Cicada wings as biotemplate and their modifications

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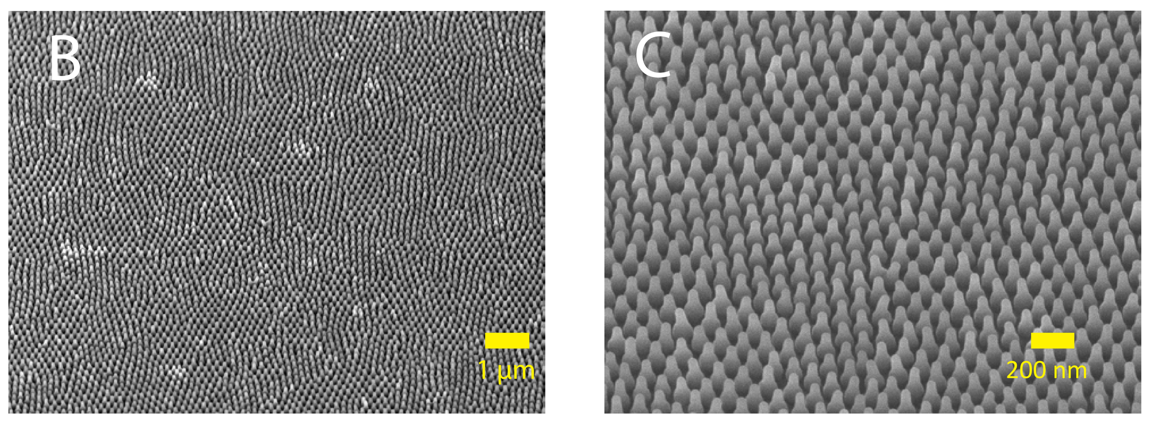
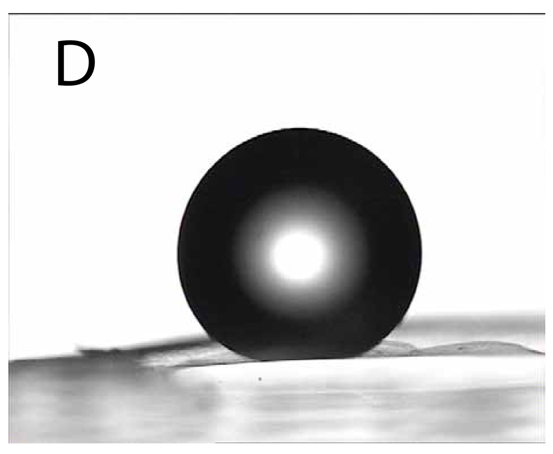
Introduction

Biomimetics is a modern discipline, which deals with the use of natural structures to create functional materials. Natural patterns can be modified, replicated or mimicked and materials with interesting properties can be created. Bioinspired nanostructured surfaces which are highly hydrophobic, and which can be found on leaves of water plants or insect wings, have already found technological applications because they are much more effective than chemically treated flat surfaces.
Surface of cicada's wings is covered with arrays of nanopillars and reveals high hydrophobicity. Using laser ablation, the chitinous nanopillars were covered by thin layers of SnO_2 or TiO_2. These chemical modifications resulted in reversibly light- and heat-switchable surface wettability. Also, the surface reliefs of wings were negatively and positively replicated by nanocasting into poly(dimethylsulfoxide) (PDMS) and into poly(methylmetacrylate) (PMMA). The PMMA replicas were sputter covered with gold or silver. The ultrathin noble metal foils appear to be promising material in research of surface-enhanced Raman scattering (SERS).

Cicada (*Pomponia intermedia*)

Cicada wing is covered with hexagonally ordered papillary. The pillars have height about 400 nm and their diameter is about 120 nm. The morphology is identical for the dorsal and ventral surfaces and between male and female specimens. Structure consisting of arrays of pillars has anti-reflection function and therefore the wings are transparent (in broad band from approximately 450 nm to 2500 nm).
Chitinous strucuture on upper side of wing shows hydrophilic properties, which are increased by epicuticular waxes. Hydrophobicity can be explained by Wenzel's model or Cassie-Bexters model. The wing is appropriate template for replication and function modifications. Cutitular waxes are very important during replication because enable easier separation of negative replica from template.

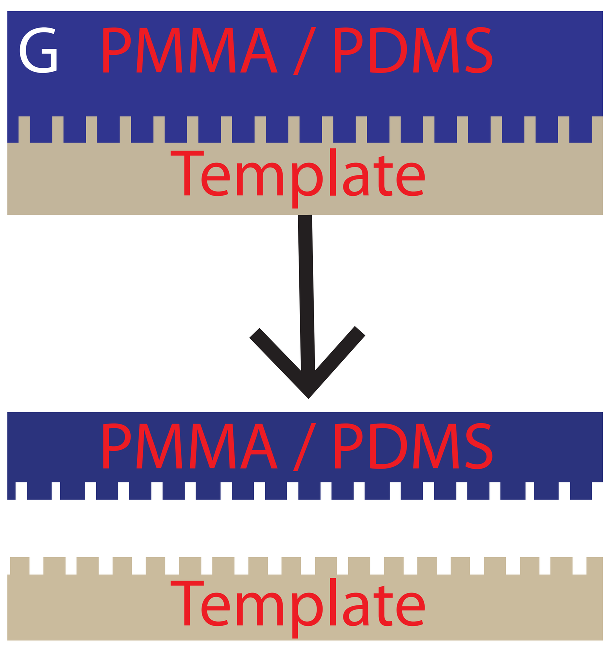


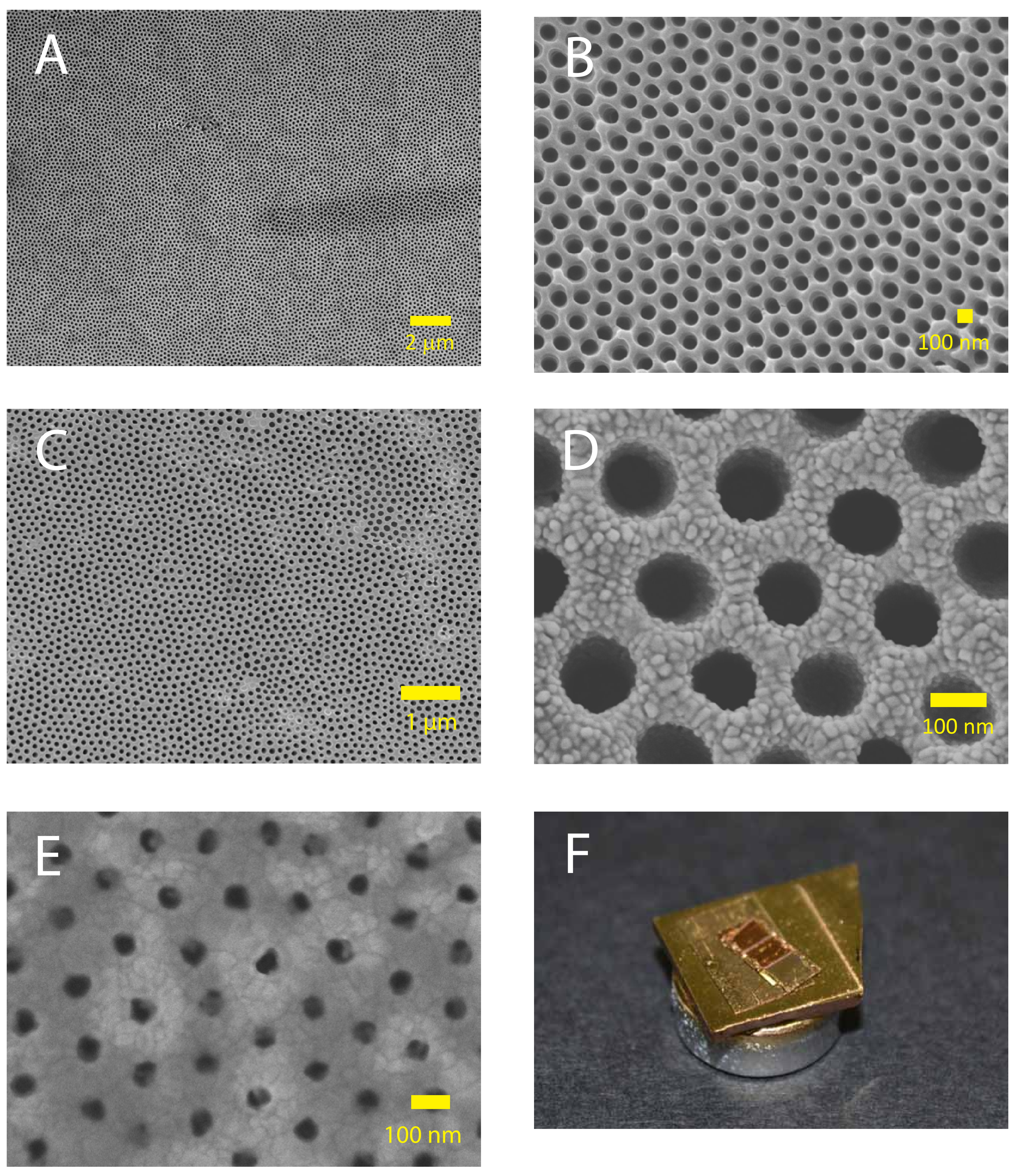


(A) *Pomponia intermedia*. (B) Large area of a dorsal side a of cicada's wing with chitinous pillars. (C) Detail of array of pillars - side view. (D) Drop of water (volume of 2 microliters) on upper side of wing.

Replications and nanocasting

Reliefs with typical dimension in the order of ten nanometers can be replicated using the method of casting (nanocasting) into suitable polymer matrice such as PMMA or PDMS. The polymer is poured on a specially prepared surface that we want to replicate. After curing, we can easily separate a negative replica in polymer from the template and manipulate with it. The polymer replica serves as the intermediate template for the preparation of self-supporting gold foil with apertures about 100 nm - dimension interesting for applications in photonics and as a substrate for SERS (Surface Enhanced Raman Spectroscopy). Large (macroscopic) areas can be reproduced in the high details. Short heating of the gold foil (about 300°C for 15 seconds) results in uniform reduction of nanoholes diameters.





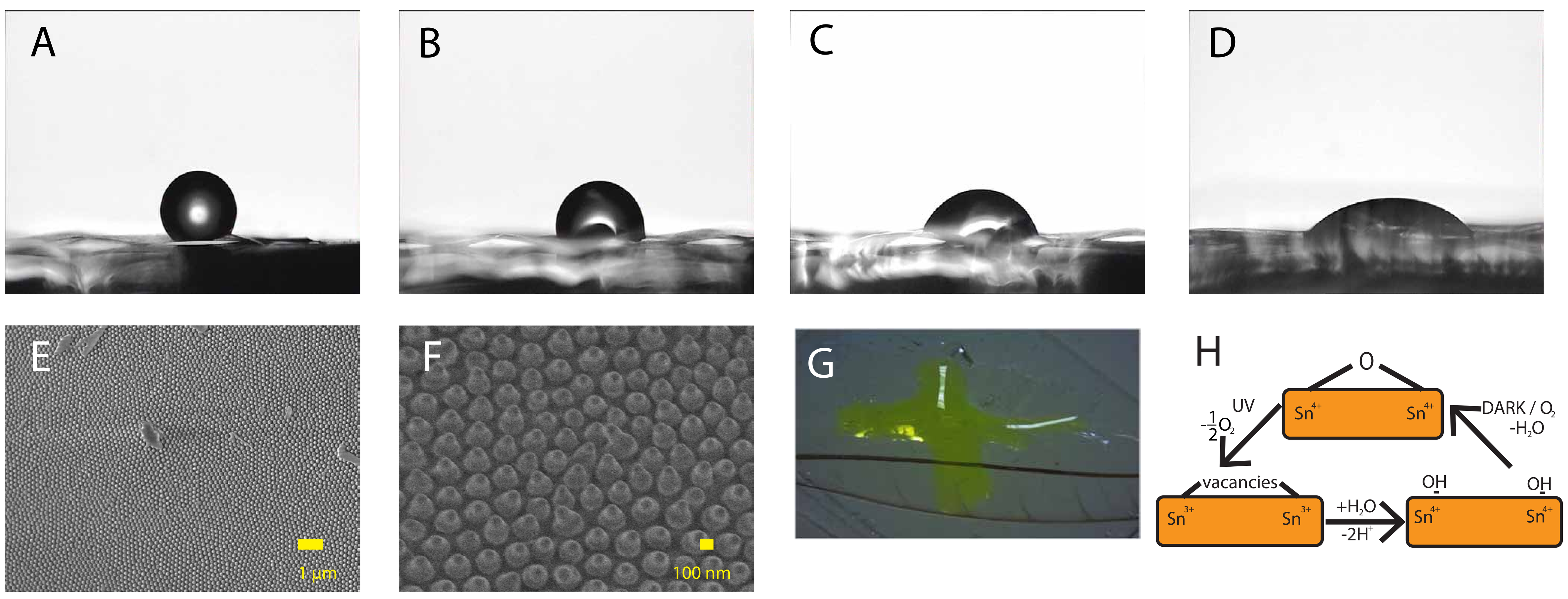
(A) A negative replica of cicada's wing cast into PMMA. (B) Detail on foil with holes done by pillars on cicadas wing. (C) Gold foil and 100 nm holes with thickness 50 nm. (D) Detailed view with distinct gold grains. (E) The gold foil after heating on approx. 300°C. (F) Gold foil with 100 nm holes. The area with "copper colour". (G) A scheme of nanocasting of biotemplate. A, B, C, D and E are SEM micrographs.

Photo-controled wettability of surfaces

Hydrophobic properties of the cicada wings can be further modified and used for another purposes. One way how to modify this natural material is deposition of thin layer of semiconductor oxides using ArF excimer laser ablation of ZnO, SnO_2, and TiO_2 targets, respectively.
After deposition of 5 nm of SnO_2 on the surface of cicadas wing, we have obtained a substrate, which was hydrophobic. However, in the presence of water (for example air humidity) and exposure to UV radiation, a chemical reaction occurs and the wing surface become super-hydrophilic.

In these inorganic oxides (ZnO, SnO_2, TiO_2), the photogenerated formation of electron-hole pairs leading to oxygen-deficient surface sites is believed to be responsible for the effect. Hydroxyl group adsorption on the defect sites is prefered to oxygen adsorption, leading to low water contact angle. The original hydrophobic state is then restored as the hydroxyl groups are replaced by ambient oxygen during storage in dark.

Irradiation was carried out 60 minutes with UV lamp with an output 2 x 8 W at a wavelength 366 nm.



(A) Drop of water with volume of 2 microliters on cicada wing with 5 nm thick layer of SnO_2. Before UV irradition (B) Water drop on the same surface as (A) after 15 minutes of UV irraditation. (C) Water drop after 30 minutes of UV irraditation. (D) Water drop after 45 minutes of UV irraditation. (E, F,) SEM micrographs of dorsal side of cicada wing with with 5 nm layer of semi-condutive SnO_2. (G) Selective wetting of cicada wing with SnO_2 layer by watter. Shape of "cross" was obtained by exposuring the wing over mask to UV radiation. (H) Scheme of photocatalyst reaction.

Conclusion

Cicada wings appear to be a suitable natural template, that can be copied or imprinted in the polymers. Very successful way, how prepare replicas in details in tens of nanometers, is nanocasting. We have developed a relatively simple and fast way to create the film with 100 nm apertures in PMMA or PDMS. Gold foils with 100 nm apertures were prepared as promising material, which is suitable for use in SERS. For preparation of such surfaces, this procedure is very good competitor to oher methods, for example nanolithography.

One possible modification of the wings of cicadas is the controlling of their hydrophobic properties. Deposition of suitable materials such as semiconducting oxides (TiO_2, ZnO, SnO_2) allowes change their surface properties by UV radiation. We can transform the hydrophobic state of a surface into hydrophilic in a relatively short time of exposure. It would be possible to control the movement of liquid over the surface by defined path of the irradiation.

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