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## Two-dimensional Platinum Nanosheets Between Graphite Layer

A variety of chemicals can be intercalated between graphite layers to produce graphite intercalated compounds (GICs) [1], because graphite has a layered structure and each layer interacts via weak van der Waals force and can accept and donate electrons from the intercalants. Metal chloride also can be intercalated between graphite layers. Transition metal particles between graphite layers could be obtained by the insertion of transition metal chlorides into graphite layers and the subsequent reduction. In this paper we report the intercalation of platinum tetrachloride between graphite layers and reduction of platinum tetrachloride between graphite layers to produce platinum nanosheets with 1-3 nm thickness and hexagonal holes.

A mixture of solid platinum chloride ( $\text{PtCl}_4$ , Sigma-Aldrich) and powder graphite (KS6, TIMREX) were treated under 0.3 MPa of chlorine at 723 K for 7 days to obtain the platinum chloride intercalated compounds (PtCl<sub>x</sub>-GIC) [2, 3]. The PtCl<sub>x</sub>-GIC sample was reduced at 573 K for 1 h under 40 kPa of hydrogen to produce the platinum metal intercalated compounds (Pt-GIC). The platinum metal loading in the mixture was 5wt%.

Figure 1 shows TEM images of the Pt-GIC sample obtained by JEOL JEM-2100 (200 keV) [3]. XMA analysis confirmed that the dark images were composed of platinum. Several rod-like platinum images in parallel are seen in Figure 1(a) while, sheet-like platinum images with hexagonal holes are seen in Figure 1(c). The TEM analysis with the rotation of the Pt-GIC sample against electron beam confirmed that the rod-like images shown in Figure 1 (a) was a side view and (c) was a top view of the platinum nanosheets intercalated between graphite layers. The platinum sheets are arranged in parallel with graphite layers (interlayer distance of 0.335 nm) in Figure 1(b), which is the magnified view of Figure 1(a).

Void spaces are also observed at the edge of the platinum sheets. Figure 1(d) is a drawing of the top view of platinum sheet. The AB side of the hexagonal holes in the

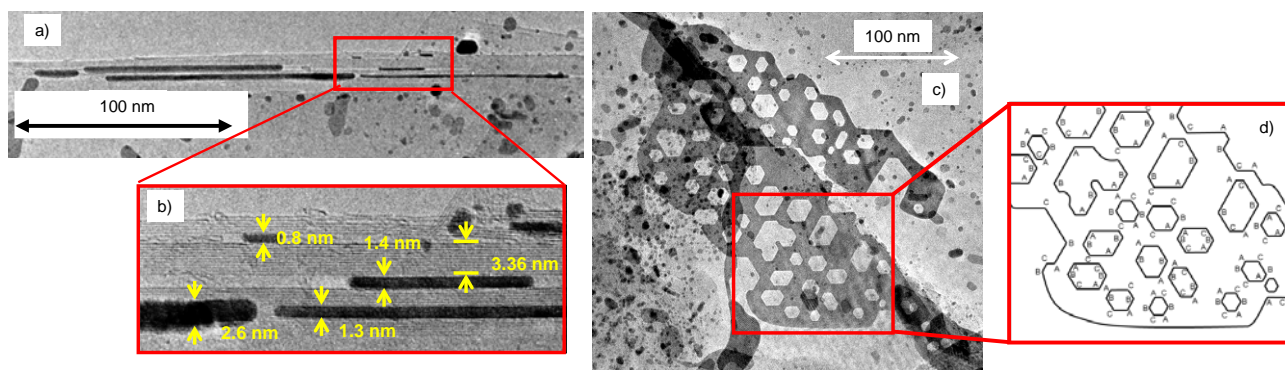
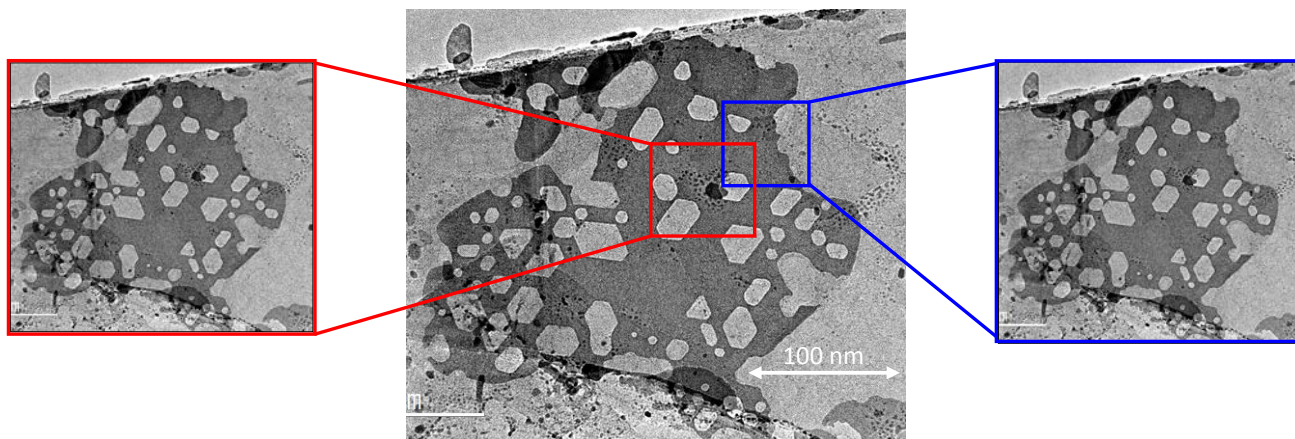


Figure 1 Pt-GIC

platinum sheet are straight and parallel to each other. The BC and AC sides in the hexagonal holes and edges at the sheet are also parallel to each other and the angles between two straight sides from three AB, BC, and AC directions are at 120°. The structure of the graphite layers would reflect on the peculiar structure (holes and edges) of the platinum nanosheets. Platinum atoms or platinum chloride molecules or both would migrate along with a regular hexagonal net of carbon atoms during hydrogen reduction at 573 K. Movement during the reduction would determine the morphology of the resulting platinum nanosheets, which have hexagonal holes.

Pt-GIC was treated under 0.3 MPa of chlorine from room temperature to 473 K at the rate of 10 K/min. TEM image of the sample is shown in Figure 2. In addition to platinum metal sheets, small platinum particles are also observed. A part of platinum nanosheets would be oxidized to platinum chloride species, which were reduced to metal by the irradiation of electron beam during TEM observation [5]. Besides the nanosheets, small platinum metal particles are also formed (Figure 2), which indicates that chlorine would intercalate between graphite layers and oxidize the nanosheets from the edge side. On the other hand, small platinum metal particles are also observed in the hexagonal holes and above (or below) of the nanosheets. One probable explanation for the oxidation of nanosheets from the inner side by chlorine is that voids would exist in a graphite layer (graphene) and chlorine molecules would pass through the voids and oxidize from the inner side of platinum sheets. The existence of the voids would be predicted by the reversibility of PtCl<sub>x</sub>-GIC and Pt-GIC. Platinum nanosheets with 1-3 nm thickness could not be produced by the agglomeration of platinum atoms from one intercalant platinum chloride layer with third stage structure during reduction. Many platinum atoms would pass through the voids and aggregate to form platinum nanosheets with 1-3 nm thickness during the hydrogen reduction process. In the chlorine oxidation process, platinum chloride species derived from the nanosheets would pass through the voids to produce third stage structure.



**Figure 2** TEM image of Pt-GIC treated under 0.3 MPa of chlorine at from room temperature to 473 K at the rate of 10 K/min.

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