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Graphene Supported Au-Pt Core-Shell Catalyst: Electro catalysis of Formic Acid Oxidation
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Introduction
Polymer electrolyte membrane fuel cell (PEMFC) is energy technology limited by the need for expensive catalysts, such as Pt.[1] Highly active graphene-supported Au-Pt core-shell (Au@Pt) catalyst with atomically thin Pt shell and low Pt loading is here used in PEMFCs for formic acid (FA) oxidation. Core-shell catalyst 20% of Pt on graphitized carbon (C-Pt20%) was a reference in all experiments. Key challenges:
1. Chemical syntheses of graphene-Au@Pt catalyst.
2. Electro catalysis of FA oxidation and oxygen reduction reactions (ORR).
3. Functional testing of graphene-Au@Pt in PEMFC.

Graphene-Au@Pt synthesis

1. Graphene synthesis

2. Au@Pt NP formation

Graphene-Au@Pt synthesis (Fig. 1) starts by graphene oxide (GO) reduction to graphene and covalent (CYS-graphene) functionalization by L-cysteine (CYS). Au cores are formed next and strongly bonded to the CYS thiol group, followed by Pt shell formation. The Au@Pt precursors ratio corresponds to an atomically thin Pt shell on the Au cores.

Graphene-Au@Pt characterization
GO reduction to graphene was followed by UV-Vis spectroscopy: 235 and 303 nm peaks are converted to a 265 nm peak (Fig. 2a), and the Au NP plasmon peak (520 nm) is damped by Pt shell formation (2).

X-ray photoelectron spectroscopy (XPS) confirms CYS-graphene bond types (pyrrolic N at 399.5 eV, Fig. 2b). Fig. 2c shows 2-ethanesulfonic acid (MES) on Au (167.98 eV) – a NP stabilizing agent, and strong covalent Au-thiol (163.52 eV) bonds which ensure catalyst stability.

Au@Pt NPs of uniform size (8 ± 2 nm) was imaged by transmission electron microscope (TEM, Fig. 3a, b). Homogeneous distribution of NPs on graphene (Fig. 3c) is based on its high surface area and ensures good Au@Pt stability. Composition of the NPs was measured by energy-dispersive X-ray spectroscopy (EDX), from which atomic ratio Au:Pt = 2.76:1 can be obtained (Fig. 3c).

Conclusions
1. Graphene-Au@Pt synthesis yielded atomically thin Pt shell, highly active for FA oxidation.
2. Chemical bonds between Au@Pt NPs and graphene improve stability.
3. FA oxidation on graphene-Au@Pt exhibits several times higher currents and 69.4 mV lower overpotential towards ORR than C-Pt20%.
4. Graphene-Au@Pt exhibits OCP of 825 ± 9.9 mV and 96.8% higher power output (122 ± 3.5 mV/cm²) than C-Pt20% at 80 °C.

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