

# Efficient palladium recovery and catalyst development from electroplating wastewater using functionalized carbon materials

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### Significance and Relevance

The study demonstrates an innovative approach for recovering palladium (Pd) from electroplating wastewater using functionalized carbon materials, such as carbon black and graphene. These materials, modified with a pyrimidine TREN derivative, exhibit high Pd recovery rates (up to 97% within 24 hours) under eco-friendly conditions. The recovered Pd forms hybrid materials that serve as efficient catalysts for the Oxygen Reduction Reaction (ORR) in alkaline media, achieving a catalytic activity comparable to commercial platinum electrodes. This work is novel in combining wastewater recovery with the production of cost-effective, sustainable electrocatalysts, promoting circular economy principles.

*Preferred and* 2<sup>nd</sup> *choice for the topic:* Water treatment; Sustainable and clean energy production and transport

Preferred presentation: Oral preferred or Short Oral

## **Introduction and Motivations**

The study addresses the dual challenges of resource sustainability and industrial wastewater management, focusing on palladium (Pd) recovery from electroplating processes. Precious metals like Pd, critical for industrial and green technologies, face supply limitations and high costs, necessitating efficient recovery methods<sup>1</sup>. Traditional approaches are energy-intensive and often unsuitable for low-concentration solutions<sup>2</sup>. Electroplating rinse waters, typically neglected, offer a valuable recovery opportunity, aligning with circular economy goals<sup>3</sup>. Functionalized carbon materials have shown promise in capturing and repurposing Pd, reducing waste while enabling the creation of effective catalysts for energy applications<sup>4,5</sup>.

#### **Materials and Methods**

Carbon black (CB) and graphene (G1) were functionalized with a pyrimidine TREN derivative (HL) to enhance Pd recovery. Recovery experiments used a Pd(II) solution (0.1 g/L) with functionalized and non-functionalized carbons, followed by quantification via MP-AES. Structural and chemical analyses included SEM, STEM, EDS, and XPS. Catalytic properties were assessed through electrochemical techniques (CV, LSV, and RRDE) in alkaline media. The materials were tested for their Oxygen Reduction Reaction (ORR) performance, focusing on parameters like onset potential, half-wave potential and the number of exchanged electrons.

#### **Results and Discussion**

The recovery of precious metals in the electroplating industry presents both economic and environmental challenges. While various methods have been proposed for treating spent electrolyte solutions, limited attention has been given to recovering metals from washing processes following metal deposition. This study focuses on evaluating the effectiveness of two carbon materials, CB and G1, in recovering palladium from washing water produced during electrochemical palladium



deposition. CB and G1 exhibit favorable properties for palladium recovery and catalyst production, including high surface area, reactive surface groups, and excellent electrical conductivity. The findings demonstrate a novel approach for palladium recovery from aqueous solutions while simultaneously developing low-cost materials for alkaline fuel cell catalysts. Additionally, the potential functionalization of CB and G1 with a pyrimidine TREN derivative ligand was explored. This ligand promotes palladium recovery through chemical complexation and creates heterogeneous single-atom catalytic sites. The functionalized materials showed catalytic properties comparable to those required for the Oxygen Reduction Reaction (ORR). Rotating ring-disk electrode tests revealed that the number of electrons exchanged per O<sub>2</sub> molecule was close to 4, indicating nearly complete conversion of O<sub>2</sub> to H<sub>2</sub>O. These promising results were achieved using heterogeneous catalysts containing only 5.21 wt% of recovered palladium, demonstrating the potential for advancing eco-friendly electroplating processes and developing efficient, low-content platinum-group metal (PGM) carbon-based catalysts.



**Figure 1** HAADF STEM images of raw carbon materials obtained after the recovery process of palladium. Pd nanoparticles are visible as bright spots, support coverage is very uniform.

## References

- 1. European Commission, Directorate General for Internal Market, Industry, Entrepreneurship and SMEs, *Publications Office*, **2020**, https://data.europa.eu/doi/10.2873/58081.
- 2. W. Giurlani et all, Sustainability, 2024, 16, 5821.
- 3. S. Massari, M. Ruberti, *Resources Policy*, 2013, 38, 36-43.
- 4. E. H. Sujiono et all, *Results in Chemistry*, **2022**, *4*, 100291.
- 5. M. Bonechi et all, *Catalysts*, **2021**, *11*, 764.

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