## Designing Gold Nanocluster Interfaces for Tailored Electrocatalytic Outcomes

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Atomically precise metal nanoclusters (NCs), particularly Au<sub>25</sub>(SR)<sub>18</sub> (AuNCs), are highly valuable in nanotechnology due to their unique quantum-size-related properties, defined stoichiometry, and discrete energy levels. This presentation explores the fundamental properties and diverse electrocatalytic and bio-hybrid applications of gold and gold-platinum clusters, emphasizing the crucial role of precise structural control and spatial organization on electrode surfaces.

We demonstrate that controlling the organization of Au<sub>25</sub>(SR)<sub>18</sub> clusters is paramount for optimizing their performance in the electrochemical CO<sub>2</sub> reduction reaction. Utilizing the Langmuir–Schaefer (L-S) method enables the fabrication of well-ordered two-dimensional (2D) assemblies on highly oriented pyrolytic graphite (HOPG) electrodes. We found that deposition at low surface pressures (10 mN/m) maximizes the catalytic efficiency, as proper dispersion minimizes aggregation, which otherwise buries active sites and decreases normalized activity. The inherent low activity of gold clusters toward the competing hydrogen evolution reaction (HER) facilitates high selectivity for CO<sub>2</sub> conversion.

Beyond surface catalysis, AuNCs are exceptional electron relays in bio-hybrid systems. Introducing neutral  $Au_{25}(SR)_{18}$  clusters into the outer leaflet of an insulating lipid bilayer (DPPTE/DOPC) on a gold electrode dramatically increases the electron transfer (ET) rate constant. This effect, observed even at concentrations as low as 0.01 mol%, proves that AuNCs function as "remote gold electrodes," restoring the reversibility of fast electrochemical probes across the barrier layer [1].

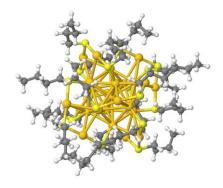


Figure 1: The structure of Au<sub>25</sub>(SC<sub>4</sub>H<sub>9</sub>)<sub>18</sub>.

Furthermore, the structural modification of the core, specifically doping with platinum to form  $Au_{24}Pt(SR)_{18}$  clusters, yields unique electrocatalytic properties. Thes clusters exhibit a strong electrocatalytic effect for the conversion (oxidation and reduction) of hydrogen peroxide ( $H_2O_2$ ). This enhanced activity, attributed to the interaction between the central Pt atom and the delocalized electron system of the gold core, permits the quantitative determination of in  $H_2O_2$  aqueous solutions with high accuracy, suggesting potential as single-use sensors for biological analysis [2].

These studies confirm that the functionality of gold nanoclusters and their doped variants is highly tunable through precise control of both their composition and, crucially, their spatial organization at the interface.

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## References

- [1] A. Wieckowska, E. Jablonowska, M. Jaskolowski, R. Bilewicz, J. Electroanal. Chem. 932, 117261 (2023).
- [2] K. Zdunek, A. Więckowska, J. Electroanal. Chem. 984, 119009 (2025).