Planar Gliding Discharge as a Tool to Study Spatially-Distributed Plasma Chemical Surface Modifications

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Abstract: A versatile planar gliding discharge setup was used to study the spatial distribution of plasma-induced chemical changes on boron nitride nanotube surfaces exposed to argon, nitrogen and air gliding discharges. The results reveal the spatial distribution of the extent of chemical modification, with the boron nitride ratio increased from 1.25 to a high of 8.1. The hydrophilicity increased throughout the surface with the increased B:N ratio.

1. Introduction

Plasmas are gaining attention for the electrification of the chemical process industry, and with gas conversion applications specifically. With in-plasma catalysis, the substrate supporting the active metal catalyst is directly exposed to the active plasma. The plasma then plays multiple roles over multiple time scales, providing intermediate excited species, enabling adsorption and desorption of reactants and products, possible electric field induced catalytic enhancements, and so on [1]. Similar plasma conditions are used for surface modifications, thus leading one to suspect that plasma catalysis conditions are also prone to chemical surface modifications of the catalytic material and its support. A planar gliding discharge (PGD) setup makes it possible to accurately characterize substrate changes with spatial distribution. Boron nitride nanotubes were chosen due their known chemical stability at high temperatures. However, BNNTs are susceptible to chemical modification by plasma functionalization [2].

2. Methods

A planar gliding discharge (PGD) setup enabling the insertion of a catalyst layer has been designed. The electrode assembly consists of an initial diverging section followed downstream by a constant-gap section, providing means to study the spatial-temporal behavior of the gliding discharge from its inception to steady gliding, and plasma-induced surface chemistry changes. Ar, N₂ and air were used as plasma gases flowing at 2.5 SLPM. An AC source, typically operating at ~7 kHz, 7 kV_{peak} and 50 mA_{peak} was used (reduced electric fields of 5-15 Td). Boron nitride nanotube sheets (BNNTs) [3] were used as test surfaces. The surface chemistry changes were analysed by XPS, FTIR and contact angle measurements.

3. Results and Discussion

XPS measurements were performed on the BNNTs at different locations along the middle of the PGD setup. One observes a clear change of the surface atomic composition, with more pronounced changes in the upstream (diverging) section, plateauing in the constant gap region. N vacancies are created, leading to O incorporation upon re-exposure to air after experiment. The B:N ratio was used to assess the loss of nitrogen vacancies (Fig. 1). At location 2 with air, the chemical modification becomes more uniform in the

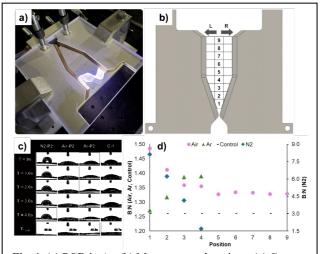


Fig. 1. (a) PGD in Ar. (b) Measurement locations. (c) Contact angle test at location 2. (d) Atomic % B:N ratio from XPS survey scans versus location and plasma gas composition.

constant gap region; the B:N ratio was 1.41 at location 2 and averaging 1.33 at locations 5-9. Every location analyzed had a B:N ratio higher than the control (1.26). Contact angle tests showed that the surface had become more hydrophilic than the control except for the N_2 at location 2 with a B:N ratio of 6.2 compared to 1.41 with air and 1.31 with Ar. FTIR and Hi-Res XPS analyses revealed the formation of B_2O_3 on the surface.

4. Conclusion

The PGD setup allows to investigate the spatial distribution of plasma-induced surface chemistry changes to a catalyst support. These initial results hint that plasma catalysis performances may be further optimized via the plasma-substrate interactions (e.g. possible surface modification for selective gas adsorption/desorption) in addition to the sought-after catalytic site activity.

References

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