface. The weak attachment makes AFM imaging difficult: images can be obtained only with the weakest tapping force. Even under such conditions, some dendrimer molecules on the terraces can still be moved by the imaging tip (note the streak in Figure 3A indicated by the arrow). With normal tapping force (set point less than 0.5 V below the resonance tuning curve), dendrimer molecules on the terrace are swept away and thus are not observed in AFM images (Figure 3B). Weak dendrimer–HOPG interactions may also be understood in terms of a low interfacial energy or

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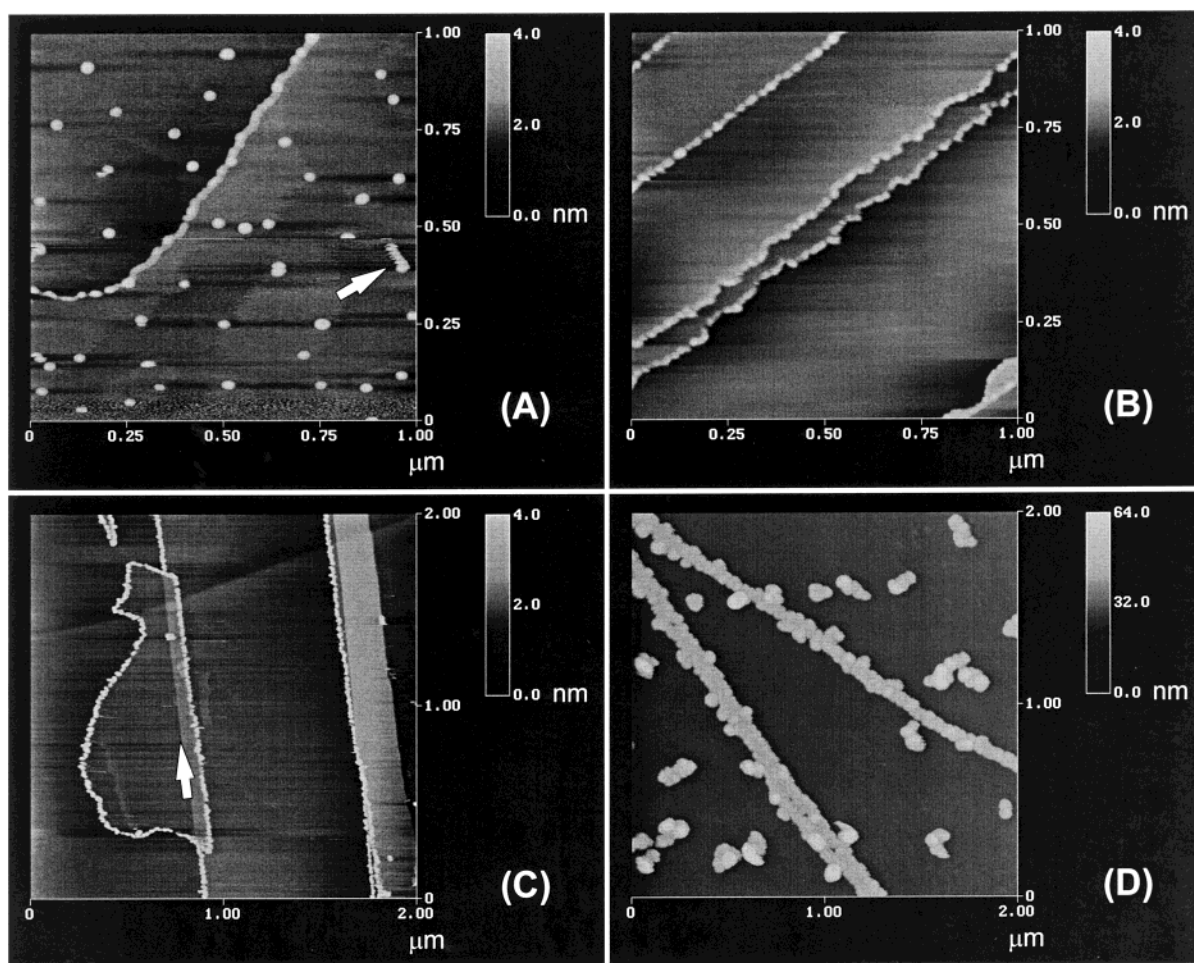


Figure 3. AFM images of HOPG substrates after being thermally oxidized at 630 °C in a flowing stream of O₂ for 15 min: (A) substrate after soaking in a 4 nM ethanol solution of G6-NH₂ for 11 min (weak tapping force); (B) same substrate as that in part A but with normal tapping force; (C) substrate after immersing the substrate shown in part A in a 0.1 mM aqueous solution of K₂PdCl₄ for 1 min and then reducing with a 1 mM ethanolic solution of BH₃·NHMe₂ for 10 min; (D) substrate in part C after electroless deposition of about 20 nm (height) of Cu.

surface tension, and it is reasonable to expect that dendrimers will assume a more spherical shape on a low-energy surface than they do on a high-energy surface such as hydrophilic mica or Au surfaces.⁴² However, the G6-NH₂ height on HOPG (2.8 nm) is still less than the diameter of a freely moving G6-NH₂ dendrimer suspended in a solution (6.7 nm). We want to emphasize again that height measurements made with a tapping tip are not completely reliable. For example, the tip will interact with a dendrimer molecule differently than it will with an HOPG surface, which leads to an error in the height measurement. Furthermore, other factors such as the magnitude of the imaging force and the presence of a capillary force can also influence the apparent height values.^{29,30,32,43}

In contrast to the situation on terraces, dendrimers strongly adsorb onto step edges, and they cannot be removed by the tip even using a very strong tapping force (set points exceeding 2 V below the resonance tuning curve). Additionally, adhesion remains strong even after loading the dendrimers with Pd precursor ions followed by chemical reduction (Figure 3C). It should be pointed out that the nodular features at the step edges are not an

imaging artifact. Sometimes an edge is covered by a graphite sheet so that it cannot be modified with acid groups during thermal oxidation. The arrow in Figure 3C points to such a buried edge, and it is apparent that dendrimers do not sorb at this location even though the height of the edge is correct for an HOPG crystal.

Pd nanoparticles immobilized at HOPG step edges according to method B are catalytically active. For example, these Pd particles can function as catalysts for electroless deposition of Cu (Figure 3D). It is clear that the copper lines (average height of 22 nm and average width of 120 nm) are reminiscent of the original step edges where Pd particles are selectively immobilized. In addition, results of cyclic voltammetric experiments show that immobilized Pd can also serve as an electrocatalyst (see Supporting Information).

Summary and Conclusions

In summary, we have shown that dendrimers can serve as a convenient mediator for immobilizing small catalytic particles onto flat model surfaces (mica and HOPG). Immobilization can be achieved either through adsorption of dendrimer-encapsulated particles or through surface synthesis reactions after adsorption of empty dendrimer hosts. At present, we are unable to remove the dendrimer mediator without causing significant structural changes such as surface aggregation. One promising approach for

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solving this problem is the use of more active substrates, an avenue we are pursuing at the present time.

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Supporting Information Available: Text and figures relating to the following topics: XPS spectra and cyclic voltammograms of immobilized Pd particles supported on HOPG. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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