



Synthesis of PtCuCo ternary alloy using laser ablation synthesis in solution-galvanic replacement reaction(LASiS-GRR)

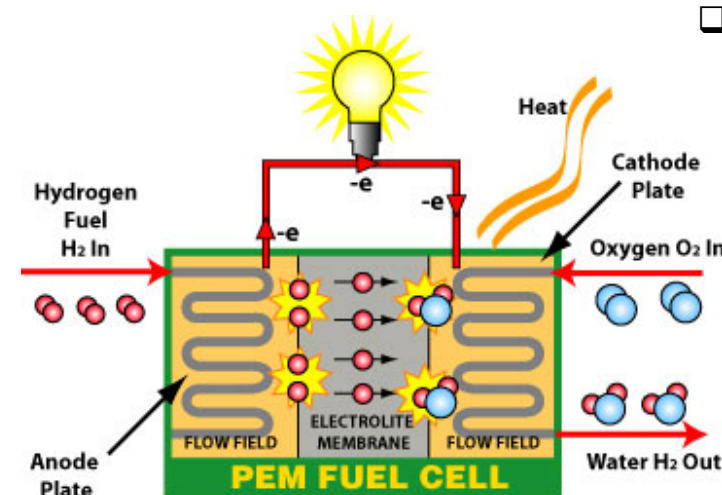
Kangmin Cheng^{1,3,4}, Sheng Hu^{2,3,4}, Dibyendu Mukherjee^{*1,2,3,4}

¹Department of Mechanical, Aerospace, and Biomedical Engineering, ²Department of Chemical and Biomolecular Engineering, ³Nano-BioMaterials Laboratory for Energy, Energetics & Environment, ⁴Sustainable Energy Education and Research Center (SEERC)

Introduction and Experimental Set-up

➤ Proton exchange membrane fuel cell (PEMFC)

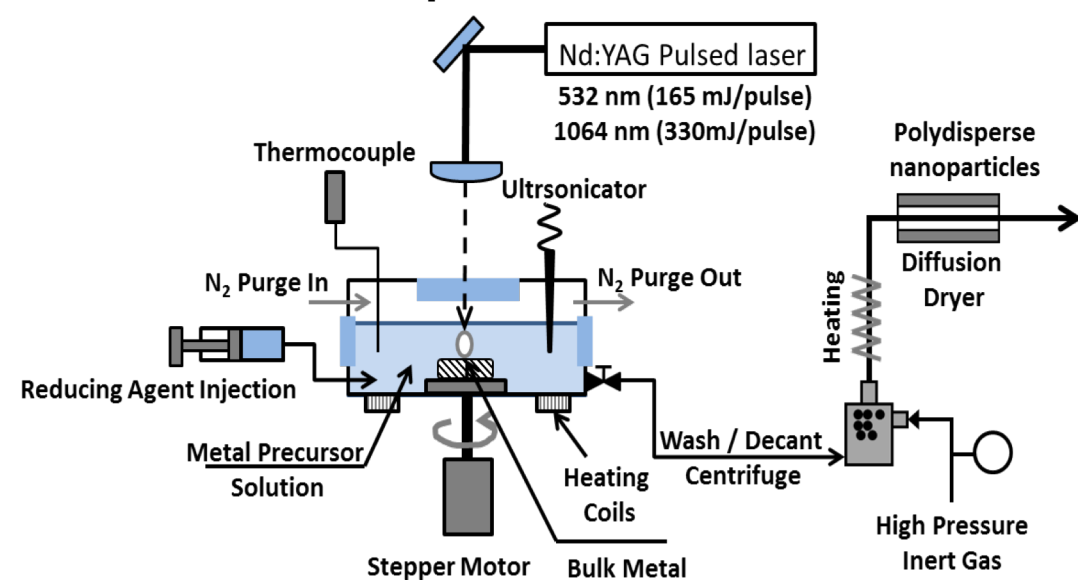
- ❑ In PEMFC, hydrogen and oxygen enters into the anode and cathode respectively. At the anode, electrons are separated from protons that flow through the external circuit towards the cathode. At the cathode, the electrons combine with protons passing through the membrane to carry out oxygen reduction that forms water. This sluggish 4-electron transport oxygen reduction reaction (ORR) plays a crucial role in determining the fuel cell efficiency. Traditionally, Pt catalysts have been used to accelerate the reaction rate. But Pt is an expensive metal, and is not very durable under acidic conditions.



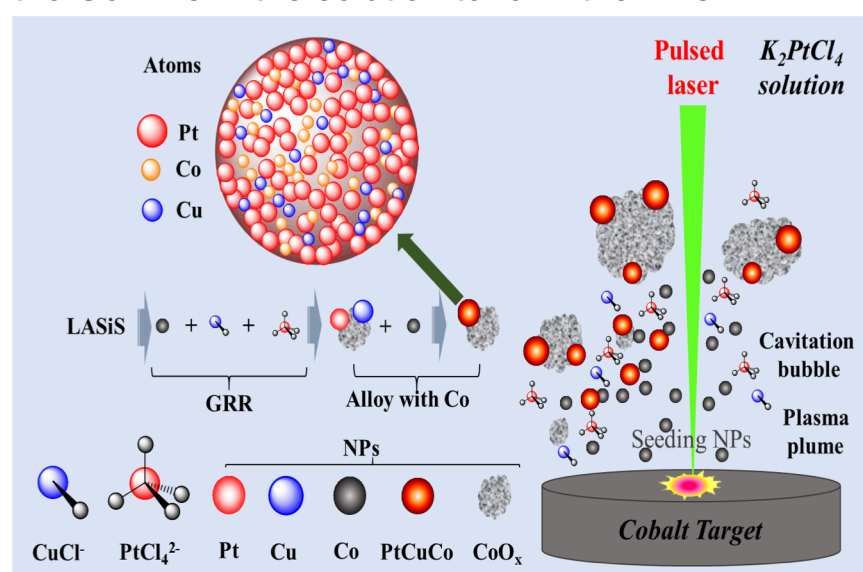
<http://www.tech-etch.com/photoetch/fuelcell.html>

- ❑ Alloying Pt with other transition metals such as Co, Cu modifies the respective oxygen and hydroxide binding energies and meanwhile increase the surface sites for the ORR to occur due to the shrinkage of lattice parameters. Besides, forming nanoalloys also lower the cost of the expensive noble metal Pt.

➤ LASiS-GRR setup and mechanism



- ❑ Tandem laser ablation synthesis in solution-galvanic replacement reaction (LASiS-GRR) is a facile, green yet, efficient route for synthesizing binary/ternary nanoalloys. An in-house designed multifunctional LASiS-GRR cell is used in the current study for the synthesis of PtCuCo ternary alloys as ORR catalysts. Briefly, a Co target is ablated by a 1064 nm pulsed laser in water with PtCl_4^{2-} and Cu^+ ions. A liquid-confined plasma plume expanding with extremely high temperature and pressure thermally vaporizes the metal target and initiates ultrafast propagation of cavitation bubbles. Seeding NPs within the bubble go through GRR with PtCl_4^{2-} and Cu^+ ions from the precursor salts to form Pt and Cu NPs. These NPs rapidly alloy with the Co NPs in the solution to form the NAs.

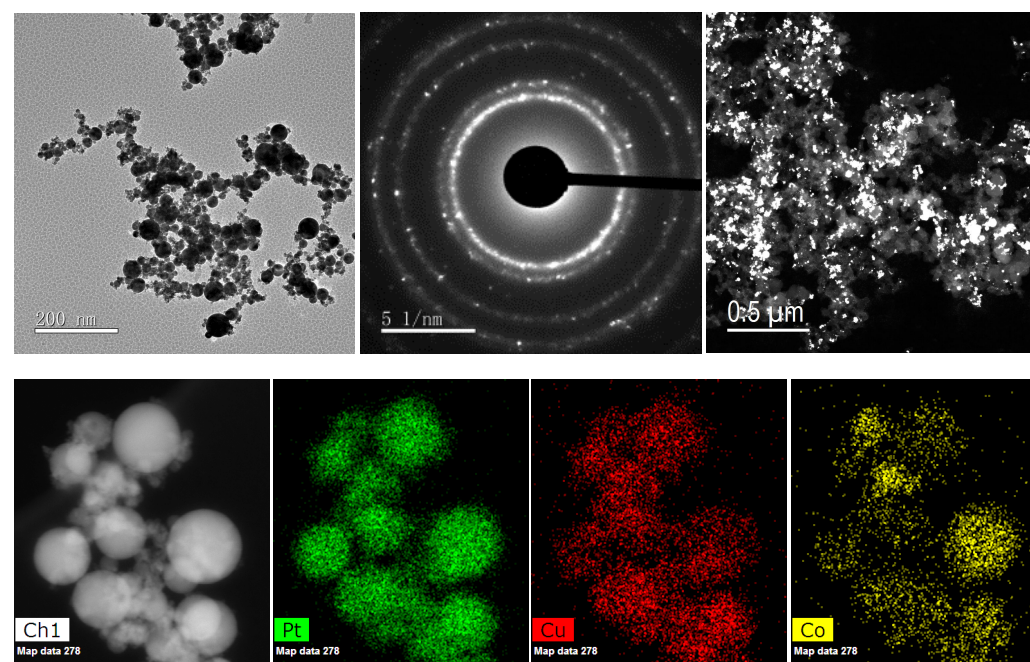


LASiS-GRR occurs when the redox potential of the target metal is less than the metal salts.

Redox Potentials
 $[\text{PtCl}_4]^{2-}/\text{Pt} = 0.755$
 $\text{Cu}^+/\text{Cu} = 0.52$
 $\text{Co}^{2+}/\text{Co} = -0.28$

Results

➤ Shapes and elemental distribution of nanoalloy (via Electron Transmission Microscopy (TEM))

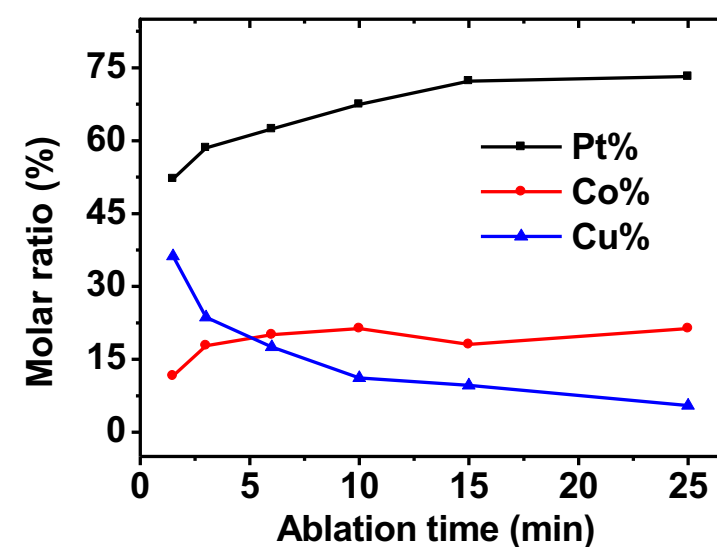


➤ Tuning of Pt:Cu:Co ratio

1. By changing CuCl salt concentration

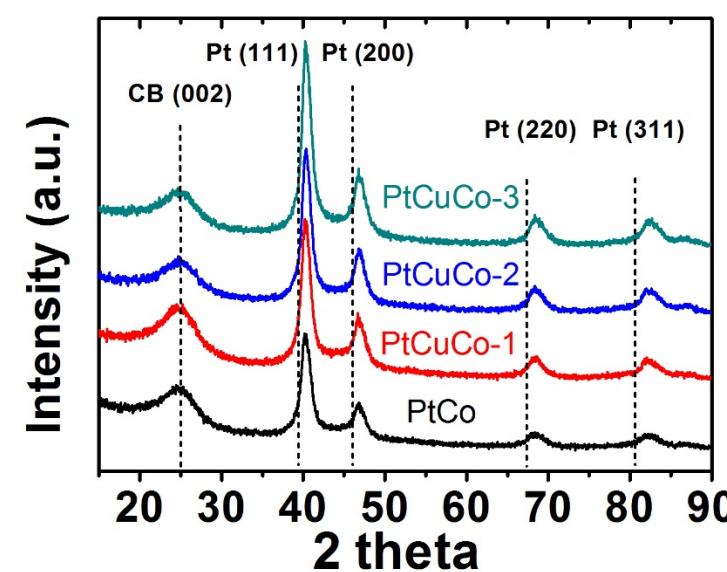
Tuning	Sample	K_2PtCl_4 (mM)	CuCl (mM)	Ablation time (min)	Pt%	Co%	Cu%
CuCl salt	PtCo	0.3	0	6	77	23	0
	PtCuCo-1		0.03		70	24	6
	PtCuCo-2		0.12		67	15	18
	PtCuCo-3		1.92		66	11	23

2. By changing ablation time



The reduced Cu atoms will go through GRR with K_2PtCl_4 during ablation, therefore the Cu ratio decreases and the Pt ratio increases with ablation time.

➤ X-ray Diffraction



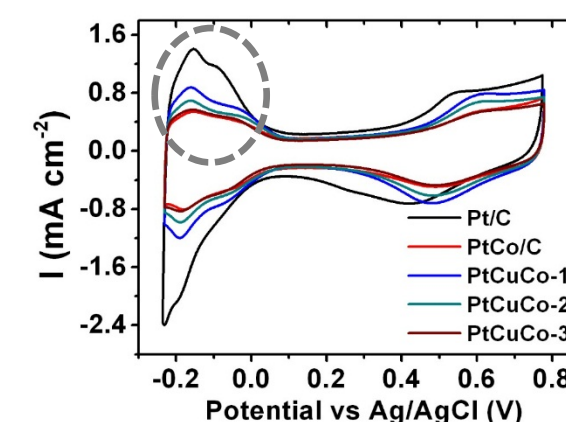
XRD patterns indicate a clear shift of PtCuCo characteristic peaks to higher angles. This indicates a shrinkage of lattice parameter of Pt due to the alloying of the three elements, as can be explained by the Bragg's law.

$$n\lambda = 2d\sin\theta$$

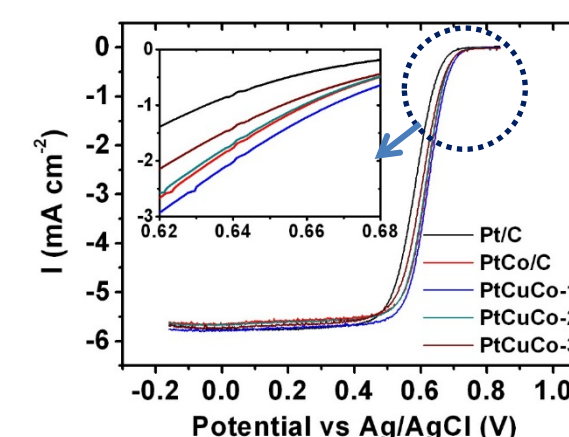
Results

➤ Catalytic activities: Electrochemistry Results

❑ Cyclic voltammetry curves



❑ ORR polarization curves



	Pt loading ($\mu\text{g}/\text{cm}^2$)	ECSA (m^2/g)	I_k at 0.9 V (mA/cm^2)	MA (A/mg)	SA (mA/cm^2)
Pt	25	38.32	1.84	0.07	0.19
PtCo	22.93	17.36	5.03	0.22	1.26
PtCuCo-1	22.09	28.13	6.06	0.27	0.98
PtCuCo-2	21.63	23.28	4.72	0.22	0.94
PtCuCo-3	21.46	18.04	3.43	0.16	0.89

- ❑ Cyclic voltammetry compares the electrochemical surface areas (ECSA) for the synthesized PtCuCo ternary alloys through the hydrogen adsorption/desorption area.
- ❑ ORR polarization curves indicate that all synthesized NAs outperform the catalytic activities of commercial Pt/C.
- ❑ While binary PtCo NA indicates the best specific activity (SA), the ternary PtCuCo-1 NAs exhibit the best ORR mass activity (MA).
- ❑ The superior MA and SA for the as-synthesized ternary PtCuCo NAs can be attributed to the green synthesis technique of LASiS-GRR that uses no harsh chemicals and surfactants that are known to be detrimental to surface catalytic activities.
- ❑ Finally, elemental ratios in the alloy can be readily tailored for optimizing the O/OH⁻ adsorption energies and therefore achieving the best catalytic performances.

Summary

- ❑ We develop LASiS-GRR as a facile, green synthesis technique for the synthesis of ternary PtCuCo NAs with tailored composition and alloying as excellent ORR catalysts.
- ❑ The combination of Cu and Co as non-precious transition metals showed promising results in lowering Pt % (wt.) while enhancing the catalytic activities, which is ascribed to the modified O/OH⁻ binding energies and increased surface sites due to alloying.

References

1. S Hu, G Goenaga, C Melton, TA Zawodzinski, D Mukherjee. **Applied Catalysis B: Environmental** 182, 286-296.
2. S Hu, M Tian, EL Ribeiro, G Duscher, D Mukherjee. **Journal of Power Sources** 306, 413-423.
3. S Hu, C Melton, D Mukherjee. **Physical Chemistry Chemical Physics** 16 (43), 24034-24044.

Acknowledgement: Partial support for Kangmin Cheng comes from the **Center for Materials Processing (CMP)**.