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## **Curcuminoid boron difluoride as TADF emitting dye for OLEDs**

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Since the development of OLEDs in the late 80's,[1] there has been a continuous effort devoted to the improvement of the structure of the stacks of the different layers constituting the OLEDs and of the dye contained in the emitting layer. Back in the 80's, only fluorescent dyes were used. However, those dyes are limited to an internal quantum efficiency (IQE) of 25% originating in the spin-statistic upon electrical excitation (*i.e.* 25% of singlets and 75% of triplets are inherently formed). In the 90's, a leap in the emission efficiency was made as phosphorescent emitters (*i.e.* Ir, Pt, ... metal complexes) were introduced in the emitting layer resulting in an IQE of 100%.

Unfortunately, this strategy was only short-lived because of the shortage in these noble metals. It was therefore necessary to find an alternative to overcome this problem and research naturally turned to the use of fully organic dyes.

The first solution appeared around 2009 when Adachi *et al.*[2] were able to show that upon a careful design of the emitting dye, the triplets could be harvested to repopulate the singlets which ended up with device with an IQE of 100%. This strategy was based on the well-known delayed fluorescence phenomenon which was then named Thermally Activated Delayed Fluorescence (TADF) when incorporated into the device. As the name suggests, TADF is sensitive to the temperature because the triplet energy level is close enough to the singlet's one to repopulate it through thermal energy ( $kT$ ).

In this talk, after a brief presentation of the TADF phenomenon, curcuminoid boron difluoride will be introduced and their properties will be explained by means of their photophysical properties in solution and in thin films.[3-4] While the properties of TADF were not expected, we clearly demonstrated that we were able to build OLEDs with high NIR efficiency, which was not possible with other TADF dyes

Finally, I will introduce the new development we are following to implement the previous work and especially, to increase the IQE of those curcuminoid boron difluoride.

### **Acknowledgements**

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## (NHC-olefin)-nickel(0) nanoparticles as catalysts for the (Z)-selective semi-hydrogenation of alkynes and ynamides

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The catalytic semi-hydrogenation of internal or terminal alkynes is useful in numerous organic syntheses by providing alkene building blocks, both at laboratory and industrial scale.<sup>1</sup> In particular, such hydrogenation is critical in the reduction of polyfunctionalized bioactive molecules and in polymerization reactions in order to eliminate alkynes and dienes from alkene raw materials. Herein, we report that the reduction of a [NiCpBr(NHCcinnamyl)] complex with an excess of MeMgBr leads to coordinated Ni(0) nanoparticles (Figure 1). The combination of a strong  $\sigma$ -donor NHC ligand with a  $\pi$ -coordinating appended cinnamyl moiety likely prevents Ni(0) particle aggregation into larger inactive species and allows rapid exchanges with reaction substrates. The resulting NHC-olefin-Ni(0) particles effectively catalyse the (Z)-selective semi-hydrogenation of various alkynes and ynamides (Figure 1), the latter being a rare example of direct semi-hydrogenation of ynamides without the use of any salt or additive.<sup>2</sup> The developed catalyst proved to be reusable over six runs.

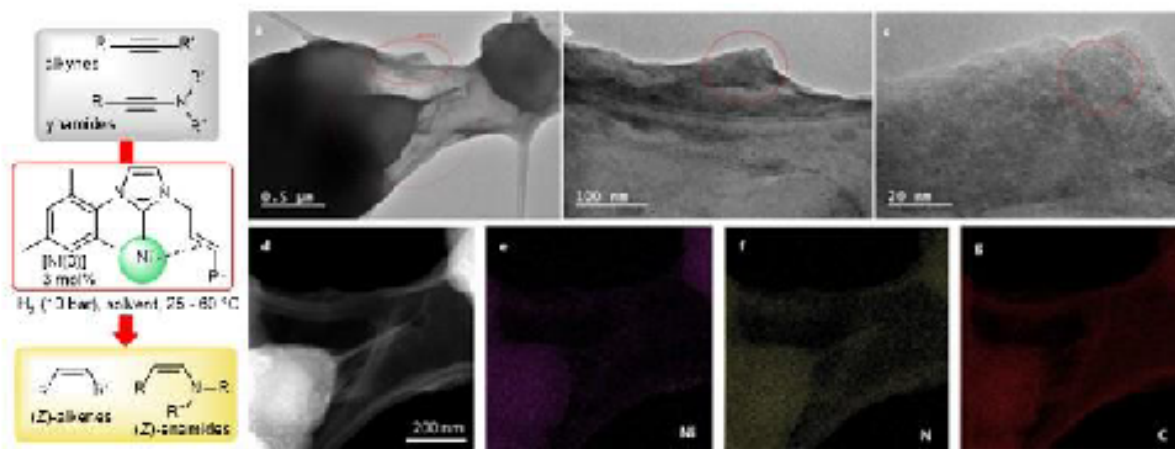


Figure 1.

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## Moisture and light responsive composite hydrogel made by DLP 3D printing

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The association of elements with 3D/4D printing to manufacture new composites is leading to an increase in the number of applications related to various fields such as robotics, medicine, pollution control, etc. The design of this type of material in 3D printing is still rare and does not result in high quality objects. In this communication, we introduce a simple route to fabricate composite materials exhibiting dual stimuli. Special attention has been paid to the design of 4D composite in order to bring a fine control to the reversible shape deformation. One of the key parameters lies in the insertion of metallic gold nanoparticles into hydrogel object to confer it a 4D feature. In a first step, a description of the synthesis of the nanoparticles followed by the analysis of the morphology/size/dispersion by UV-vis spectrum and TEM imaging is performed. Several mixtures were prepared by varying the concentration of nanoparticles, with the aim of observing its impact on the photoreactivity/viscosity of the formulations and their printability. Resolution and fidelity criteria regarding the CAD model were assessed by investigating printed objects by SEM microscopy. Finally, camera tracking combined with different mathematical models are used to understand the swelling and thermal properties of these objects. By playing with the light intensity or the nanoparticles concentration, the increase of temperature can be controlled in a precise manner leading to the production of a 3D object that responds to a dual stimuli: moisture for swelling and heat for returning the printed object to its initial size. By taking advantage of the synergy between these dual properties, progress to various fields such as soft robotics can be envisioned.

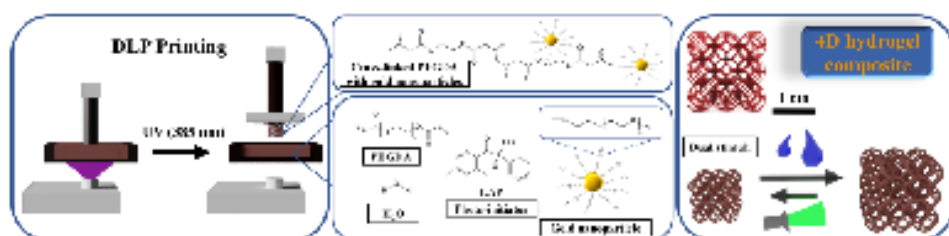


Figure : Global outline of the subject.

### Acknowledgements

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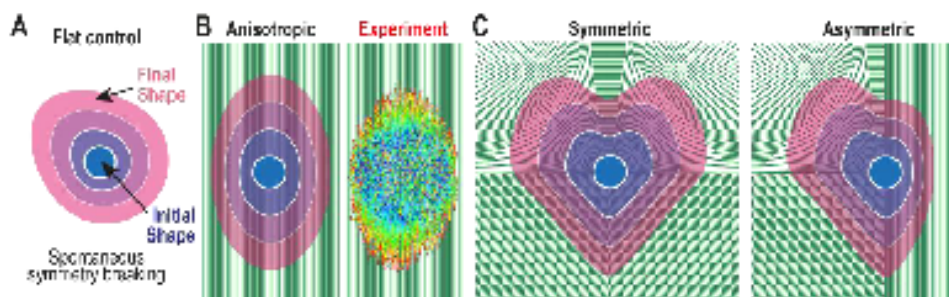
## Influence of substrate curvature in cell migration and tissue morphogenesis

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Tissue and organ establishment requires some complex cell migration processes at the individual cell and collective level. Identification and characterization of the mechanisms which regulate these processes are crucial for developmental biology as well as regenerative medicine. Some recent work carried out in the Biointerfaces lab showed that cell migration can be affected by substrate curvature<sup>1</sup>. The causes of this phenomenon are poorly understood. We have already demonstrated that during epithelium elongation on a surface made of hills and valleys, migration and cell division are oriented along the concave line (figure 1). The aim of my project is to study how a complex curvature network (figure 1) affects epithelium elongation and directs cell migration based on some prior work and modeling<sup>2</sup>. To this aim, I use lithography techniques to print a 3D-pattern in a resin and replicate it on polydimethylsiloxane (PDMS). Cell migration and epithelium elongation on this 3D topographical surface are imaged by time-lapse confocal microscopy and immunostaining followed by a quantitative analysis with an image processing software. Different parameters can be analyzed, among which migration speed, focal adhesions, and also nucleus deformation.



**Figure 1:** Epithelial colony elongation controlled by complex symmetric or asymmetric curvature networks. **A:** Epithelial colony elongation on flat PDMS, **B:** Epithelial colony elongation on simple substrate curvature with result of the experiment, **C:** Epithelial colony elongation on more complex substrate curvature network.

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## Electrosynthesis of TiO<sub>2</sub> nanotubes electrodes with variable thickness and localized rapid analysis of their photoelectrochemical properties

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Recent advances in materials science have opened up great opportunities for the design of heterostructures associating two or more components that could lead to highly efficient photoelectrodes usable for photoelectrochemical (PEC) solar to chemical energy conversion.<sup>1</sup> However in these complex heterostructures, any change in terms of morphology or composition will impact all steps of the PEC reaction,<sup>2</sup> making the quest for the best structure a difficult process. Therefore, to assist in the rational design of PEC devices, there is an urgent need for characterization methods to rapidly determine in operando the properties of photoelectrode materials and understand how any structural or physicochemical changes impacts the overall PEC efficiency. Until now, no method allows determining simultaneously several of these properties in operando for these complex systems, and the optimization of photoelectrodes efficiency in terms of material composition, film thickness, or co-catalyst loading is still largely achieved through a trial-and-error approach by synthesizing and analyzing a set of different electrodes, which can be time and resource-consuming.<sup>3</sup>

We recently developed a new approach that allows the growth of aligned TiO<sub>2</sub> nanotubes (NTs) with length increasing gradually from 0 to 10 μm, on a single electrode.<sup>4</sup> This simple anodization method allows, in one step, to tune the length of the tubes by controlling the immersion time within the electrolyte during the synthesis. This method was employed to synthesize TiO<sub>2</sub>-NTs with variable length but also nanotubes doped with cations (Nb<sup>5+</sup>, Ta<sup>5+</sup>) and/or anions (N<sup>3-</sup>).<sup>5</sup> The PEC efficiency of these electrodes were analyzed using a small light beam as a local probe scanning the surface with variable length of NTs.

Therefore, with one synthesis and one measurement, we were able to determine the optimal length of the NTs for PEC applications. The experimental data measured for the different samples exhibit different behaviors that can be ascribed to changes of electronic conductivity and light absorption depending on the doping species. Furthermore, by using scanning photoelectrochemical microscopy (SPECM),<sup>6</sup> we were able to confirm these results at higher spatial resolution and to identify some defects present in these photoelectrodes.

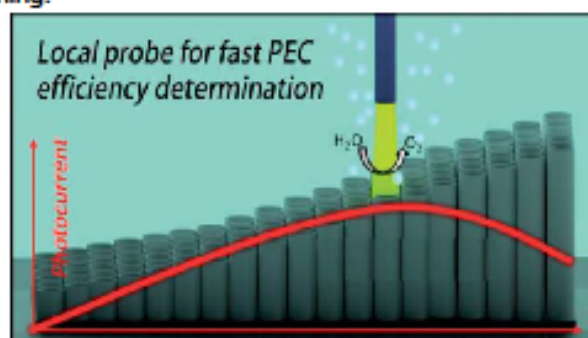


Figure 1: principle of the local probe PEC measurement on variable NTs length electrode.

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## 3D-PRINTED EOSIN Y-BASED HETEROGENEOUS PHOTOCATALYST FOR ORGANIC REACTIONS

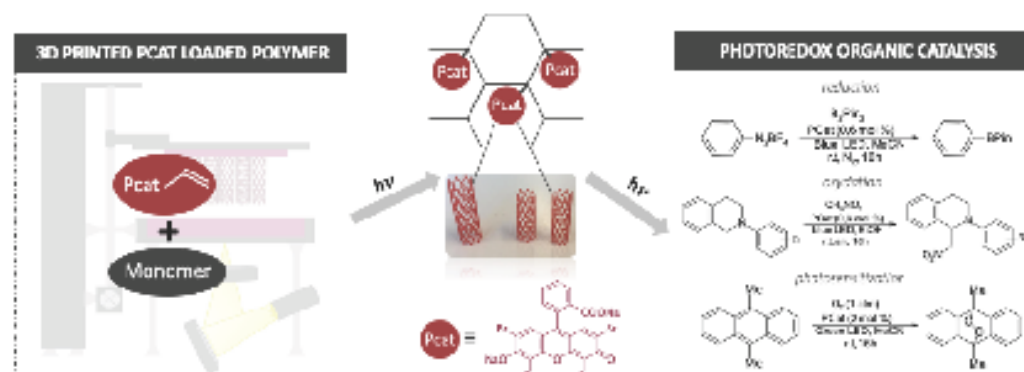
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Photoredox catalysis for organic transformation has been considered as a powerful tool in organic synthesis since its revival in 2008 [1-2]. This innovative field of chemistry relies on the excitation of a photocatalyst (PCat) giving an excited state with unique properties, including the ability to transfer electrons or to transfer energy. However, most of the photocatalysts are prepared and used in homogeneous phase which limits the applications since the photocatalyst is not recover at the end of the reaction. The solution is to switch from homogeneous to heterogeneous catalysis using a support with high accessibility to PCat [3-4]. The approach of this project is the fabrication and evaluation of new 3D printed polymer-based supported photocatalysts [5-6]. Polymeric supports are synthesized via free radical polymerization to yield a recyclable hierarchical polymeric network including a non-toxic PCat (eosin Y) covalently bounded. The photocatalytic activity of this new object was then evaluated through model organic reactions in oxidation, reduction, and photosensitization.



**Figure** : 3D-Printed heterogeneous photocatalyst for organic reactions.

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**'Tous Chercheurs': a school laboratory experience**

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Sharing scientific, technical and industrial culture is more important than ever. Because the word of science is increasingly being questioned, because young people are less and less interested in science, because the spread and impregnation of fake news will have consequences in the fight against the major challenges of the 21st century (climate, environment, health, etc.). Rather than trying to combat such 'conspiracy', which is often counterproductive, several international institutions recommend that researchers re-engage with citizens by including them in the research process and through more transparency about the issues and the possible impacts of science and technology, both positive and negative. This includes developing citizen science processes that include different audiences, and using them as a mean to transmit the precepts of scientific questioning and reasoning. Such approaches are encouraged by the *France 2030* LPR.

Developing these projects nevertheless requires a place to welcome, for assistance in setting up the project, as well as a platform for implementation and follow-up. Based on an existing model, 'Tous chercheurs' (<https://www.touschercheurs.fr/sciences-participatives/>), we would like to create a multi-purpose reception area for the public as well as for the researchers, to help raising awareness on scientific approaches among citizens, teachers and schoolchildren in Alsace.

The objective of the school laboratory is to help setting up citizen projects, to offer a neutral meeting place between scientists and citizens, to establish a dialogue without barriers and to contribute to the training of young people in the challenges of science. Through a few examples, I will show what can be achieved around this experimental site.



## WATER-SOLUBLE RESIST FOR 193 NM PHOTOLITHOGRAPHY BASED ON A CHITOSAN BIOPOLYMER

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The negative effects of the traditional resists can be minimized by using more ecologically friendly resists for the photolithography process. For instance, some more recent photoresists have a lower environmental impact because they are produced from water-soluble, biodegradable and renewable materials<sup>1</sup>. Moreover, they can be made utilizing less wasteful and energy-intensive production techniques.

In our earlier research, we investigated the effect of deep ultraviolet light on chitosan thin films by using a variety of characterization techniques, including FTIR-ATR, XPS, ToF-SIMS, SEC, and EPR<sup>2</sup>. Based on these findings, we put forth a mechanism for photoinduced alteration of photoresist obtained from natural sources. But, in order to compete with industrial standards, the sensitivity of the resist needs to be increased. The dose-to-clear of the resist formulation is reduced by roughly two times with the introduction of a photoacid generator (PAG)<sup>3</sup>. To fully understand the role of PAG and the proposed photo-modification mechanism, comparative study was done.

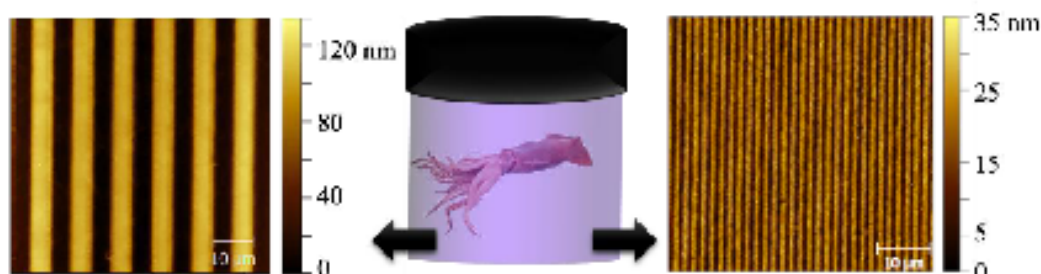


Figure: Examples of patterns obtained using chitosan-based resist: AFM scans of 5  $\mu\text{m}$  and 0,8  $\mu\text{m}$  lines.

### Acknowledgements

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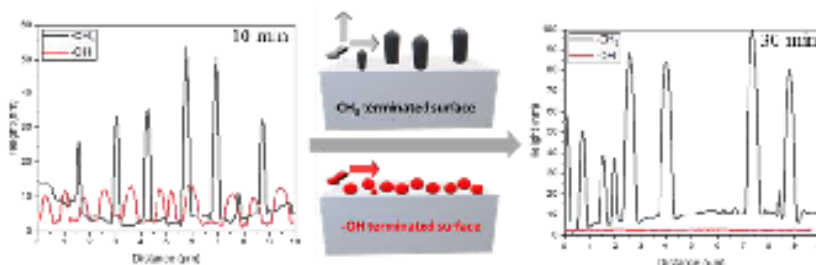
## PLASMA POLYMERS FROM CITRONELLAL: TOWARDS NANOSTRUCTURATION OF BIO-BASED THIN FILMS

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The use of bio-based precursors for plasma polymerization allows to bring a recognized coating technology closer to the demands for sustainable procedures. One type of promising bio-based functional polymers derives from plant secondary metabolites<sup>1</sup>. Among those, a component of several essential oils, citronellal is a monoterpene containing an aldehyde functional group. Those chemical properties make citronellal a prospective precursor for functional polymers. In this work, the deposition rate and the chemistry of citronellal plasma polymers were evaluated at different input powers, duty cycles and spatial distributions in the reactor. Furthermore, the effect of the chemistry of the substrate's surface on the morphology of the plasma polymers was assessed. At the same deposition condition and position in the reactor, the formation and growth of plasma polymers was affected by the substrate chemistry that was either methyl- or hydroxyl-terminated. The analysis of the growth of the nanostructures formed in methylated surfaces revealed a distinguishable growth in the normal direction to the surface, leading to nanostructures that grow with increasing deposition time. A different behavior was observed in hydroxyl-rich surfaces, in which by increasing the deposition time the nanostructures disappeared and a homogeneous thin film was formed (Figure 1). Those results highlight that tailoring surface chemistry is an effective strategy to control the formation and growth of nanostructures through plasma polymerization. The formation of nanostructures during plasma polymerization have been previously analyzed as a function of some characteristics of the plasma phase<sup>2</sup>, but the consideration of the surface chemistry diversifies the variables that have to be considered in such complex analysis. This work is part of initial efforts from our research group to complement that knowledge.



**Figure 1** : AFM roughness profiles for plasma polymers deposited over -CH<sub>3</sub> and -OH terminated surfaces.

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## **HEXAGONAL ARRAYS OF CARBON MICROPYRAMIDS FORMED BY SELF-ASSEMBLY OF SOOT NANOPARTICLES**

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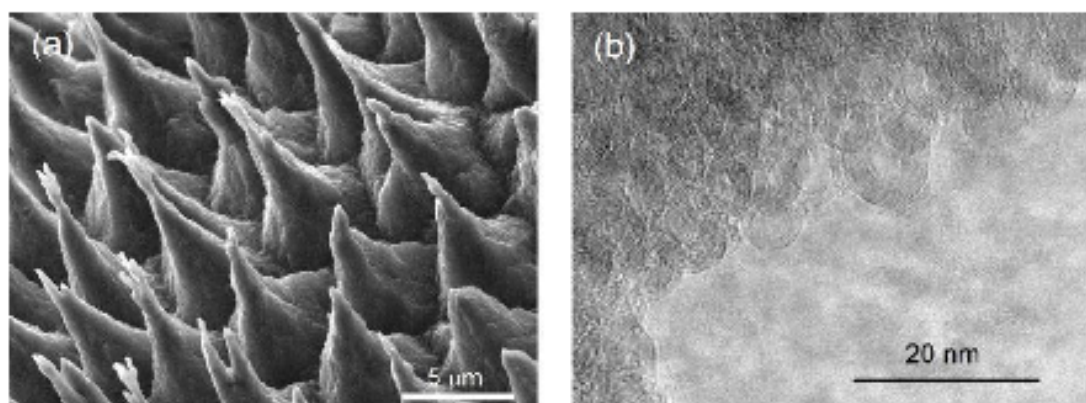
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Almost regular hexagonal arrays of microscopic pyramids consisting of soot nanoparticles are formed on the surface of graphitized filaments of chitosane, which are resistively heated to ~1800–2400 °C under an Ar atmosphere containing trace amounts of oxygen (~300 ppm) [1]. At higher temperatures ( $T > 2300$  °C, approximately) the soot particles are represented mainly by multishell carbon nano-onions. The height and width of the pyramids are strongly dependent on the temperature of the resistive heating, diminishing from 5 to 10  $\mu\text{m}$  at  $T \approx 1800^\circ\text{C}$  to ~1  $\mu\text{m}$  at 2300–2400 °C. The pyramids always point normally to the surface of the filaments. They are soft and can be easily destroyed by touching them but can be hardened by annealing under an oxygen-free atmosphere. It is supposed that thermophoretic force generated by a strong temperature gradient near the resistively heated surfaces is the cause of the self-assembly of the soot nanoparticles in the micropyramids.

The new carbon-based morphology is perspective for a number of advanced applications. We have demonstrated that the individual carbon micropyramids emit a tunneling current upon generation of a local electrical field. This indicates on the possibility to create field emitter arrays by a simple bottom-up approach, avoiding the expensive and hazardous techniques such as photolithography and reactive ion etching. The pyramid arrays may be also investigated as superhydrophobic coatings and ultrablack metasurfaces.



**Figure :** (a) SEM image of an array of the micropyramids on the surface of a resistively heated carbon microtube. (b) Soot nanoparticles (carbon nano-onions) forming the micropyramids.

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