Submerged Microplasma Jet in Microwells with Particle Beds – Synthesis of N-doped Carbon Quantum Dots

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Abstract: N-doped carbon quantum dots are synthesised by immersing a microplasma jet into a gas–liquid reactor of the size of a microwell, containing an aqueous solution of folic acid (Vitamin B9). Three studies are reported here [1-3]. The first study concerns the bulkand surface-analytical characterization of the quantum dots for a rational material design [1]. The second study is about the engineering of the plasma process to achieve process intensification of the synthesis and demonstrates nanomaterial purification [2]. We discovered a bespoke hydrodynamic formation of the plasma-liquid-solid interface under operating conditions; both in presence of a solid interface (metallic bed or glass beads) or without. The third study aimed at fundamental understanding of the hydrodynamic profile of the plasmaliquid interface, discovered in [2], and varies systematically process conditions to decipher mass transfer and kinetic effects [3]. This last study aims also to answer the question if catalytic effects arise from the solid metal alloy material forming the bed.

Keywords: plasma jet, submerged jet carbon quantum dots, multiphase processing, hydrodynamics

1. Motivation: intensifying plasma-liquid reaction

The key issue around plasma and plasma catalysis is the short lifetime of the active species. This hampers especially the effectiveness of plasma-actived multiphase reactions, as additional mass transport issues arise.

At best, the plasma phase is in direct contact with the catalyst, rendering superfluous any matter transport. Yet that may deteriorate the catalyst by thermal action or cause abrasion, and even then, a major part of the plasma phase will remain as unused bulk volume. Rather than using a pure plasma gas phase, we investigate here plasma in presence of a small liquid volume hold by a microwell, in which a catalyst might be immersed as packed bed. The liquid solution is the reaction medium containing the reactant molecule (to be converted with or without a catalyst). In all three studies [1-3], we have used a submerged microplasma jet that triggers the gas–liquid reaction with or without bed of metal particles. The reaction investigated produces N-doped carbon quantum dots (NCQD)

2. N-doped carbon quantum dots – nanomaterial characterization (study I, [1])

N-doped carbon quantum dots (NCQD) were rationally designed and synthesised, for the first time, from folic acid (Vitamin B9) by a non-thermal microplasma jet [1]. A new conceptual design was developed to synthesise the desirable NCQD for three main applications (nanopesticides, water purification, and theranostic treatment). The structural and analytical characterisation confirmed an average size of 3.1 nm for the synthesised NCQD with the multi-functional groups (-OH, –COOH, –NH₂) on their surface. The TEM results indicated that the core of NCQD was a multilayered structure, including single defected graphene sheets of graphitic-nitrogen and pyrrolic-nitrogen. In addition, fluorescence performance and stability of the as-prepared NCQD were determined. The quantum yield

of NCQD was 35%, which is relatively high, with a strong blue fluorescence. A basis for predicting colloidal behaviours based on balancing molecular attractive and repulsive forces was elucidated by applying the Derjaguin, Landau, Vervey, and Overbeek (DLVO) theory. Finally, compared with other similar microplasma-assisted synthesis processes, this developed method has proven the ability to provide a tailored and scalable synthesis process of high-quantum-yield NCQD at gram-scale production.

3. Process intensification of the plasma-liquid process (study II, [2])

Process intensification of the submerged-plasma process to NCQD was achieved by varying the distance of the tip of the microplasma jet to the water surface in three steps, named distant, contact, and deflection modes. As a further variation, the liquid volume was either stirred or unstirred and may contain glass beads or metal flakes. In this way, the mass transfer, hydrodynamics, and the electrical field are influenced and define the specific gas-liquid interface, possibly including plasma-catalytic effects. A thermosfluidic analysis confirmed a uniform temperature profile and a positive temperature effect on the mass transfer. In this way, the research demonstrated notable process intensification, elevating the synthesis towards 1 g nanoproduct per day, while maximising the intended performance, the photoluminescence intensity. Recycling of the nanomaterial allowed to further increase the mass yield via reusing it for synthesis up to five times. A pure NCQD product was achieved by a combined precipitation-dialysis purification approach. An analysis by optical emission spectroscopy reveals the formation of the plasma species from which a reaction mechanism is proposed.

4. Reaction system characterization of bespoke plasmaliquid hydrodynamics with or without solid bed (study III, [3])

Triphasic plasma systems in literature, alike the one we used, are not well designed and understood. The third study aims at fundamental investigation of the principal effects in the plasma-activated triphasic catalyst system, used in the studies I and II for NCQD synthesis; to decipher reaction (kinetic) and mass transfer effects. Kinetics and mass transfer play a critical role in many chemical reactions and are essential for the cost and environmental profile of processes derived from the reactions.

We monitored and documented changes in the abovementioned bespoke plasma-liquid hydrodynamic regime, upon variations of the operating conditions; especially how the almost flat, large specific interface of the thin liquid layer changes, with or without a (catalyst) bed underneath. The solution properties were systematically varied concerning the density, polarity, surface tension, and viscosity; by adding ingredients to the aqueous solution. In this bespoke, plasma-activated hydrodynamic regime, plasma can penetrate to the catalyst bed via the thin liquid film and polarize the plasma-liquid interface.

We monitored reaction rate for the different hydrodynamic regimes. The results show that the reaction rate is determined by the diffusion of the vitamin B9 reactant in the aqueous solvent and by the interfacial area. This confirms our hypothesis that the formed thin liquid layer, by compression of the microplasma jet, is the effective reaction medium (and not the bulk liquid volume); acting as a 'microreaction zone'. This thin layer can be stabilised by wetting a particle bed underneath (metal alloy flakes, glass beads). Results are also indicative of an electrocatalytic effect of the alloy flakes.

5. Acknowledgement

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6. References

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