What is the reason why gold nanoparticles synthesized by Laser Ablation in Liquids are stable?

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Laser ablation liquid (LAL) is an alternative technique for forming metal nanoparticles (NPs) in solution.[1] LAL involves focused laser pulsed irradiation of a bulk metal target in a liquid. Due to the absence of capping agents and of chemical precursors, LAL is environmental friendly and has an easy set-up. Fundamental studies have been focused on the impact of the laser-induced plasma induction and of the cavitation bubble generation in the nucleation processes leading to the formation of NPs.[2] At variance, the stability of the NPs generated by LAL is still an open issue. The Hamaker constant for gold in water is close to 100 k_bT and, in absence of any capping layer, Au NPs should be totally instable. On the contrary, "naked" gold NPs prepared by LAL are stable for months. Nowadays it is assessed that such a stability is due to a strong negative Z-potential but the origin of the surface negative charges is still matter of debate. Some authors ascribed the negative charge to the presence of partially oxidized gold species (AuO^- and $AuCO_3^-$).[3] However, the presence of oxidized gold species for NPs prepared in pure water has been questioned by others [4]. Recent investigations, suggest that the negative surface charge density is dominated by ion adsorption and not by surface oxidation.[5]

To clarify this issue, we have undertaken a systematic study synthesizing Au NPs through LAL using as liquid phase deionized water and aqueous solutions of salts, acids and bases. Synthesis in HCl (pH=4), NaOH (pH=10) and NaCl (10^{-4} M) results in stable NP with the same size (10 nm in diameter) while the Z-potential has a very weak dependence on the pH passing from about -45 mV at pH=3 to about -55 mV at pH=10. Also the nature of the acid has negligible effect on the NPs features (HCl, HNO_3 and H_2SO_4 lead to indistinguishable NPs). Experiments with pH indicators demonstrate that the procedure of LAL is associated with an increase in the pH of the starting solution.

The reason for the NPs stability will be discussed tacking into account their reactivity immediately after the generation in the plasma medium.

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