A Density Functional Theory Approach to Unusually High Electrocatalytic Activity of Platinum Clusters on Palladium-Shell Nanoparticles

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Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
First published on the web Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

S1 Additional TEM and HRTEM images of Au@Pd@Pt NPs

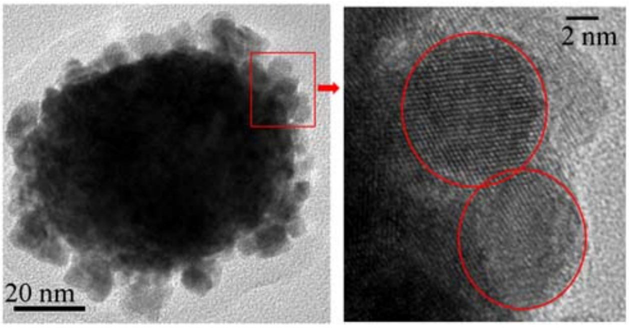

Figure S1. The TEM image (left) and the HRTEM (right) of the 55 nm Au@Pd@Pt NPs with 2 monolayers of Pd and θ_{Pt} ~20.

As for the epitaxial growth of the Pd on Au NPs surface, we have explained it in our previous paper.[1] The SEM show clearly that Pt would grow by the cluster or island.

S2 Bond displacement vector method

The Raman intensities should be calculated as[2]

$$I_{Raman} \propto \left|\frac{\partial \alpha}{\partial Q}\right|^2$$

where α is the polarizabilities of considered system and Q the mass-weighted vibrational normal mode of specific frequencies. Generally, the Q would be expressed as

$$Q = \sum_i l_i q_i$$

where $q = \sqrt{m_i}\Delta x_i$ is the mass-weighted Cartesian coordinate and l_i the corresponding displacement. Apply this, we have rewritten Raman intensities as

$$I_{Raman} \propto \left|\sum_i l_i \frac{\partial \alpha}{\partial q_i}\right|^2 = \left|\sum_i \frac{l_i}{\sqrt{m_i}} \frac{\partial \alpha}{\partial \Delta x_i}\right|^2$$

Here we only considered that Q is related to the C-O stretching. In this situation, the displacements belong to one CO molecules could be summarized first. As a result, we have

$$I_{Raman} \propto \left|\sum_i \frac{\vec{l}_i}{\sqrt{m_i}} \frac{\partial \alpha}{\partial \Delta S_i}\right|^2 = C\left|\sum_i \frac{\lambda_i \vec{l}_i}{\sqrt{m_i}}\right|^2$$

where ΔS_i represents the CO bond length vector, $\vec{l}_i$ the corresponding displacement vector, C the quantity of square of polarizability derivate corresponding specific C-O bond, and λ_i relative value between polarizability derivate corresponding arbitrary C-O bond and specific C-O bond . Here we ignored the mass different between oxygen and carbon atoms. This assumption would bring a relative error of 2.4% which is suitable for semi-quantitative analysis. The experimental observation show that the Raman intensity of CO molecules adsorbed on Pt atop sites is larger than it on Pd bridge sites. We considered this difference by an arbitrary factor $\sqrt{3}$ for calculating Raman relative intensities. In more specifically, λ_i equals to 1 when ΔS_i relate to PdC-O and $\sqrt{3}$ to PtC-O. This method is called the bond displacement vector method in the text. Finally all calculated relative Raman intensities are memorialized to the same area.

Notes and references

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