Synthesis of Ag and Au Nanoparticles in Aqueous Solutions Mediated by Naturally Occurring Compounds in Common Sprouting Seed Exudates

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The potential biomedical applications of elemental Ag and Au nanoparticles comprising a metal nanocore (with at least one valuable dimension between 1 and 100 nm) encapsulated by an organic layer have attracted significant interest [1-4]. However, the environmental costs associated with existing chemical-reliant and energy-intensive synthesis routes, and the adverse repercussions of chemical residues on the nanoparticle surface could have on human health [5], make biological reductant and stabilizer more suitable agents in the fabrication of benign and affordable nanomaterials. Moreover, as is often the case, the inadequacy of one chemical to serve all functions (i.e. reductant, shape-guiding, and stabilizer), finds recipes calling for a mixture of compounds. For these reasons, our holistic approach harnesses the synergistic effect of naturally occurring phytochemicals (i.e. exudates) discharged by common sprouting seeds during imbibition, to reduce metal ions and subsequently forming metallic nanoparticles in aqueous solutions. This method is more favorable from an environmental and economical point of view.

Rapid generation of spherical silver nanoparticles (Figure 1A) was achieved by mixing 0.01 M silver nitrate ($AgNO_3$) solution with crude alfalfa (*Medicago sativa*) seed exudate at 30°C under non-photomediated conditions. The reaction reached completion in 2.25 h, comparable to the kinetic rates of wet chemical reduction methods. Interestingly, simple dilution of the seed exudate with deionized (DI) water prior to reaction led to the formation of some silver nanoparticles with triangular shape (circled in red in Figure 1B) ranging between 85.6 and 108.0 nm in edge length. A typical selected area diffraction (SAED) pattern of the triangular silver nanoparticle is depicted in Figure 1C, verifying its single crystallinity. The three sets of spots (box, circle, triangle) could be assigned to {220}, {422}, and the forbidden 1/3{422} planes of face-centered cubic (FCC) silver crystal on the basis of their d-spacings. The six-fold symmetry of the diffraction spots is a clear indication that the surface was highly oriented in the [111] direction, consistent with previous studies on silver (and gold) nanocrystals bounded by atomically flat surfaces [5-6].

Gold nanocrystals of similar anisotropic morphology could also be fabricated by similar approach described above. Subjecting 0.01 M potassium tetrachloroaurate ($KAuCl_4$) with lentil (*Lens culinaris*) seed exudate yielded an appreciable number of triangular shaped gold nanoparticles with edge length of less than 100 nm (Figure 2A). The corresponding SAED pattern (Figure 2B) shows intense circular rings corresponding to the {111}, {200}, {220}, and {311} planes revealing a high crystalline structure with FCC phase [7].

Our findings provide evidence of the reducing, shape-directing, and stabilizing activities of the concoction of phytochemicals in *M. sativa* and *L. culinaris* seed exudates. Simple modulation of reactant strength by dilution had a profound effect on the final product, which allowed a degree of control over nanoparticle size and shape.

References

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Figures

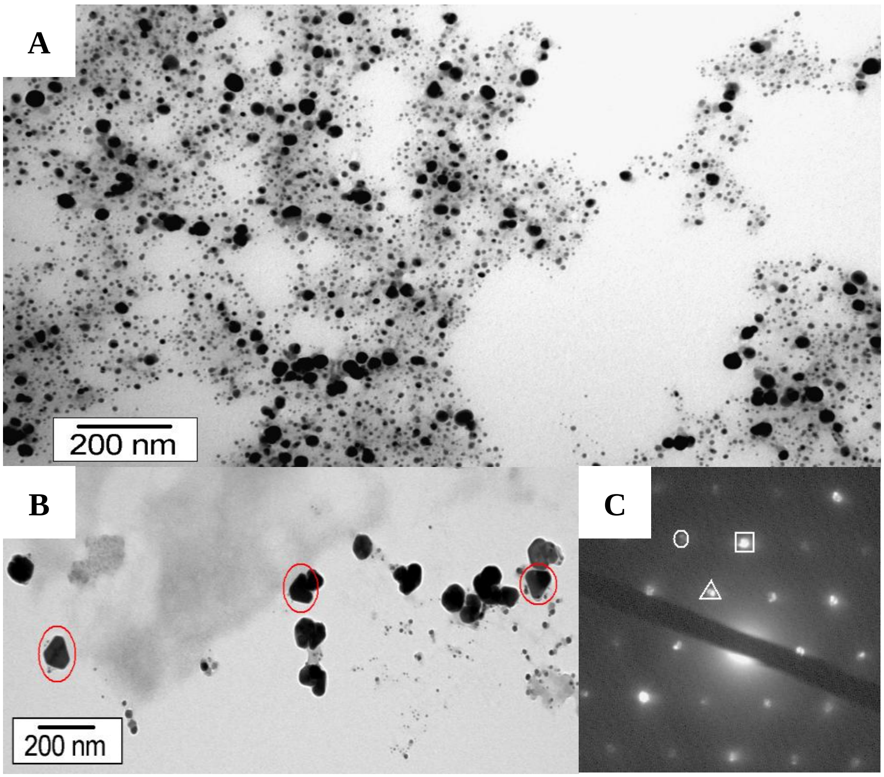

Figure 1. Representative transmission electron images of the silver nanoparticles of A) spherical and B) triangular shape synthesized by the reaction of 0.01 M $AgNO_3$ with crude and diluted aqueous alfalfa (*Medicago sativa*) seed exudate, respectively, in the dark at 30°C. C) The corresponding selected area diffraction (SAED) pattern of a triangular shaped nanoparticle with the boxed, circled, and triangular spots ascribed to the {220}, {422}, and the forbidden 1/3{422} reflections, respectively.

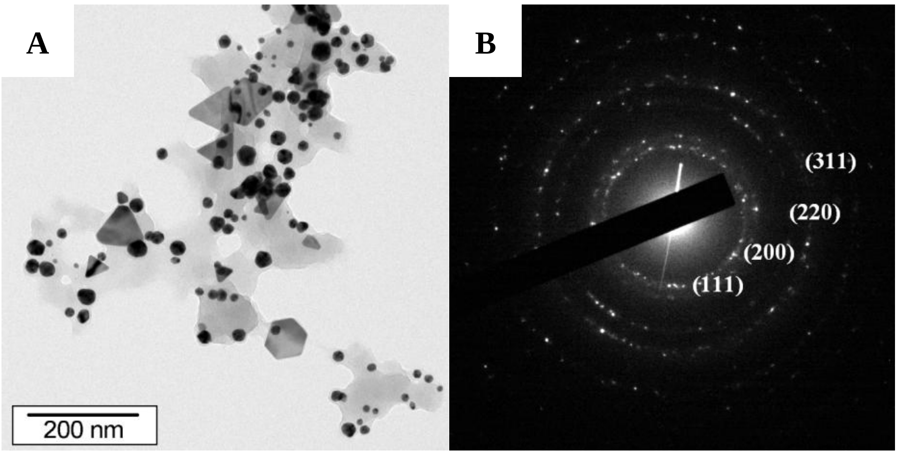

Figure 2. A) Representative transmission electron image of the gold nanoparticles generated from the reaction of 0.01 M $KAuCl_4$ with green lentil (*Lens culinaris*) seed exudate in the dark at 30°C and B) the respective SAED pattern showing {111}, {200}, {220}, and {311} reflection rings.