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The COSY Working Group 3: "Confined Metal and Metal-Oxide Nanoparticles and Clusters Down to the Subnanometer Scale"

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We will present a report on the achievements of WG3 in the last Grant Period. WG3 has delivered a coordinated and high-impact research program advancing the fundamental understanding, predictive modeling, and application of atomically precise clusters and nanostructured materials across catalysis, energy conversion, optoelectronics, and biomedicine. Through tight integration of first-principles theory, machine learning, synthesis, and operando spectroscopy, WG3 has established robust structure-property-function relationships spanning subnanometer clusters to mesoscale assemblies.

A central focus has been the mechanistic role of size, support, and ligand effects in cluster catalysis. Size-selected Pt clusters on TiO_2 and SnO_2 revealed how metal-support interactions and size govern CO oxidation activity/stability (Valtera *et al.*, *Small Struct.*, 2025). MD simulations of Au nanoparticles demonstrated orientation- and support-dependent melting (Pavloudis *et al.*, *Small Struct.*, 2025). Ligand-protected Au nanoclusters exhibited support- and pretreatment-dependent selectivity in alkyne hydrogenation (Banu *et al.*, *Nanoscale*, 2025), while Cu-doped Au clusters showed how staple flexibility and partial deligation govern electrochemical CO_2 reduction (Ibáñez-Alé *et al.*, *Small*, 2024). Methane-to-methanol conversion over CeO_2 identified the cooperative role of water and oxygen in sustaining reactive hydroxyl species (Li *et al.*, *ACS Catal.*, 2025). $SrFe_{0.9}Mo_{0.1}O_{3-\delta}$ perovskite was demonstrated as a robust catalyst for nonredox water splitting (Anemone *et al.*, *Small Struct.*, 2025). At the atomic scale, DFT studies identified graphdiyne and boron-graphdiyne as platforms for single-atom/cluster catalysis (Sandoval Menjívar *et al.*, *Small Struct.*, 2026). High-level *ab initio* benchmarking clarified the electronic origins of fluxionality, linking Jahn-Teller distortions, conical intersections, and stability (Krupka *et al.*, *Small Struct.*, 2026), while systematic DFT studies of transition-metal tetramers and hexamers revealed cross-scale correlations between structural motifs, energetics, and "magic" patterns (Garcia-Alfonso *et al.*, *Small Struct.*, 2026). A defining contribution of WG3 lies in methodological innovation. Conformal sampling of catalytic processes achieved subchemical accuracy with high-throughput capability (Roongcharoen *et al.*, *J. Chem. Theory Comput.*, 2025; Melani *et al.*, *J. Phys. Chem. C*, 2025), enabling transferable MLIPs for alloy screening. Dispersion-corrected MLIPs accurately reproduced structural, thermodynamic, and dynamical properties of water and aqueous $MgCl_2$ (Ferretti *et al.*, *J. Chem. Inf. Model.*, 2025). Beyond catalysis, WG3 explored functional nanomaterials, e.g., Mn-doped perovskite supercrystals with spatially resolved emission (Dibenedetto *et al.*, *Small Struct.*, 2025); defect-engineered hybrid perovskites for enhanced electromagnetic wave absorption (Cai *et al.*, *Small Struct.*, 2025); tunable nonlinear optical response in perylene diimides (Skentzos *et al.*, *Mater. Adv.*, 2026); and iron oxide nanoclusters enhanced phosphate transport under dialysis conditions (Lucante *et al.*, *Small Struct.*, 2026).

These results establish predictive, mechanistically grounded design principles for confined metal and metal-oxide nanostructures, bridging atomic-scale insight with functional performance in catalysis, materials science, and biomedicine.