

## Investigation of Reactive Atmospheric Pressure Plasma deposition of Nano-particulate Film

Yu Xu, Tao He, Yu Zhang, Chaoliang Wang, Ying Guo, Qinyu Yang,  
Ke Ding, Chengran Du, Jianjun Shi and Jing Zhang  
Department of physics, Donghua University  
email(speaker):jingzh@dhu.edu.cn

These years, nonthermal reactive atmospheric pressure plasma has attracted a lot of research attention for plasma enhanced chemical vapor deposition (PECVD) of films in a continuous way. The reactive atmospheric plasma is composed of charged particles and excited neutrals with high reactive energy. It can provide a unique environment for chemical reactions and film growth, which is distinct from the ordinary condensed chemical reaction driven by single hot source. All the reactions are far from chemical equilibrium and take place at low gas temperature. Much research has found dense or porous nanoparticulate films could be obtained and have similar structure with that deposited by vacuum PECVD.

The reactive particle growth in plasma gas phase is very important for understanding deposition process and modulating the film structure. In this work we use pulsed-radio frequency (RF) He/TiCl<sub>4</sub>/H<sub>2</sub>O plasma to visualize the nanoparticles grown in a plasma and the process of the film deposition. The collective dynamics of the particles driven by the electric field in the initial stage of the plasma-off phase is revealed using video microscopy.

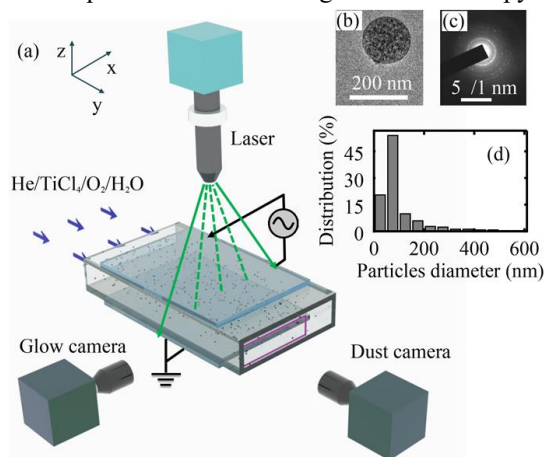


Figure 1: Illustration of the discharge, (a) experiment setup, and (b) an after-glow particle appearance characterized by TEM, and (c) TiO<sub>2</sub> SAED pattern, and (d) TiO<sub>2</sub> particles diameter distribution.

In Fig.1, two fluorine-doped tin oxide glass plates were used as electrodes, where the upper one was driven and the lower one was grounded. The particles were illuminated by a laser with wavelength of 532 nm. Two CMOS cameras were used to record the particle dynamics and the evolution of the discharge glow with a frame rate of 100 frames per second (fps). The dust-camera was installed in front of the discharge chamber with a 532 nm band pass filter to record the particle movement, while the glow camera was installed beside the chamber to record

the plasma discharge. The two cameras were synchronised by a signal generator. Our research shows that the whole procedure of the porous film deposition was observed directly at a kinetic level in the first time. Varying the plasma-off time allows to control the size of the deposited particles.

The reactive atmospheric pressure plasma containing Ar/O<sub>2</sub>/HMDSO (hexamethyldisiloxane) is applied to coat polyethylene (PE) separators for lithium-ion batteries. The separator moves through the plasma region continuously, and its top and internal fiber surface is coated with a thin SiO<sub>2.01</sub>C<sub>0.23</sub>H<sub>x</sub> film composed of nanoparticulates grown in plasma phase with an average size of about 100 nm.

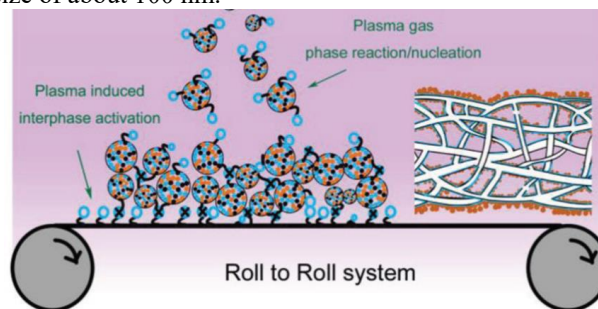


Figure 2 Schematic diagram of the reactive plasma and deposition process on fibrous PE separator

As shown in Fig. 2, this deposition process is composed of a plasma gas phase reactions/nucleation and plasma-induced surface reactions. The active species were revealed by optical emission spectroscopy (OES) and include: Ar at 750 nm (4p<sup>1</sup>-4s<sup>1</sup>), atomic O at 777 nm (3s<sup>5</sup>S<sup>0</sup>-3p<sup>5</sup>P), OH at 309 nm (A<sup>2</sup>Σ<sup>+</sup>-X<sup>2</sup>Π), and Si at 288.2 nm (3p<sup>11</sup>D-4s<sup>1</sup>P<sup>0</sup>). The surface of the nanoparticles and the PE is activated in the plasma. Then, the active nanoparticles react with each other or with the active PE surface to form a thin SiO<sub>x</sub>C<sub>y</sub>H<sub>z</sub> nanoparticulate layer. This reactive coating provides good adhesion of the nanoparticulate film on the surface and a shell-supporting framework for the fibrous PE. A mere 3 min coating of PE separator endows the lithium-ion battery with a lower interface resistance and improved C-rate and cycling performances. This roll to roll reactive atmospheric deposition provides a modulated and eco-efficient binder-free coating method for temperature sensitive substrates.

### References

- [1] Xu Y, et al., Plasma Chemistry and Plasma Processing, 39, 937(2019).
- [2] S. Qin, et al., Advanced Mater. Interfaces, 5-9, 1800579(2018)..