

CO Stripping as a Simple and an Accurate Tool for the Characterization of Ru@Pt Core@Shell Nanoparticle Structures

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Pt-Ru nanoparticles, either alloy or core-shell structures, have attracted significant interest because of their application as catalysts for the electro-oxidation of methanol in direct methanol fuel cells (DMFCs), in the preferential oxidation of CO in hydrogen feeds (PROX), and the during electro-oxidation of hydrogen in proton exchange membrane fuel cells (PEMFCs) when the hydrogen fuel contains some CO. The catalytic properties of PtRu nanoparticles depend mainly on their particle size and composition, the distribution of Pt and Ru sites at the atomic level, and the surface population of Pt and Ru¹.

Ru-Pt nanoparticles with a Ru@Pt (core@shell) structure are reported to have noticeably different catalytic properties from nanoparticles composed of PtRu alloys or monometallic Pt and Ru mixtures, due to the unique Ru@Pt core/shell electronic structure². It is known that the coupling between the adsorbate valence states and the transition metal d-states defines the value of the adsorption energy³. Therefore, it is possible to modify the activity of these catalysts (i.e. their electronic properties) by altering the composition and the arrangements of atoms within the nanoparticle structure.

In this study, the adsorption/desorption of CO is used as an analytical tool for the determination of the Ru@Pt surface structure when the Pt coverage switches from one monolayer to multilayer. Ru@Pt catalysts with different Pt coverages were synthesized by the sequential chemical reduction of RuCl₃·3H₂O and H₂PtCl₆·6H₂O. Ethylene glycol (EG) was used as both a solvent and a reducing agent, while polyvinyl pyrrolidone (PVP) was used as a capping agent. 10% Ru@Pt /VC catalyst was prepared by adding the catalyst colloid solution to a homogeneously mixed VC/ethanol solution, followed by stirring for 2-4 hours. After Ru@Pt /VC powder collection and washing, it was dried under vacuum at room temperature. The catalyst ink was made by mixing 0.3 ml of a 1% w/w Nafion solution, 0.6 ml of isopropanol, 0.1 ml of water, and 10 mg of the Ru@Pt /VC powder and then sonicating for ≥ 30 min.

Wavelength dispersive X-ray spectroscopy (WDS) was used to determine the composition of the Ru@Pt nanoparticles, while XRD revealed the effect of Pt coverage on the Ru core lattice parameters. TEM, accompanied with EDX, was used to confirm the formation of Ru@Pt core@shell structures, rather than individual Pt and Ru particles. TEM was also used to establish the particle size distribution and to confirm good dispersion of the catalyst nanoparticles on the VC support.

Figure 1 (inset) shows that CO stripping peaks for pure Ru/VC and Pt/VC appear at 0.62 and 0.83 V vs. RHE, respectively. When these catalysts were mixed together, CO stripping seen in same two peaks, at indicating the absence of any effect of Ru on the Pt activity when they are physically mixed together. However, in the case of Ru@Pt nanoparticles, when the Pt coverage ranges from a sub- to full monolayer, CO stripping appears as a single peak, as shown in Figure 1, indicating the strong interaction between the Pt shell atoms and the Ru core. Surprisingly, with more Pt in the shell (less than 2 monolayers), two CO stripping peaks appear due to the existence of two Pt surface sites with different electronic properties. At one, Pt is in direct contact with Ru and therefore the electronic effect is high. Thus, the CO stripping peak for these sites appears at 0.62 V vs. RHE. At the other type of Pt sites, the Ru electronic effect on the surface Pt atoms is buffered by the existence of an underlayer of Pt atoms. When the Pt shell exceeds the limit of two monolayers, a single peak is observed, but shifted positively until it reaches a value close to that of pure Pt. This demonstrates of the weak effect of Ru on the electronic properties of the surface Pt atoms.

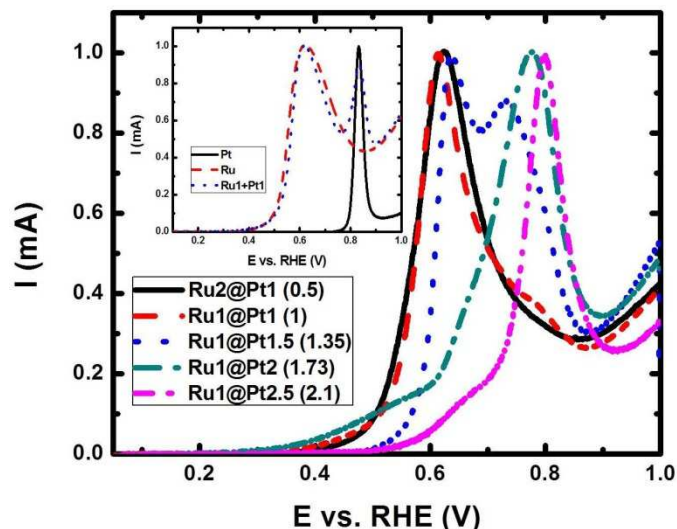


Figure 1: CO stripping voltammetry (20 mV/sec) of Ru@Pt/VC NPs with different Pt coverages (indicated in brackets) in RT 0.5 M H₂SO₄. The CO was pre-adsorbed at 0.05 V for 15 min and the current has been normalised to the height of the largest peak. Inset: CO stripping voltammetry of Ru/VC, Pt/VC, and physically mixed Ru/VC and Pt/VC NPs.

In order to confirm that the CO stripping behavior is unrelated to the Ru core particle size, β -propylene glycol (PG), which has a higher boiling point than ethylene glycol (EG), was used, giving larger Ru nanoparticle sizes. Figure 2 shows that, independent of the Ru core size, a single CO stripping peak is seen at 0.62 V vs. RHE when the Ru core was covered with one monolayer of Pt (Ru1@Pt1 (EG) or Ru1@Pt0.6 (PG)). When the Pt shell was increased from one to less than two monolayers ((Ru1@Pt1.5 (EG) and Ru1@Pt1 (PG)), two CO stripping peaks are seen again independent of the Ru core size.

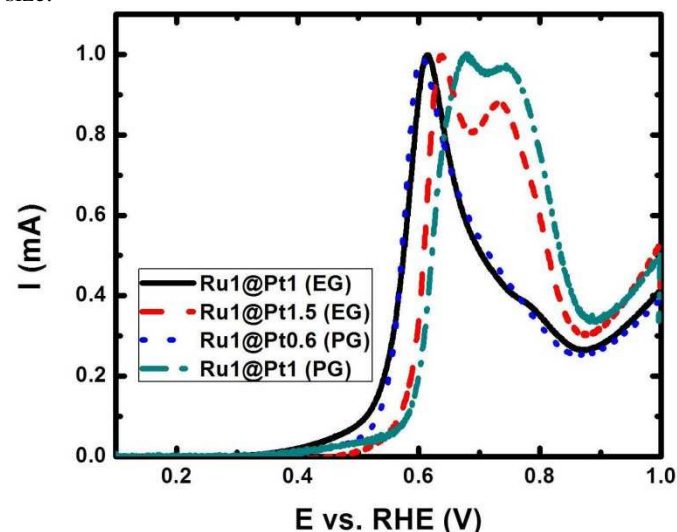


Figure 2: CO stripping voltammetry (20 mV/sec) of Ru@Pt/VC NPs with different Pt coverages in 0.5 M H₂SO₄. The solvents used in the core@shell synthesis are indicated in brackets. The CO was adsorbed at 0.05 V for 15 min and the current has been normalised to the height of the largest peak.

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