

Carbon Supported Pd-Pt-Cu Nanocatalysts for Efficient Formic Acid Electrooxidation: Facile Syntheses, Componental Functions and Structural Evolutions

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Pd-based nanoalloys supported on carbon black with favorable sizes and structures as well as homogeneous dispersions are receiving a great interest owing to their potential applications in various catalytic reactions including anode reactions in low-temperature fuel cells [1]. In order to get a significant and balanced improvement on the catalytic activity and durability of a Pd-based nanocatalyst for a specific reaction, rational design and synthesis, structural analysis, performance evaluation and insightful understanding of multi-component nanoalloys are essential, and yet remain as a challenge.

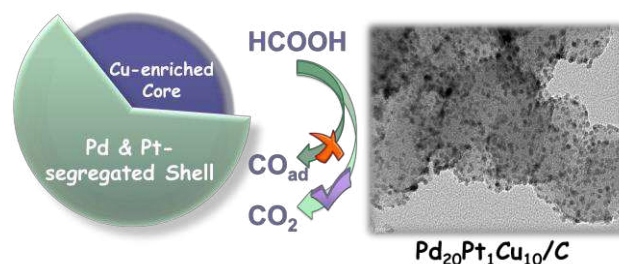
In the present work, we have comparatively screened several one-pot synthetic methods for preparing highly dispersed carbon-supported low Pt-contented Pd-Pt-Cu nanocatalysts with readily cleanable surfaces and different alloying degrees by varying reducing agents, solvents and stabilizers. Pd₂₀Pt₁Cu₁₀/C synthesized with ethylene glycol and sodium citrate has been identified to exhibit the best electrocatalysis towards formic acid oxidation (FAO) among all the tested samples including mono-, bi-, and tri-metallic Pd nanocatalysts. Moreover, a comprehensive investigation with combined XPS, electrochemical and ATR-IR measurements enables a better understanding of the compositional and structural origins [2] leading to such an enhanced electrocatalysis. It is revealed that the cheaper Cu functions mainly as the “core filler” to expose a Pd and Pt-segregated active surface and a deliberately controlled small fraction of Pt on the surface minimizes the undesired dehydration of formic acid [3], in addition, a weak electronic effect from Cu and Pt promotes FAO on Pd. Surface restructuring with Pt agglomeration due to intense Cu dealloying procedure [4] degrades the performance of the ternary nanocatalysts. The current work may lend new hints for the development of high performance multi-component electrocatalysts towards better clean energy utilization.

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References

- [1] Rice, C. A.; Wieckowski, A. “Electrocatalysis of Formic Acid Oxidation.” *Electrocatalysis in Fuel Cells*. Springer London, 2013. 43-67.
- [2] Bradley, J. S.; Via, G. H.; Bonneviot, L.; Hill, E. W. *Chem. Mater.* 1996, 8, 1895-1903.
- [3] Cuesta, A.; Escudero, M.; Lanova, B.; Baltruschat, H. *Langmuir*. 2009, 25, 6500-6507.
- [4] Koh, S.; Strasser, P. *J. Am. Chem. Soc.* 2007, 129, 12624-12625.



Scheme 1. Schematic structure and TEM images of the trimetallic Pd-Pt-Cu/C nanocatalysts.