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Crystalline Nanoscale Platinum(0) Clusters in Glassy Carbon

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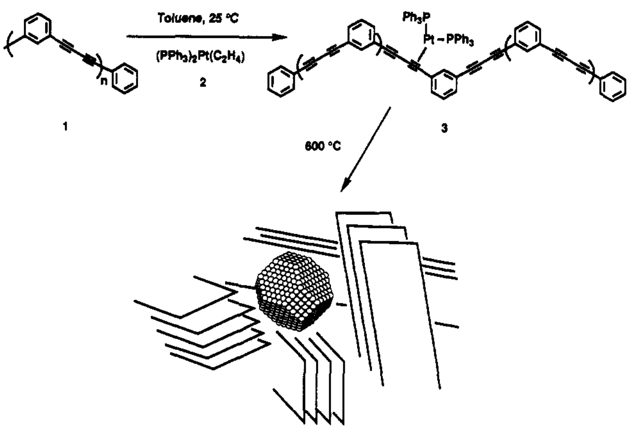
The preparation of highly dispersed metal clusters on various supports is desirable in order to maximize the use of the metal and to derive high activity from the catalyst.[1] While the choice of metal for a particular reaction is of obvious importance, the catalytic activity and chemical selectivity of a catalyst are strongly dependent on the size and shape of the metal particles, as well as on the support material utilized in the reaction.[2] In particular, effecting control of the size and dispersion of platinum particles is critically important for their use in fuel-cell applications.[3–9] In addition to the importance of preparing small clusters as related to catalysis, nanoscale metal particles exhibit properties which deviate from those of the bulk metal and represent structural intermediates between single atoms and crystalline solids.[6,10–14]

Scheme I



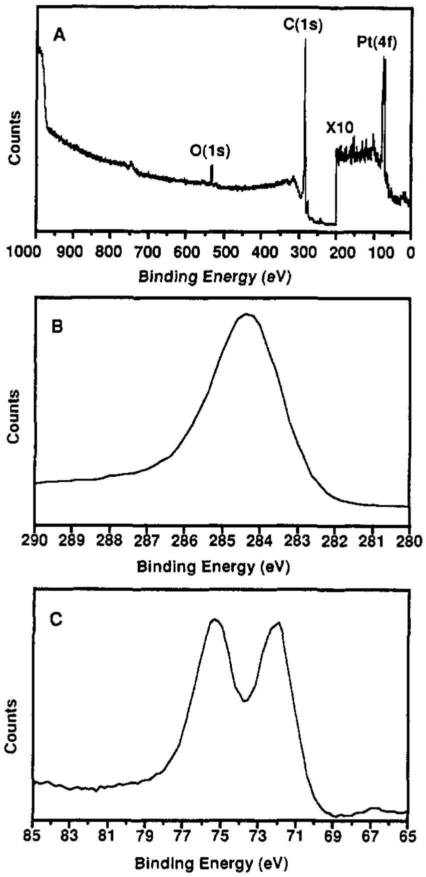


Figure 1. XPS spectra of Pt-DGC: (A) survey after an argon ion sputter treatment; (B) high-resolution spectrum of the C(1s) line; (C) high-resolution spectrum of the Pt(4f) line.

Previous methods of synthesizing small metal clusters include the deposition of metals onto the surfaces of various supports,[15–19] incorporation of metals in polymer films on electrodes,[20–27] or the generation of clusters in gels.[28] We have approached the preparation of nanoscale metal clusters with the goal of incorporating the metal clusters *in* a carbon support matrix rather than on the surface of a support with the expectation that the homogeneous incorporation of metal clusters will result in stable, high-

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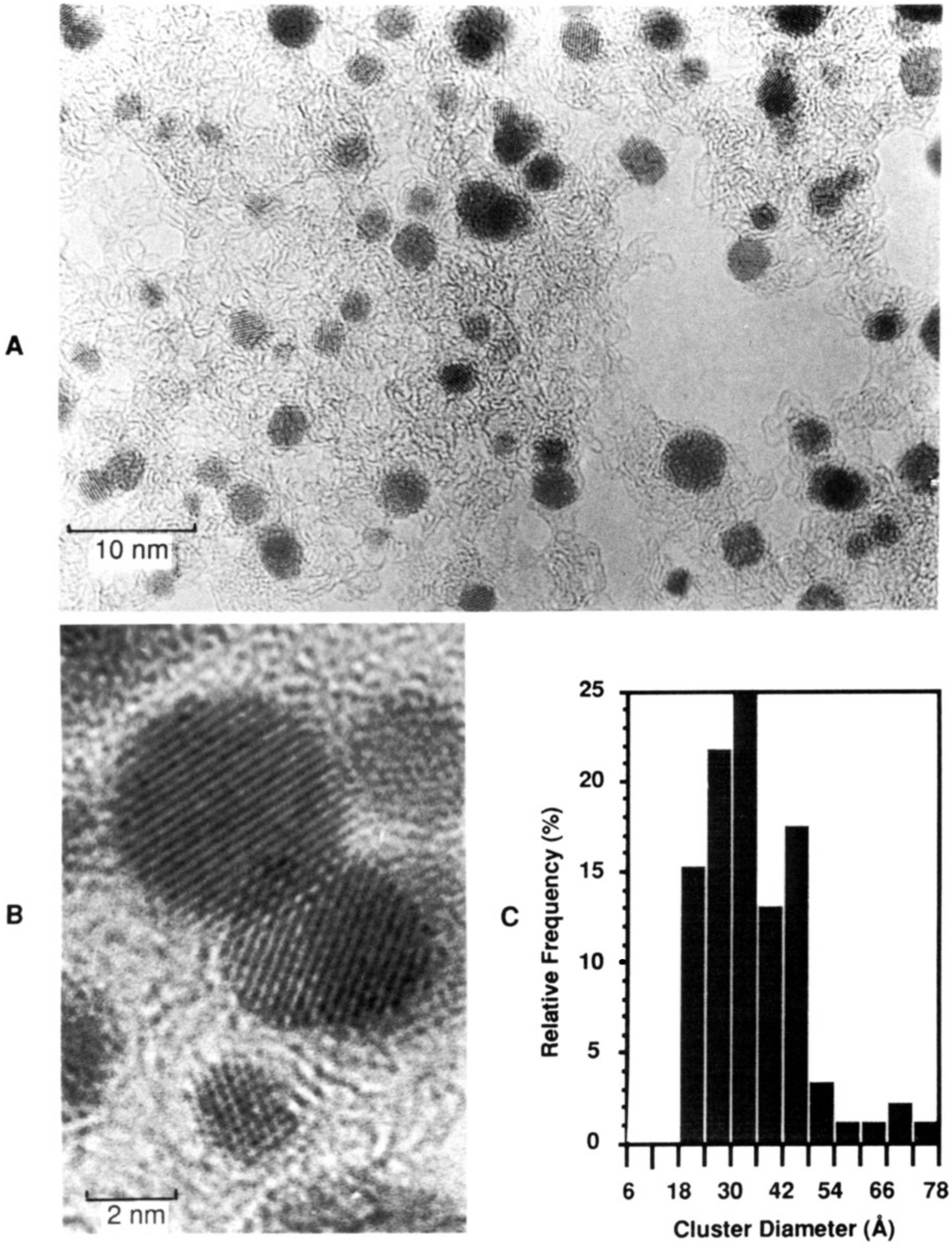

Figure 2. (A) TEM image of a representative area of Pt-DGC which was deposited on potassium bromide and then lifted onto a copper grid. The dark spots represent platinum clusters. (B) TEM image of single platinum particles revealing lattice fringes. (C) Cluster size distribution of platinum particles in Figure 2A. The average particle diameter is 32 Å.

activity catalysts. We have previously reported a low-temperature synthesis of glassy carbon and that the incorporation of platinum on the molecular level in a carbon precursor, followed by thermolysis, results in a conductive, dimensionally stable carbon matrix containing platinum clusters with high catalytic activity.[29-31] A valid concern is that these materials could retain a sufficient level of phosphorus from the platinum precursor, as well as other elements, and possibly result in the formation of heterogeneous clusters. We report here the surprising observation that these nanoclusters are, in fact,

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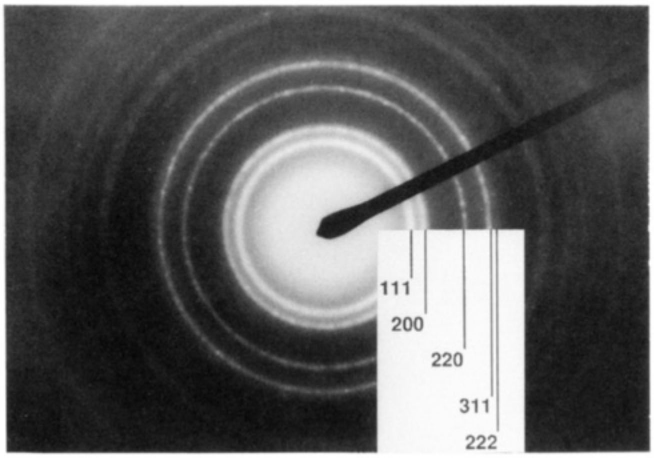

Figure 3. Electron diffraction pattern of Pt-DGC.

crystalline platinum(0).

Platinum was introduced to the carbon matrix at an atomic level by coordination of platinum to the carbon-carbon triple bond of poly(phenylene diacetylene). As illustrated in Scheme I, reaction of poly(phenylenediacetylene) (**1**) with ethylene bis(triphenylphosphine)platinum (**2**; 0.1 mol equiv of **2** relative to diacetylene functionality contained in **1**) in toluene at 25 °C under an argon atmosphere for 6 hours resulted in the consumption of **2** and the formation of a red-brown solution of **3**. As depicted in the generalized drawing of **3**, this reaction allows the atomic dispersion of platinum along the glassy carbon polymer precursor backbone. Note that the platinum in **3** is bound only to the alkyne functionality and to triphenylphosphine ligands. Addition of the reaction solution to an excess of petroleum ether resulted in the precipitation of **3** as a green-yellow solid in 69% yield.[32,33] This solid was air-stable and soluble in toluene and benzene. Prolonged reaction (3 days) under the same conditions resulted in the formation of an intractable solid, presumably resulting from displacement of triphenylphosphine ligands from platinum by alkynes on other polymer chains.

Conversion of **3** to platinum-doped glassy carbon (Pt-DGC) was accomplished by casting a thin film of **3**, dissolved in toluene, onto a potassium bromide disk followed by thermolysis at 600 °C (1 °C/min ramp rate, 6 h at final temperature) at 10^{-6} Torr, giving a black, highly reflective, conductive film of Pt-DGC (the idealized structure shown in Scheme I is explained below). Raman spectroscopic analysis confirmed the microcrystalline carbon structure of Pt-DGC and the presence of platinum in the solid was revealed by X-ray photoelectron spectroscopic (XPS) analysis.[34] Figure 1A is an XPS spectrum of Pt-DGC showing the expected C(1s) and Pt(4f) electrons and residual levels of oxygen and phosphorus. Clearly, the bulk of the triphenylphosphine ligands contained in **3** are lost in the formation of Pt-DGC since the original platinum complex contained 2 equiv of phosphorus for every platinum atom. High-resolution scans of the C(1s) (Figure 1B) and Pt(4f) (Figure 1C) regions indicate that the solid contains approximately 0.2 atom % platinum. The binding energy of the C(1s) electron was used as an internal reference (284.6 eV) for determination of the binding energies of the Pt(4f$_{7/2}$) and Pt(4f$_{5/2}$) electrons which gave values of 72.2 and 75.5 eV, respectively. These values are 1.2 eV higher than that reported in the literature for bulk platinum. However, this difference in binding energy is not attributed to the presence of oxidized platinum, but rather the result of the effect of small particles on binding energy[35-38] and/or the result of the intimate interaction between the conductive carbon substrate and the metal clusters.

A sample suitable for transmission electron microscopic (TEM) analysis was obtained by dissolving the supporting potassium bromide disk in water and then capturing the free-floating film of Pt-DGC on a copper TEM grid. Figure 2, parts A and B, shows bright-field images of Pt-DGC obtained near the optimum Scherzer defocus.[39] The dark dispersions in these micrographs correspond to platinum clusters whereas the lighter features arise from graphitic carbon which constitutes the glassy carbon support. The platinum clusters present in this Pt-DGC sample possess an average diameter of 32 Å and a relatively narrow size distribution, with no clusters observed with a diameter of less than 18 Å (Figure 2C). Close examination of Figure 2A reveals that many of the platinum clusters exhibit lattice fringes, indicative of crystalline order. These fringes are more easily discernible at higher magnification as shown in Figure 2B. The composition of the platinum clusters was confirmed by analysis of the Pt-DGC sample with selected-area electron diffractometry (Figure 3). Spacings were observed at 2.23, 1.88, 1.37, 1.17, and 1.12 Å, which are all within 2% of the values reported for the 111, 200, 220, 311, and 222 reflections, respectively, for metallic platinum.[40]

The idealized structure shown for Pt-DGC in Scheme I represents our finding that the carbon matrix is similar to glassy carbon which is illustrated by the small domains of graphitic ribbon. The scheme also shows one platinum cluster with a defect-free cubo-octahedral structure containing 1289 atoms. This cluster possesses a diameter of approximately 33 Å, which lies close to the average nanocluster size obtained by TEM analysis.[6,11,41] Undoubtedly, the platinum clusters contained in the Pt-DGC solid are not defect-free, a feature which may have a significant impact on catalysis mediated by these materials.

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