Laser-Synthesised Cu, Ag, Au, and Al Nanoparticles for Catalytic Enhancement in Energy Accumulation Devices

Danishevskyi V.A., Hnilitskyi Y.M.
Lviv Polytechnic National University, 12 Bandery str., Lviv, 79013, Ukraine E-mail: vladyslav.a.danishevskyi@lpnu.ua

Recent advances in electrochemical energy storage have underscored the need for highly active and stable catalyst materials that can accelerate the redox processes in devices such as lithium-ion batteries, supercapacitors, fuel cells, and metal–air systems. Metal nanoparticles (NPs)—particularly copper (Cu), silver (Ag), gold (Au), and aluminium (Al)—have demonstrated considerable promise as catalytic additives or as primary catalyst components due to their large surface area, tunable surface chemistry, and capacity to foster faster electron transfer. By reducing reaction overpotentials and mitigating electrode degradation, these nanoparticles can significantly enhance both power output and cycling stability. However, their performance largely depends on the method of synthesis and the resultant purity and structure of the NP surfaces. This thesis investigates pulsed laser ablation in liquid (PLAL) as a "green" method for producing ligand-free Cu, Ag, Au, and Al nanoparticles, and highlights how these materials can improve electrochemical and catalytic reactions in energy accumulation systems.

Laser ablation of metals in a liquid environment (e.g. water, ethanol, organic solvents) has received growing attention for the creation of stable metal nanocolloids without chemical reducing agents or stabilisers [1]. In PLAL, high-intensity laser pulses (for instance, from a Q-switched Nd:YAG laser at 1064 nm, 7 ns pulse width) are focused onto a submerged metal target. The rapid heating causes a plasma plume, and its subsequent cooling in the surrounding fluid condenses vapourised metal into nanoscale particles. Crucially, PLAL bypasses the use of surfactants or capping ligands, so the resulting nanoparticles feature pristine surfaces—immediately available for catalytic applications. This process also enables control of particle size through the adjustment of laser fluence and repetition rate: shorter pulses and moderate fluences often yield smaller, more uniform nanoparticles, whereas higher fluence or longer pulses can yield larger or partly molten aggregates [2]. Additionally, the liquid medium plays a key role, influencing surface oxidation, colloidal stability, and eventual catalytic performance.

The primary goal is to produce and characterise Cu, Ag, Au, and Al nanoparticles by PLAL for catalytic enhancement in energy devices, focusing on how purity and nanoparticle morphology affect electrocatalytic performance in model systems. Specific aims include: (1) optimising laser ablation parameters (pulse width, energy, solvent choice) to minimise oxide formation and agglomeration in the colloids, (2) evaluating the structural and morphological properties of each nanomaterial via scanning electron microscopy (SEM) and X-ray diffraction (XRD), and (3) measuring the catalytic contribution of these nanoparticles in half-cell or full-cell configurations related to supercapacitors, Li–S batteries, Li-ion cells, and fuel cell electrodes. It is hypothesised that Cu NPs, especially if partially oxidised to Cu_2O, will offer strong interactions with sulphur-based redox species in lithium–sulphur batteries, while Ag and Au NPs may enhance oxygen reduction reaction (ORR) kinetics for metal–air or conventional proton-exchange membrane (PEM) fuel cells [3]. Al nanoparticles, though prone to oxidation, may function as reactive energy carriers or hydrogen producers when partially stabilised in organic solvents [4].

Targets of high-purity Cu, Ag, Au, and Al were immersed in glass cells containing deionisedwater or ethanol. A pulsed Nd:YAG laser (1064 nm, 7 ns, up to 200 mJ per pulse) was focused onto each target, producing intense plasma. The ablation continued for 15–20 minutes per sample, forming a distinct metal–colloid suspension with minimal sediment. Laser fluence and repetition rate were systematically varied to influence particle size distribution. The resulting colloids were stored for immediate use or further analysis.

After synthesis, small aliquots of each metal colloid were drop-cast onto silicon wafers and driedunder ambient conditions for SEM analysis. SEM images revealed predominantly spherical particles ranging from ~10 to 40 nm in diameter, depending on the laser parameters. Under certain conditions, copper exhibited core–shell structures (metallic Cu core with a Cu_2O shell), especially when ablation took place in water for prolonged periods [5]. Silver and gold nanoparticles presented narrower size distributions and less oxide contamination, consistent with their lower reactivity. Al nanoparticles, by contrast, were partially coated with an amorphous oxide/hydroxide layer, evidenced by a broad XRD peak at ~38° and a visible morphological "shell" in SEM micrographs. Figure 1 (not shown here) exemplifies the morphology of Ag nanoparticles, illustrating the uniform, spherical shapes achievable with moderate fluence.

XRD measurements corroborated the SEM observations: Ag and Au displayed sharp metallic peaks, while Cu and Al showed evidence of oxide phases. For copper, distinct Cu_2O reflections near 36–39° were evident, while Al revealed an additional broad feature indicative of Al_2O_3-like layers. Although these oxide components can impact catalytic behaviour, in some electrochemical settings (e.g. water–gas shift catalysis) such interfaces can be beneficial, creating active metal–oxide junctions.

Electrodes for supercapacitor testing were prepared by mixing carbon black with a small amount of PLAL-synthesised nanoparticles and pressing them onto current collectors. Cyclic voltammetry (CV) in a three-electrode cell revealed improved current response and somewhat higher specific capacitance when Au or Ag NPs were introduced, likely because the metallic nanoparticles facilitated charge transfer and possibly added pseudocapacitance. In lithium–ion half-cells (using Li foil as a counter-electrode), Cu-based electrodes displayed faster charge–discharge kinetics and better retention after 50 cycles than identical electrodes without Cu NPs. Additional experiments focusing on Li–S cathodes suggested that core–shell Cu/Cu_2O particles helped reduce the shuttle effect of lithium polysulphides, presumably by binding these species at the metal–oxide interface, thus increasing Coulombic efficiency [6]. Fuel cell catalysts tested in alkaline conditions showed that Ag NP-based cathodes achieved improved oxygen reduction reaction (ORR) activity over plain carbon or sputtered silver references. This effect is attributed to the high fraction of accessible active sites on the ligand-free Ag surfaces. Gold nanoparticles were similarly effective, yielding stable ORR currents in acidic media with minimal performance loss over hours of operation. Though cost is a concern for precious metals, their nanoscale usage can be minimised while maintaining catalytic benefits.

Al NPs ablated in water were quickly passivated by oxide/hydroxide, limiting immediate hydrogen output. However, ablation in low-polarity solvents (e.g. hexane) or doping with minor additives lowered oxide formation, leading to more reactive particles that could generate H_2 upon contact with moisture. The possibility of storing Al-based colloids or powders and releasing hydrogen on demand is noteworthy for portable or auxiliary energy systems [4]. Although such Al systems need further stabilisation and scale-up testing, the synergy between laser ablation control and chemical passivation might pave the way for safer, more efficient hydrogen generation strategies.

The data confirms that PLAL yields **clean-surface** metal nanoparticles (Cu, Ag, Au, Al) in stable colloidal form with minimal residual contaminants, which are directly applicable to electrochemical energy storage devices. Surfactant-free NPs often display higher catalytic activity than chemically synthesised analogues, owing to unobstructed active sites [1]. Here, $Cu–Cu_2O$ core–shell structures enhance Li–S battery performance, Ag and Au show promising ORR activity for fuel cells, and Al exhibits potential as a reactive energy carrier if managed to minimise extensive oxide formation. Further refinements, such as applying external electric or magnetic fields during ablation, or selecting more inert solvents, can shift particle size distributions and modulate oxide layers, customising the NP surfaces for targeted applications.

Subsequent work will focus on producing bimetallic nanoparticles (e.g. Au–Cu, Ag–Al) via co-ablation or sequential ablation and examining their synergy in catalysis. Additionally, advanced in situ techniques (fast optical diagnostics or small-angle X-ray scattering) could be employed to capture real-time particle formation dynamics, guiding improved parameter selection. In terms of scale-up, continuous-flow PLAL reactors are under development to produce gram-scale yields, critical for bridging the gap between laboratory results and commercial viability. Overall, these findings highlight PLAL as a robust, eco-friendly approach for generating metal-based nanocatalysts that facilitate key electrochemical reactions in sustainable energy technologies.

Acknowledgements. This work was supported by NOVINANO LAB Ltd., Laboratory of Nanotechnology.

1. Forsythe, R.C. et al. Nanoparticle Catalysts by Pulsed Laser Ablation in Liquid for Catalysis and Energy. Chem. Rev. 2021, 121, 7568–7637.
2. Rao, S.V.; Podagatlapalli, G.K.; Hamad, S. Ultrafast Laser Ablation in Liquids for Nanomaterials and Applications. J. Nanosci. Nanotechnol. 2014, 14, 1364–1388.
3. Fajín, J.L.C.; Illas, F.; Gomes, J.R.B. DFT Study of Synergistic Catalysis of the Water–Gas–Shift Reaction on Cu–Au Bimetallic Surfaces. ChemCatChem 2016, 8, 1208–1217.
4. Czech, E. & Troczynski, T. Hydrogen generation via massive corrosion of deformed Al in water. Int. J. Hydrogen Energy 2010, 35, 1029–1037.
5. Zhang, D. et al. Laser Synthesis and Processing of Colloids: Fundamentals and Applications. Chem. Rev. 2017, 117, 3990–4103.
6. Lo Pò, C. et al. Cu-based nanocatalyst by pulsed laser ablation in liquid for water splitting: Influence of solvent on Cu/Cu_2O ratio. J. Phys. Chem. Solids 2024, 193, 112162.