Evidence of nanoparticle catalyst reorganization and enhanced NH3 yield with a ns-pulsed tube-to-plane DBD in N2:H2

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Abstract: We investigate the gas conversion performances and reorganization of metal nanoparticle films on the dielectric of a tube-to-plane ns-pulsed DBD for NH_3 synthesis. Metal deposition is controlled to form three structures: sparse nanoparticle coating, thin (t<50 nm) and thick conformal metal nanoparticle films (t>50 nm). The coatings increase power delivery to the bulk plasma, while heavier loaded samples undergo surface reorganization forming fractal structures up to 700 nm in height with accompanying higher NH_3 yields.

1. Introduction

The study of plasma-catalytic gas conversion processes in dielectric barrier discharges is traditionally performed using a combination of non-invasive optical emission spectroscopy paired with kinetic modelling. Another approach to this problem involves the simplification of a reactor configuration to a diagnosable analogue with consideration for retaining reactor properties of interest. A single-pellet reactor [1] provided insight on interfacial effects near the edge of catalytic pellets contributing to both plasma enhancement and energy deposition. Recent work evidenced that the plasma-catalyst interactions may lead to enhanced catalytic activity, but possible plasma-induced physical rearrangement and chemical changes haven't been studied. This work implements a strategy with a 2D axisymmetric dielectric barrier discharge allowing to study the effects of metal nanoparticle loading and restructuring under the action of the discharges on gas conversion performances in N_2-H_2 mixtures for NH_3 synthesis.

2. Methods

Various Fe nanoparticles-loaded quartz discs (t=1/16") were prepared via pulsed laser ablation in a low pressure (10^{-5} Torr) Ar environment. The fluence of the 10 Hz Nd-YAG laser (355 nm) was held constant (~122 mJ mm^{-2}). The samples were prepared through a variation in laser shot counts (n_{shots}) to control the formation of three different coatings: sparsely nanoparticle-coated, clustered non-conductive metal nanoparticle films under 50 nm, and thicker nanoparticle coatings forming a conductive surface. The samples formed an electrode of an atmospheric pressure 1:1 molar ratio N_2:H_2 DBD sustained with a dual-polarity nanosecond pulser operating at a 3 kHz pulse repetition frequency (PRF). The quartz substrate served as dielectric barrier between a fixed metal bottom electrode and a stainless-steel tube electrode separated by 300 μm from the thin film surface (**Fig. 1a**). The processing gas was fed directly through the tube electrode, maximizing plasma exposure.

3. Results and Discussion

Energy deposition per pulse into the plasma at similar pulser operating conditions for highly-loaded samples (n_{shots} > 2000) increased (900 +/- 34 μJ) relative to blank quartz discs (675 +/- 12 μJ) (**Fig 1c**.). Thinly-coated (500 ≤ n_{shots} ≤ 2000) samples made minor improvements to the energy per pulse delivered to the discharge (702 +/- 18 μJ). Transient measurements of the power deposition for surface-conductive samples showed an increase in discharge power by up to 40 % over a timespan of 5-10 min. Optical microscopy of these samples revealed fractal structure formations (**Fig. 1b**) on the surface with measurable heights up to 700 nm. These structures, akin to Lichtenberg figures, are characteristic of increased surface charging and demonstrate a surface reorganization past a critical current density.

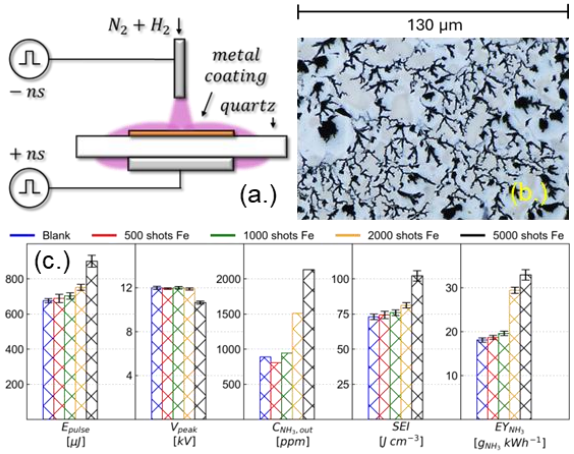

Fig. 1. Setup (a.) and resulting fractal surface structure (b.) formed from a heavily loaded (5000 shots) quartz disc after exposure to the ns pulsed N_2-H_2 DBD for 50 min. Improvements in power deposition and gas conversion performance were observed for fully-coated samples (c.).

4. Conclusion

Varied plasma-catalytic conditions were obtained with metal nanoparticle coatings exposed to an atmospheric pressure ns-pulsed N_2-H_2 DBD. Increases in NH_3 yields were observed in correlation with the increasing plasma energy deposition. Plasma-induced surface modifications hint at a contribution of improved surface conductivity to discharge intensity and gas conversion.

References

[1] T Butterworth and R W K Allen 2017 *Plasma Sources Sci. Technol.* **26** 065008.