

# From liquid conversion to nanoparticle synthesis by submerged spark discharges.

H. Kabarra<sup>1</sup>, C. Noël<sup>2</sup> and T. Belmonte<sup>2</sup>

<sup>1</sup>Université de Lorraine, Institut Jean Lamour, UMR CNRS 7198, NANCY, F-54011, France

<sup>2</sup>CNRS, Institut Jean Lamour, UMR CNRS 7198, NANCY, F-54011, France

Keywords: Spark discharges, dielectric liquids, nanoparticles, chemicals

Presenting author email: Thierry.Belmonte@univ-lorraine.fr

The utility of submerged discharges to create original molecules has been demonstrated by several groups – see *e.g.* (Oshima *et al.*, 2014) or (Cataldo, 2004).

It is well-known that discharges in carbonaceous liquids like acetonitrile, n-hexane or methanol for instance lead to the synthesis of nanoparticles that have compositions varying from hydrogenated amorphous carbon to diamond.

Submerged spark discharges transform liquid molecules into by-products that can further react to create new molecules, clusters and nanoparticles. However, till now only little is known about chemical processes in these media that are far from equilibrium.

In the sketch of processes that succeed during one discharge event, one finds (i) dielectric breakdown, (ii) shockwave emission, (iii) streamer propagation, (iv) transition to spark and (v) bubble oscillations.

Chemical transformations induced by the shock wave might contribute significantly to liquid modifications, the part of the energy released in the shock wave being relatively large, typically from 20 to 40% of the deposited power for nanosecond pulsed plasmas, the rest being essentially dissipated as thermal energy. However, to the best of our knowledge, no study was devoted to this question till now.

At the beginning, matter must be almost fully ionized. The streamer propagates in a straight line till electrodes are connected. The gas ionization degree decreases and the high pressure is so high that the liquid is repelled outside the plasma volume. Then, the plasma volume expands isotropically.

Sano *et al.* (2008) showed that a specific interface exists between the plasma and the liquid phase. Based on observations performed in microgravity conditions, they found out that a gas film is generated in the gas phase at the gas–liquid interface, and this film acts as a barrier between the two phases, limiting reactions between species of each domain.

The specific structure of the plasma-liquid interface, where huge gradients prevail, is responsible for the synthesis of specific molecules with limited chain lengths. Recently, Wagener *et al.* (2013) resorted to small angle X-ray scattering to study *in situ* the dynamics of nanoparticles synthesized by laser ablation. Just after the plasma pulse, two populations of particles are formed: primary particles with sizes in the range 8–10 nm and agglomerates with sizes in the range 40–60 nm. Only a weak fraction of primary particles are transferred into the liquid after the first rebound. On the other hand, agglomerates strongly increases in number density during the first bubble collapse and the following

rebound. Most of the nanoparticles are trapped inside the bubble and follows its oscillation, even before its final collapse.

Electrode erosion contributes to producing nanoparticles and this combines with liquid transformation. In figure 1, we show a surprising example where a core-shell Al@C nanoparticle is partly oxidized in air, the shell being not completely protective.

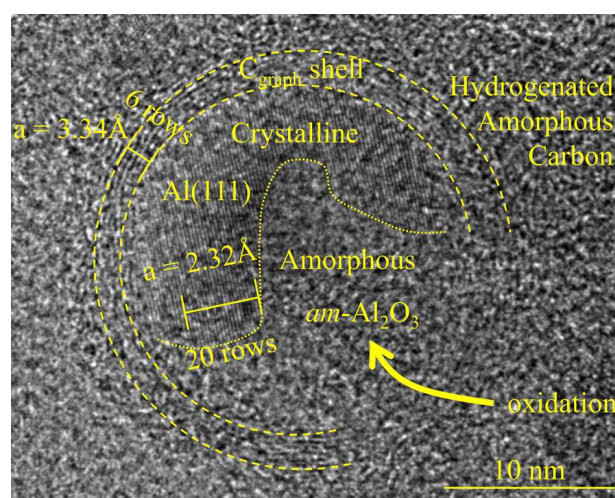


Figure 1. Half-oxidized Al nanoparticle synthesized in heptane. A graphite shell coats partly the Al nanoparticle. The uncoated part is transformed into amorphous alumina by air oxidation of the raw Al nanoparticle.

We cannot exclude that a metallic nanoparticles expelled from the plasma at high temperature might contribute to catalytic transformations of the liquid. In figure 1, whereas carbonaceous nanoparticles from the liquid are hydrogenated amorphous carbon, the carbon shell is here made of graphite. This argues in favour of specific chemical processes driven by nanoparticles from electrodes. However, this aspect has hardly been studied to date.

Cataldo F. (2004) *Carbon* **42**, 129.

Oshima F., Stauss S., Inose Y., Terashima K. (2014) *Jap. J. Appl. Phys.* **53**, 010214.

Sano N., Kawanami O., Charinpanitkul T., Tanthapanichakoon W. (2008) *Thin Solid Films* **516**, 6694.

Wagener P., Ibrahimkuty S., Menzel A., Plech A., Barcikowski S. (2013) *Phys. Chem. Chem. Phys.* **15**, 3068.