Controllable fabrication of ion-induced Au-nanoprotrusion arrays for energy- and bio-applications

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Ion irradiation to solid surface is well-known to entail the various types of surface nanostructures, such as cones, nanoneedles and ripples, even at room temperature (RT). So, this is very fascinating as a basic tool for the green (environmentally friendly) synthesis of nanomaterials. For the practical application of ion-induced nanostructures, the controllable fabrication in shape, number density, crystallin structure, and composition is essential. Here, we tackled this subject.

For the formation of ion-induced nanostructures, sputtering yield is one of the most important parameters. The clustered material of lower sputtering yield sometimes acts as the protection against the ion-irradiation, resulting in the selective erosion of the surrounding to form conical structures. Au and C are the typical examples of the materials of the highest and lowest sputtering yield, respectively. For the 600 eV Ar⁺ ion irradiation onto Au foils with a simultaneous C supply during ion irradiation at RT, densely distributed nanostructure array ranging from slender needles to cones were successfully fabricated depending on the C supply rate from 1.2 to 0.6 nm/min, respectively, under the constant sputtering rate of 49 nm/min [1]. Such Au cones were promising as a substrate for surface enhanced Raman spectroscopy for the ultrafast and ultrasensitive detection of COVID-19 virus [2].

Such a nanostructures could be formed also on Au foil edges, and the further thin film deposition thereon and cross-sectional-like observation by transmission electron microscopy (TEM) was possible without any post-thinning treatment. Fig. 1(a) shows a typical TEM image of Li-C film deposited onto Au cones on an Au foil edge. In Fig. 1(a), for the in-situ TEM observation of the electrochemical process between Li-C and graphene, a W probe coated with multilayer graphene is contacted to the Li-C film. After the voltage application between the Li-C and graphene coated W (corresponding to the charging process of nano-battery), the intercalation of Li into graphene was clearly observed in lattice images.

The composition of Au cone surface could be further modified by the simultaneous supply of the "third" element during ion irradiation. Fig. 1(b) and 1(c) show typical TEM images of an Au cone fabricated with C and Ni supply at RT, revealing that the Au cone was covered with tiny Au and Ni nanoparticles and spontaneous partial graphitization also occurred. Such Au cones covered with Ni nanoparticle showed the excellent supercapacitor property [3].



Fig. 1 (a) TEM image of Li-C/Au cones and graphene coated W for the charge-discharge process analyses. (b) Low and (c) high magnification TEM images of an Au cone fabricated with simultaneous Ni and C supply at RT.

[1] W. M. Lin. et al., Appl. Surf. Sci. **613**, 156011, (2023). [2] Y. Yang, et al., Nano-Micro Lett. **13**, 109, (2021). [3] T. Akiyama, et al., RSC Advances, **12**, 21318, (2022).