IIIa (SRU), 137091-72-6; IIIa (copolymer), 57468-87-8; IIIb (SRU), 57468-80-1; IIIb (copolymer), 57469-13-3; IIIc (SRU), 137091-73-7; IIIc (copolymer), 137059-51-9; IIId (SRU), 137091-74-8; IIId (copolymer), 137059-52-0; IIIe (SRU), 137091-75-9; IIIe (copolymer), 137059-53-1; IIIf (SRU), 137091-76-0; IIIf (copolymer), 137059-54-2; IIIg (SRU), 137091-77-1; IIIg, 137059-55-3; DBP, 1623-08-1; DDP, 298-06-6; $AlCl_3$, 7446-70-0; $GaCl_3$, 13450-90-3; NEt_3, 838-85-7.

Transformation of Platinum Carbonyl Clusters on Graphite under Laser Irradiation and Their Scanning Tunneling Microscopy Observation

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Scanning tunneling microscopy (STM) images were obtained from an isolated aggregate of Pt carbonyl clusters $[NEt_4]_2[Pt_{12}(CO)_{24}]$, which were adsorbed from the tetrahydrofuran solution onto the surface of a freshly cleaved HOPG (highly oriented pyrolytic graphite) under the nitrogen atmosphere. The in situ STM images demonstrated the morphological changes of the surface-bound Pt_{12} carbonyl clusters under the pulse laser irradiation (532 nm; 2–3 mJ), resulting in the effective decarbonylation and fragmentation which was implied by the diffuse reflectance FTIR, coupled with mass. The Pt_{12} carbonyl clusters were converted by the successive pulse laser activation into a highly dispersed Pt microcrystalline (18×50 Å^2), which was imaged by STM.

Introduction

Grafting of molecular metal clusters on solid-surfaces has been a subject of recent interest in molecular approaches for preparation of the tailor-made metal catalysts having uniform distribution of particle sizes and metal compositions.[1] The composition and morphology of the grafted clusters is profoundly controlled by the nature of supports, temperature, and atmosphere;[2] absorption or diffraction spectroscopies are employed as tools to characterize the local structure of the clusters. In the extensive effort to directly observe the surface-grafted clusters, Iijima and Ichikawa succeeded in imaging individual Rh_6 clusters derived from $Rh_6(CO)_{16}$ attached on top of (111) oxide layer of alumina by the high-resolution electron micrograph,[3] however, some of the clusters grew larger due to electron irradiation during the TEM observation.

Scanning tunneling microscopy (STM)[4,5] is a powerful tool for the observation of solid surfaces and polymers.[6] In particular, the great advantage of STM in the study of catalysis is its applicability to imaging the surfaces under in situ conditions, e.g., under the reactant gas atmosphere. In some cases, the structural changes of electrode surfaces in solutions under operating conditions have been studied with STM.[7]

The photoactivation of transition-metal clusters is an important area of catalysis due to the potential usefulness of the activated species as catalyst precursors.[8] In addition, controlling the size of metal fine particles as small as nanometer-order is a recent topic to create highly functionalized materials.[9] As part of our continuing research on catalysis by grafted clusters,[10] it has been previously reported[11] that the STM images of the individual carbonyl clusters such as $Rh_4(CO)_{12}$ and $[NEt_4]_2[Pt_{12}(CO)_{24}]$ are observed on HOPG. There is considerable interest in the in situ observation of the metal complexes or clusters on solid surfaces activated by photon emission[12] or laser irradiation.[13] In this study we have conducted the photoactivation of $[NEt_4]_2[Pt_{12}(CO)_{24}]$ adsorbed on graphite by laser excitation and imaged the conversion of the Pt carbonyl clusters with an STM operating in situ. The diffuse reflectance FTIR, coupled mass spectroscopy is also performed on the Pt_{12} carbonyl clusters deposited on HOPG. We report here the morphological transformation of an aggregate of $[NEt_4]_2[Pt_{12}(CO)_{24}]$ on HOPG induced by the pulse laser irradiation to give a Pt microcrystalline in the size of ca. 18×50 Å^2.

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Experimental Section

Our STM system is based on the NanoScope 1 (Digital Instruments, Inc.) and is equipped with a personal computer (PC-9801 RA5, NEC). The microscope unit of NanoScope 1 was covered with an aluminum shield which enabled us to perform the STM observation in flowing inert gases such as N_2 and Ar. The aluminum shield has a window of optical glass; a laser beam passes through the window to reach a sample on the microscope probe. STM images were recorded in the constant-current mode with a platinum–iridium (80:20%) alloy tip that was mechanically sharpened. We have modified the original control unit of NanoScope 1 to interfere it to the computer for data acquisition and processing. Data are transferred through an analog-to-digital converter and the linear amplifier from NanoScope 1 to the computer in direct memory access mode. The lengths of X and Y axes are estimated from the voltage applied to the piezo scanner and calibrated by the 2.46-Å spacing of graphite.[6a] The carbonyl IR spectra of $[NEt_4]_2[Pt_{12}(CO)_{24}]$ deposited on HOPG were observed by Shimazu FTIR-8100M with a MCT detector, equipped with the in situ diffuse-reflectance IR cell (SSU-8000) with KBr windows before and after the exposure to YAG laser pulse irradiation through a quartz window, where CO evolution was monitored by ULVAC-200 QP-mass spectrometer.

Platinum carbonyl cluster $[NEt_4]_2[Pt_{12}(CO)_{24}]$ was synthesized and purified by several recrystallization according to Chini et al.[14] with minor modification and identified by FTIR[14] and UV–visible spectroscopies.[15] $[NEt_4]_2[Pt_{12}(CO)_{24}]$ was dissolved in tetrahydrofuran (THF) under CO, and a few drops of the solution (0.1 mM) were placed onto a freshly cleaved HOPG (highly oriented pyrolytic graphite, ca. 5 × 5 mm); then the sample was dried in CO flow overnight. The sample was transferred to the microscope unit of STM under N_2 using a glovebag, and the STM observation was carried out in slow N_2 stream to avoid contamination by air. The 532-nm line of an Nd:YAG laser (Quanta Ray DCR-11, Spectra Physics) was used as light in the photoactivation and each pulse had a power of 2–3 mJ.

Results and Discussion

We have investigated the morphology of $[NEt_4]_2[Pt_{12}(CO)_{24}]$ adsorbed on graphite under the irradiation of laser light (532 nm). Figure 1 shows the photoinduced changes of STM images of $[NEt_4]_2[Pt_{12}(CO)_{24}]$ on HOPG. In all images of Figure 1, the tunneling current, the bias voltage, and the scan area are constant at 0.14 nA, 91 mV, and 160 × 150 Å^2, respectively. An aggregate of $[NEt_4]_2[Pt_{12}(CO)_{24}]$ (ca. 35 × 60 Å^2) was observed before the laser irradiation (Figure 1a). In contrast, such a feature was not observed when THF was simply dropped onto a graphite surface, implying that the aggregate in Figure 1a originated from the Pt_{12} carbonyl cluster. The overall morphology of the initial cluster deposit on HOPG is commonly seen by STM as the isolated aggregate consisted with a small number of rod-shaped unit (ca. 10 Å × 20 Å), similarly as reported previously.[11] From the X-ray crystallography[14a] of $[Pt_{12}(CO)_{24}]^{2-}$ in TPPM salt crystal which was estimated at ca. 10 × 12 Å^2 in van der Waals size, as depicted in Figure 3, it was suggested that the observed STM image of the initial aggregate may consist of 2–3 molecules of $[NEt_4]_2[Pt_{12}(CO)_{24}]$. Basically, no appreciable change of morphology for the cluster aggregate on HOPG was observed in several repeating runs by STM. We fixed the scan area and focused on this aggregate in the subsequent experiments. Under the laser irradiation, the laser beam reached the sample surface as well as the probe tip. Although it was generally difficult to keep the STM observation due to pulse noises synchronized with the laser, a series of snapshots was successfully obtained as shown in Figure 1 after each subsequent laser exposure (up to 40 pulses) to the sample under the N_2 atmosphere. Figure 1b was obtained after 10 pulses of irradiation where the image made more sharp and intense, and the size of the aggregate was relatively shrunk and became smaller (18 × 50 Å^2). The resulting STM image of the aggregate may correspond to naked Pt crystalline consisting of 24–38 Pt atoms, if they are ordered in a close-packing model. Interestingly, further laser irradiation made the size of the aggregate smaller and arranged it along the top-left to bottom-right direction in Figure 1c–e. Furthermore, it was suggested that the Z-axis height of the aggregate image by biding the bias voltage was relatively decreased after an additional 10–20 pulses of the laser as shown in the Figure 1a–c line scans. The temperature of the sample surface was not increased during the laser irradiation, which was measured with a thermocouple on the sample. In the continued irradiation after 40 pulses, an excess amount of tunneling current (above 50 nA) flowed due to the pulse noise synchronized with laser. Then the probe tip came away from the sample surface by an anticrash feature of the feedback circuit of NanoScope 1.[16] There was not a tip crash after 40 laser pulses; in fact, we reproducibly observed a carbon lattice image of the HOPG surface in the high resolution.

Additionally, we demonstrated no appreciable change of the STM image of cluster-free HOPG surface before and after the YAG laser under the similar conditions. A clear image of the graphite surface with the 2.46-Å spacing was obtained, which also suggested that there was no change of the graphite structure during the laser irradiation, indicative of being free from artifacts in the observed STM images on HOPG.

To get more information about the laser-induced behavior of $[NEt_4]_2[Pt_{12}(CO)_{24}]$, the carbonyl cluster was deposited on the HOPG and diffuse-reflectance FTIR spectra were observed in vacuum before and after the YAG pulse laser irradiation. In situ IR spectra were recorded with coaddition of 500 interferograms at resolution of 2 cm^{-1} to improve the signal/noise ratios. After removal of THF under vacuum, the resulting sample gave two intense and sharp bands at 2055 (s) and 1860 (m) cm^{-1} (Figure 2a) due to the linear and edge-bridging CO characteristic of $[Pt_{12}(CO)_{24}]^{2-}$ in solution.[14a] The successive addition of a pulse laser irradiation under evacuation (10^{-6} Torr) at 300 K resulted in the marked reduction of the intensities of both carbonyl bands as shown in Figure 2b–d, indicative of an efficient decarbonylation of the Pt_{12} carbonyl clusters on HOPG. Upon the admission of CO (100 Torr) onto the resulting decarbonylated sample at 300 K the intense carbonyl band at 2010 cm^{-1} and weak band at 1840 cm^{-1} reappeared in the diffuse reflectance FTIR spectra.

It was also demonstrated by QP-mass spectroscopy that CO (m/e = 28) was subsequently evolved by the laser illumination with a 532-nm line upon the graphite-adsorbed $[NEt_4]_2[Pt_{12}(CO)_{24}]$. The amount of CO was linearly developed by the successive pulse laser irradiation (10–120 pulses/exposure). A trace of C_2H_4 was also detected in the gas phase by GC–mass spectrometry using Porapack Q (1 m) column, possibly due to the photolysis of NEt_4 ions. A small amount of CO_2 (m/e = 44) was formed under the laser illumination, while H_2O (m/e = 18) was slightly decreased. The results suggest that the Pt_{12} carbonyl clusters on HOPG is efficiently decarbonylated by the pulse-laser activation with 532 line.

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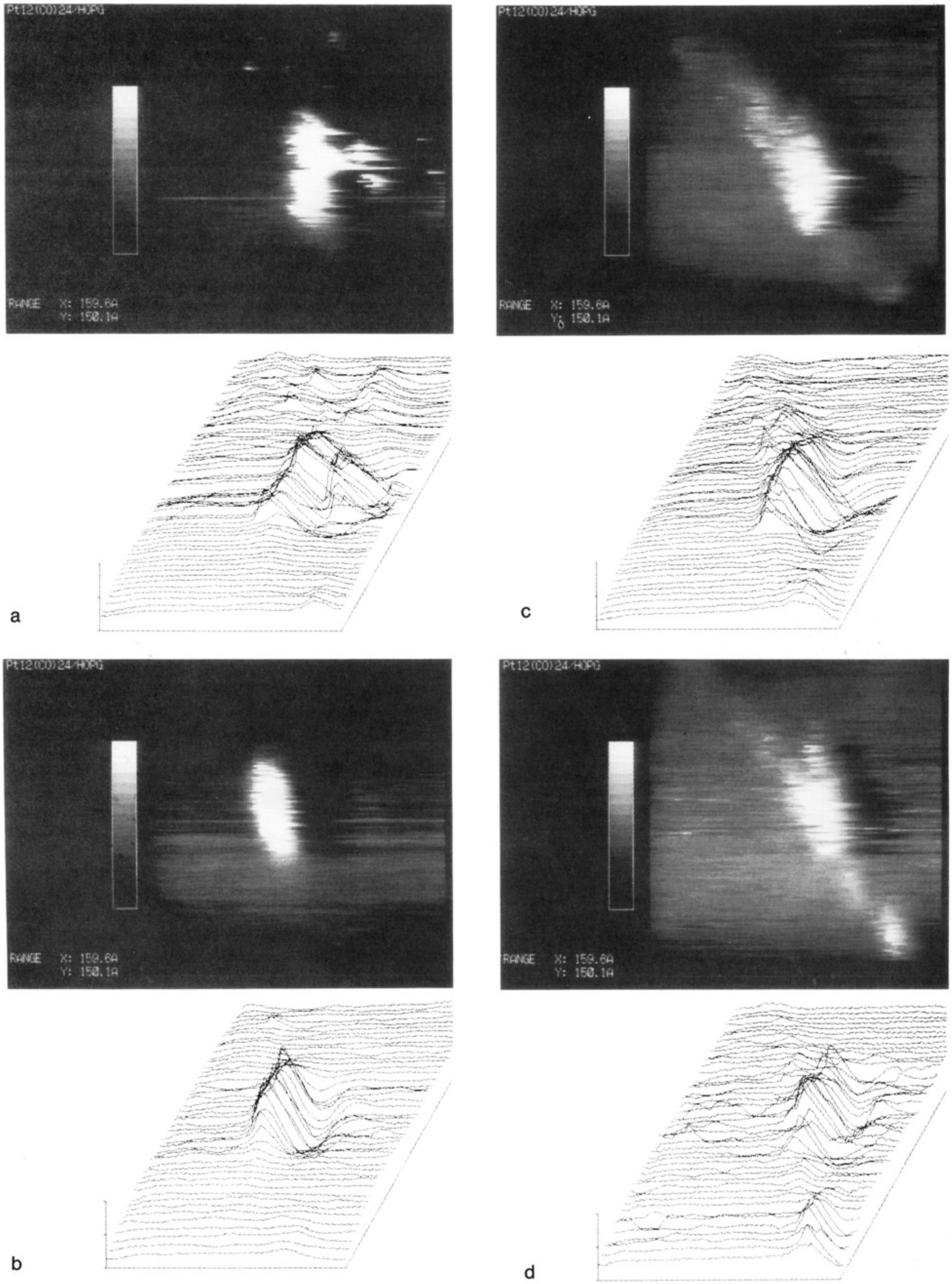

Figure 1. Changes of the STM images of $[NEt_4]_2[Pt_{12}(CO)_{24}]$ on graphite under laser irradiation. The upper figures are topographic images and the lower ones are line scan STM images. The image area of all figures: $x = 160$ Å, $y = 150$ Å. Bias voltage 91 mV, tunneling current 0.14 nA. (a) Before irradiation, (b) after 10 laser pulses, (c) 20 pulses, (d) 30 pulses, (e) 40 pulses.

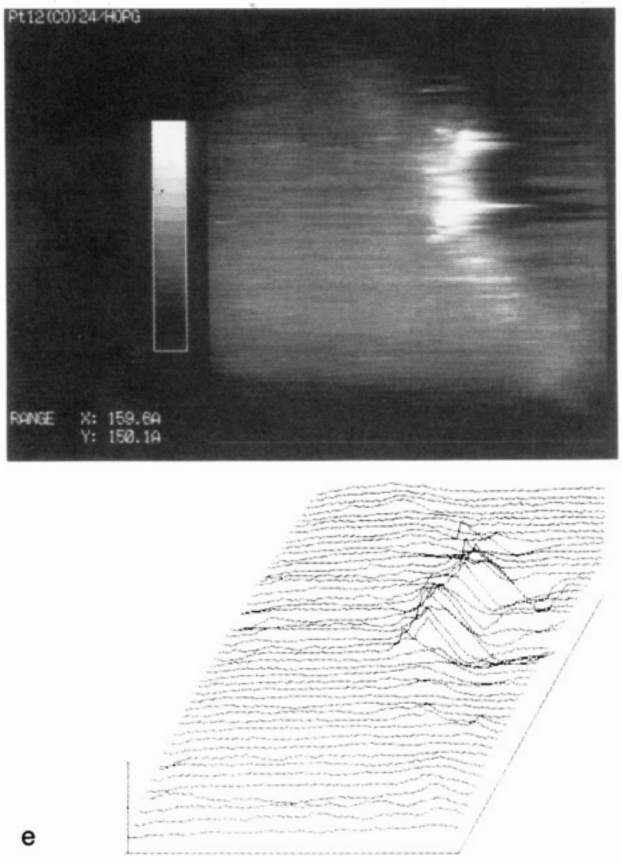

Figure 1. Continued.

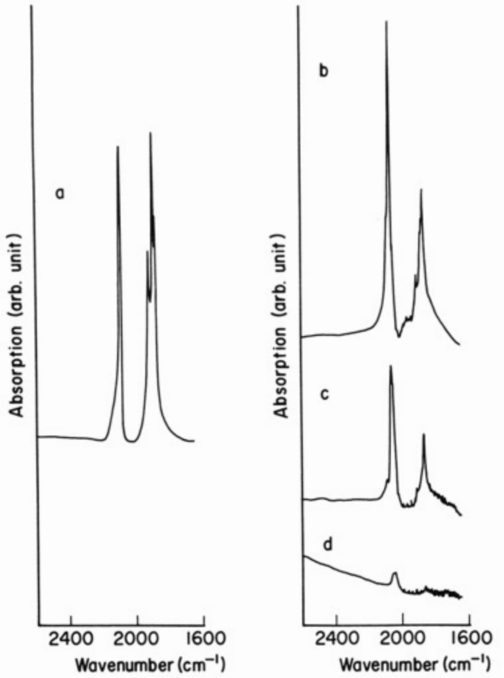

Figure 2. Change of IR carbonyl spectra of $[NEt_4]_2[Pt_{12}(CO)_{24}]$ deposited on HOPG: (a) deposition of the complex from THF solution at 300 K, followed by evacuation for 1 h; (b) after 10 pulses of 532-nm line laser irradiation; (c) 50 pulses of irradiation; (d) 100 pulses of irradiation.

As depicted in Figure 3, the X-ray crystal structure of $[Pt_3(CO)_6]_n^{2-}$ (n = 3–5) consists of the trigonal-prismatic metal framework:[14a] the intratriangle Pt–Pt distance is 2.7 Å, and the intertriangle Pt–Pt distance is about 3.0 Å; the latter interaction is weak and less than that of a single Pt–Pt bond.[17] This suggests that the intertriangle Pt–Pt bond is somewhat facile to dissociate. In fact, Heaton et al. have inferred from ^{195}Pt NMR studies that the outer triangle "$Pt_3(CO)_6$" of $[Pt_3(CO)_6]_n^{2-}$ (n = 3, 4) is mobile and rotates about the principal 3-fold axis; interexchange of the Pt_3 triangles occurs in mixtures of $[Pt_9(CO)_{18}]^{2-}$ and $[Pt_{12}(CO)_{24}]^{2-}$ even at 25 °C.[18]

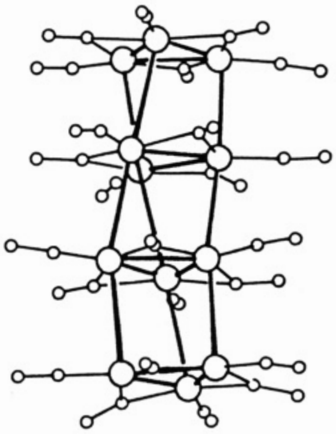

Figure 3. Pictorial representation of $[Pt_{12}(CO)_{24}]^{2-}$ by X-ray crystallography.

Accordingly, we suggest from the STM and FTIR, coupled with mass observation, that decarbonylation and skeletal fragmentation of the Pt_{12} cluster were induced by 532-nm laser irradiation, which led to the formation of a Pt microcrystalline on graphite surface.

The Pt_{12} carbonyl cluster on the graphite surface is a molecular precursor for fabrication of Pt_{12} aggregates in atomic level which are possibly evaluated by STM. Thus the photoactivation of metal carbonyl clusters by laser has a great potential for the preparation of ultimate micro metal crystalline on surfaces as an electronic device.

Conclusion

Pt_{12} carbonyl clusters $[NEt_4]_2[Pt_{12}(CO)_{24}]$ adsorbed on graphite (HOPG) were observed by diffuse reflectance FTIR and scanning tunneling microscopy which was performed under N_2 atmosphere. An aggregate of the Pt_{12} carbonyl clusters were gradually decarbonylated and effectively transformed into a smaller Pt crystalline (18 × 50 Å^2) on HOPG by the successive pulse irradiation of the 532-nm line of the laser. The successive irradiation resulted in effective decarbonylation, followed with the degradation of Pt_{12} clusters to give a fine Pt particle on the graphite surface.

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Registry No. $[NEt_4]_2[Pt_{12}(CO)_{24}]$, 61111-78-2; graphite, 7782-42-5.

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