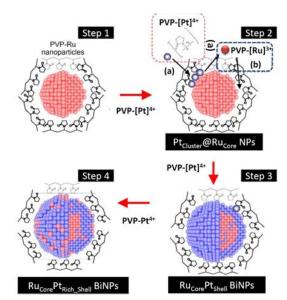
## Ru<sub>Core</sub>-Pt<sub>Shell</sub> Bimetallic Electrocatalysts over Methanol Oxidation Applications

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Nanoparticles comprising a Ru core covered with precisely controlled 1.5-to-3.6 atomiclayer (ALs)-thick Pt atoms are synthesized. These electrocatalysts show up to a 3.3-fold improvement in CO-tolerance performance with conventional all-Pt nanoparticles. In addition, the activity of core-shell electrocatalyst at a conventional battery operation potential (I<sub>300</sub>, at 300 mV vs Ag/AgCl) are substantially enhanced to optimum value about 50% and 3.3-fold better than that of other core-shell NPs with thicker shell crystals and Pt NPs, respectively. The origin of their performances, correspond to atomic structure evolution, as affected by the thicknesses of shell crystal was elucidated through a combination of experimental characterizations, employing electrochemical techniques, X-ray scattering, X-ray small-angle absorption spectroscopy, and X-ray photoelectron spectroscopy. A atomic structure evolution with surface electrochemical property varying with shell thicknesses is systematically investigated. Our results combining structural information (by SAXS, XAS, and HRTEM) with electrochemical measurements (CV analysis) probe the insight of shell thicknesses on the atomic structure evolutions so as to the surface MOR activities over  $Ru_{Core}$ - $Pt_{Shell}$  BiNPs. Results of SAXS demonstrate that the nanoparticles were successfully grown in uniform size distribution with precision control of Pt shell thicknesses using a proposed simple dual stepped polyol redox reaction. Upon growing Pt crystals as shell, the Ru atoms are stabilized in core region when shell crystals less than 2.7 atomic layers. A further growth of shell crystal to 3.6 ALs will induce the relocation of Ru atoms to their near surface region<sup>1-4</sup>.



**Scheme 1:** Schematic representations for the atomic structure evolutions of RuCore-PtShell bimetallic nanoparticles with increasing Pt shell crystals in different atomic layer thicknesses using polyol redox reaction. Pathways (a) and (b) refer to the transmetalation reaction of PVP-[Pt] $^{4+}$  + Ru  $\rightarrow$  Pt atoms + PVP-[Ru] $^{3+}$  and redox reduction reaction of PVP-[Pt] $^{4+}$  and PVP-[Ru] $^{3+}$  in a presence of CH3CHO:, respectively.

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