Laser synthesis of ultra-small Fe nanoparticles influenced by various liquid environments

Ondřej Havelka (ondrej.havelka@tul.cz), Rafael Omar Torres-Mendieta

In this work, laser fragmentation in liquids (LFL) is exploited to produce highly pure and stable iron ultra-small nanoparticles (NPs). The versatile synthesis is done by reducing the size of carbonyl iron microparticles in different solvents. The final colloids include 3 nm in size Fe-based (Fe, FeO_x or FeC) NPs with high Zeta potential value. The whole process avoids chemical waste generation or hazardous chemicals use, and thus, the described methodology represents a green chemistry alternative to all wet chemical methods. Besides, the lack of ligands on NPs' surfaces can be advantageous for applications, which requires many chemically active sites, e.g., catalysis.

Key words: Fe-based nanoparticles, ligand free nanoparticles, zero valent iron, particle stability, LFL

Introduction

In recent years, great progress has been made in the field of advanced NPs research. Unfortunately, many toxic and dangerous chemicals have been used during their production [1]. The scientific community is now concerned with finding alternative methods for nanomaterials synthesis. Laser fragmentation in liquids is one way to sustainably prepare NPs. Besides, the LFL represents the unique method, which enable production of even NPs below 10 nm size.

The nanomaterials that can be produced by LFL should exhibit also other interesting features compared to the chemical way prepared counterparts. The uniqueness comes from their ligand-free surface and versatility in liquid environment choice for production of NPs [2]. As the best benefit coming from it, the NPs can be used for many possible applications. Especially, in the case of iron NPs, the widely known applications are catalysis [3], magnetorheology [4], targeted drug delivery [5].

Methodology

The prepared samples consisted of 10 mL of each solvent and 0.4 mg / mL of carbonyl iron microparticles with a nominal size of 2 um. The prepared colloids were irradiated by a ns pulsed laser at a 527 nm central wavelength. According to the Pyatenko model calculations, the selected fluence value surpass the full evaporation threshold of iron microparticles [2]. The irradiation took place according to the experimental architecture displayed in the Figure 1.

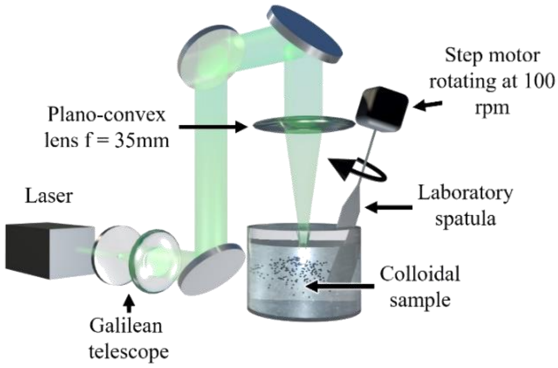

Figure 1: Scheme of iron colloid nanofabrication, Source: Under an open access CC BY license [2]

In brief, the LFL mechanism in our case consists of focusing a pulsed laser beam into a colloid composed of microparticles immersed in a liquid medium, in order to reduce the particle size. And in our case, the size reduction is prompted by photothermal vaporization. In this process, the energy absorbed by the particles is distributed through their whole electronic lattice, promoting their heating, melting, and further surface evaporation.

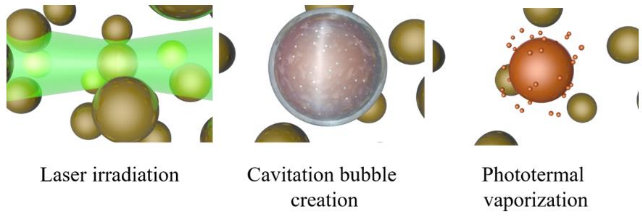

Figure 2: Scheme of photothermal vaporization mechanism, Source: author Ondrej Havelka

Results and discussion

The generated particles can be found in different forms, such as ultra-small NPs as it is in the case of ethylene glycol sample (Figure 3), or ultra-small NPs together with zero-valent iron, iron carbide, or iron oxide NPs in matrices, depending on the employed solvent and its dipolar moment (Figure 4).

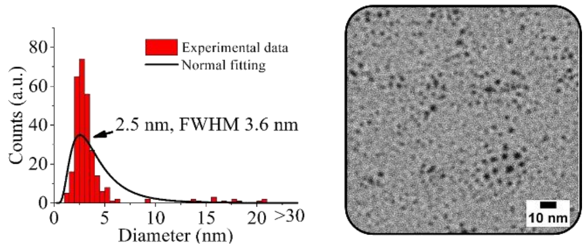

Figure 3: Ultrasmall iron NPs prepared, Source: Under an open access CC BY license [2]

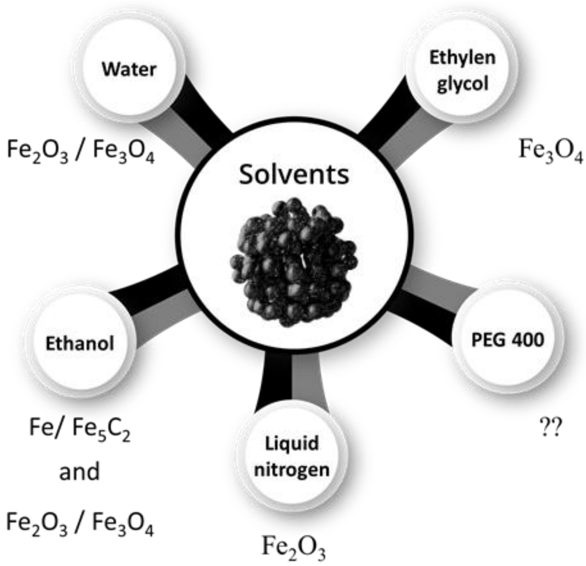

Figure 4: Chemical composition based on XPS and SAED analysis, Source: author Ondrej Havelka

Conclusions

In summary, the research proves that the methodology of laser fragmentation in liquids (LFL) can be employed to synthesize ligand-free ultra-small iron NPs in solvents with different dipolar moments. The solvents with a high dipolar moment, such as ethylene glycol or polyethylene glycol 400, possess the optimal parameters for producing highly stable colloids composed of the largest amount of ligand-free ultra-small iron NPs.

Moreover, it also reveals that the solvent's selection can enable precise control over the nanomaterial's chemical structure and production rate. Since this work brings new insights to the waste-free production of extremely small materials with controlled surface and composition, the current findings will be of fundamental interest to the scientific community involved in the materials and nanoscience fields.

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