Strain Induced Core-Shell Inversion on Bimetallic Pt-Ru Nanocrystallites

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A sequential designed process was utilized to deposit Pt atoms in different compositions on surface of the Ru-core upon Polyol reaction. In this project we successfully synthesized Ru/Pt nanocrystallites with core-shell structures for the composition ratios of Ru to Pt from 10/1 to 10/30. The Ru core size was estimated by means of TEM. The transition of crystal structure for bimetal nanocrystals (BiNCs), as a function of the Ru/Pt ratio, was elucidated by the XRD characterization shown in Figure 1. As can be seen, from Pt = 0 to 20, the deposition of Pt atoms are incorporated into the structure of Ru crystals which induce the blue shift of main diffraction peak of samples from position of Ru (101) hcp to that of Pt (111) fcc. An obvious Pt (200) fcc peak was found in addition to the much larger (111) fcc peak when Pt in the BiNCs is up to 30 and it indicats the building up of Pt phase on the surface of the nanocrystals.

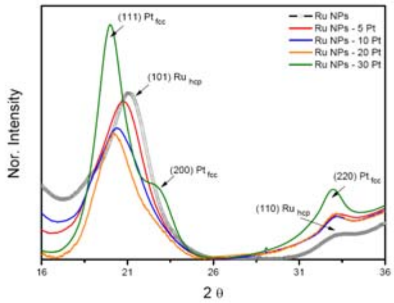

Figure 1. XRD patterns for samples of core-shelled Ru-Pt nanocrystallites at different atomic ratios.

Figure 2 shows the XANES spectra of BiNCs samples at Pt L_3 and Ru K-edge. The insects in the XANES diagrams show the Radial Structure Function (RSF) for spectra of samples by Forward Furious Transformed in selected appropriated *k* range. Patterns of Fig. 2a indicats a highest density of *d*-band vacancy (highest Whiteline intensity) for Pt = 1 BiNCs and can be assigned to the maximum exposure ratio to the air when most of the Pt were located on the surface. In addition, the *d*-band vacancy of Pt decreased when the amounts of Pt was increased from 0 to 30. Comparing with pure Pt NPs, the RSF intensity for BiNCs of Pt from 10 to 30 shows strong surface alloying effect between Pt and Ru components (relatively lower interference intensity on the BS peak). Figure 2b shows that the small amounts of Pt might be incorporated into the core and induce a large inter-atomic hybridization between Ru atoms (see the merge of two absorption peaks on Absorption trace of Pt = 1). When the Pt content was increased, the splitting of absorption peaks become obvious which can be attributed to the protection of Ru from oxidation by the coverage of Pt on the surface (see traces of Pt = 5 to 20). However, the two separated peaks on XANES tends to merage a little bit which might be due to the strain induced core-shell inversion when size and surface effect alloying bcome obvious in the nanocrystallites.[1-3] This assumption can further be confirmed by the drop of BS interference peak for Pt 30 samples (see the RSF trace in yellow).

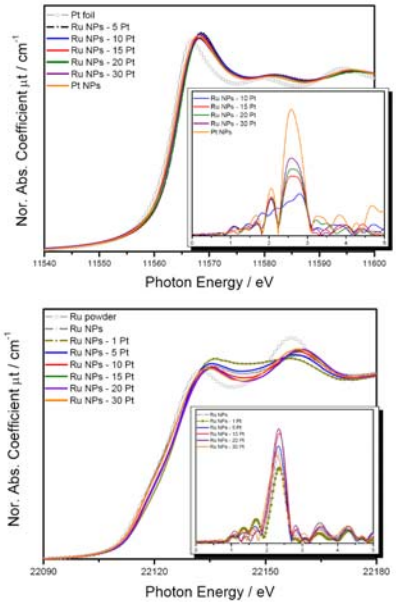

Figure 2. Pt L_3 (a) and Ru *K*-edge (b) XANES spectra of bimetal catalysts in different PtRu ratios.

To sum up, four steps for the transition of crystal phases were found and controlled by means of the sequential designed Polyol reaction on BiNCs. 1st: incorporation of Pt atoms into Ru core; 2nd: surface deposition of Pt atoms on Ru core; 3rd: surface alloying induced by increasing Pt coverage; 4th: strain induced core-shell inversion. The sechme for the four step are summarized in Figure 3.

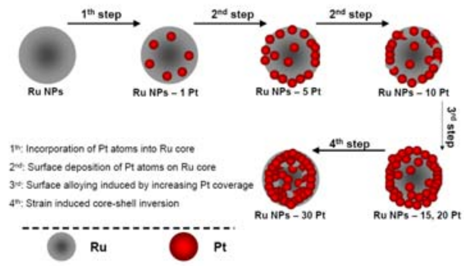

Figure 3. Scheme of Ru/Pt nanocrystallites at different ratios prepared by sequential designed Polyol reaction.

Reference:

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