Supplementary information

Evidence of unique electron donor-acceptor property for platinum nanoparticles as studied by XPS

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The procedure for preparation of the Pt-PVP nanoparticles is as follows: in a 50 ml beaker, 0.5 ml of an aqueous solution of H₂PtCl₆•6H₂O (2.5×10^{-5} mol) and 0.0052 g of PVP (MW 40 000) were dissolved in 24 ml of ethylene glycol under stirring. All the chemical reagents are in analytical grade. The beaker was then heated for 35 s in a microwave oven (Galanz WP 700). The solution changed color from orange to black and a Pt-PVP colloid (A) with the particle size 2-3 nm was obtained. For preparation of Pt-PVP nanoparticles with size 6-7 nm, an additional 0.5 ml aqueous solution of H₂PtCl₆•6H₂O was added into the colloid A and then heated in microwave oven. This operation was repeated for 8 times. A black colloid solution with precipitate of Pt-PVP nanoparticles was formed. Specimens for XPS analysis were prepared by depositing Pt-PVP nanoparticles onto a silicon wafer by spin-coating from the colloid solution. For powder of 6-7 nm Pt-PVP nanoparticles, the precipitate was separated with centrifuger, washed with alcohol to remove ethylene glycol and excess PVP, then dried in air and finally pressed into pellet for XPS measurement.

Pt nanoparticles larger than 25 nm were purchased from Aldrich Co., and it was described as nanosize activated powder with a purity of 99.9+%. The product is basically composed of Pt nanoparticles of size ca. 25 nm and ca. 300 nm. As for the sample preparation, the product was firstly immersed in aqueous solution of PVP (0.1 % w/w) for 2 days, then it was ultrasonic oscillated for 2 h to have the particles dispersed sufficiently. After that, the product was centrifuged with a rate of 3000 rpm

for 12 min to separate the particles of size 25 nm (in the solution) and 300 nm (precipitate). Then the sample with size ca. 25 nm was precipitated through a centrifuging rate of 12000 rpm. Following that, both precipitates were washed with water for 2 times to remove the excess PVP, and dried in the vacuum at room temperature. Finally, the powders were pressed into pellets for XPS measurement.

In order to make reliable BE comparison, a thin PVP film was also prepared on the surface of a piece of smooth bulk Pt by spin-coating from dilute aqueous solution of PVP (0.1% w/w).

Figure 1 shows angle-resolved N1s spectra from PVP film on bulk Pt. It can be seen that the relative intensity of the peak at 397.9 eV is lower at grazing angle of collection, indicating that the N atoms corresponding to lower N1s peak are not in the surface but in the interface of bulk Pt and PVP films and that the BE lowering is due to the charge transfer from Pt atoms to PVP side chain.

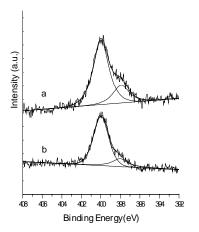


Figure 1 Angle-resolved N1s XPS spectra from PVP film on bulk Pt. a). $\theta=90^{\circ}$, b). $\theta=10^{\circ}$ (θ represents the angle between the direction of photoemission and the sample surface).