# Surface modification of diamond and cubic boron nitride films for sensing applications

**Joint Laboratory:**

Joint Laboratory of Nano-organic Functional Materials and Devices

**Principal Investigators:**

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**Summary of the project:**

Cubic boron nitride (cubic F43m) is structurally analogous to diamond (cubic Fd3m); both of them have strong covalent bonds and high atom density that make them distinctive materials with extreme physical and chemical properties. This project is focused on the controlled growth, the surface modification and characterization of diamond and cubic boron nitride (cBN) films for sensing applications. By combining the multi-disciplinary expertise among the two parties of the Joint Laboratory, we have made significant impact in the following areas:

i) **Controlled synthesis and characterization of diamond and cBN films (CityU)**

We have synthesized and characterized diamond and cBN films with controlled microstructures and morphologies. Various diamond nanostructures including nanocones, nanopillars, and nanowhiskers have been constructed on poly-D and nano-D films by employing bias-assisted reactive ion etching (RIE) in hydrogen/argon plasma. More significantly, following our success in synthesizing high-quality and high-purity cBN films on various substrates including silicon, diamond, nanostructured carbon films, and highly ordered pyrolytic graphite, we have further achieved, for the first time, high-density, uniform cBN nanocone and nanopillar arrays from cBN-diamond composite films by bias-assisted RIE with the assistance of gold dot masks.

ii) **Surface modification and functionalization of diamond and cBN surfaces (CityU and TIPC)**

Various precursor compounds with special receptors have been designed and prepared for modification of diamond and cBN surfaces. We have introduced a novel method for immobilizing Cytochrome c (Cyt c) covalently on B-doped nano-D films via surface functionalization with undecylenic acid methylester and subsequent removal of the protecting ester groups to produce a carboxyl-terminated surface. The photochemical functionalization of cBN surfaces using allylamine and the subsequent immobilization of gold nanoparticles (AuNPs) have been demonstrated. Such nanoparticles-modified cBN surfaces are expected to have applications in the areas of electronics, catalysis, and sensing. A method to modify cBN surfaces with self-assembled monolayers (SAM) of 3-aminopropyltriethoxy silane (ATPES) has also been developed by us.

iii) **Theoretical simulation and modeling (CityU and TIPC)**

We have studied the adsorptions of F4-TCNQ molecule on the perfect and defective C(100)-2×1:1H surfaces using a density-functional tight-binding and first-principles methods. The density functional theory (DFT) within the generalized gradient approximation was employed to investigate the diamond (100) surfaces with hydrogen and ethylene terminations. The computational results are in good agreement with the experimental work, and guide the design of experiments in more accurate and economic ways.

iv) **Evaluation of diamond and cBN based devices for sensing applications (CityU and TIPC)**

An application of amine-terminated cBN surfaces in DNA sensing has been illustrated. Clear fluorescence with high density and high brightness was observed only on amine-terminated cBN surfaces, indicating that amino groups introduced on surfaces are indeed a useful addition to biomolecules immobilization. We have also fabricated dansyl chloride or rhodamine B isothiocyanate modified cBN film sensors for detecting $Hg^{2+}$ or $H^{+}$, respectively. These two cBN film sensors can be used repeatedly via regeneration after each test.

**Publications:**

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**Suggested photographs:**

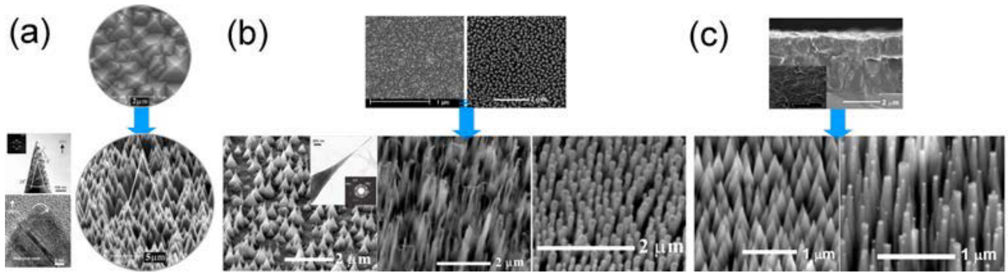


**Fig. 1** (a) Single-crystal diamond cones from [001]-textured pyramidal-shaped diamond films, (b) diamond nanocones, nanowhiskers, and nanopillars from nanodiamond films, (c) cBN nanocones and nanopillars from cBN/diamond composite films.

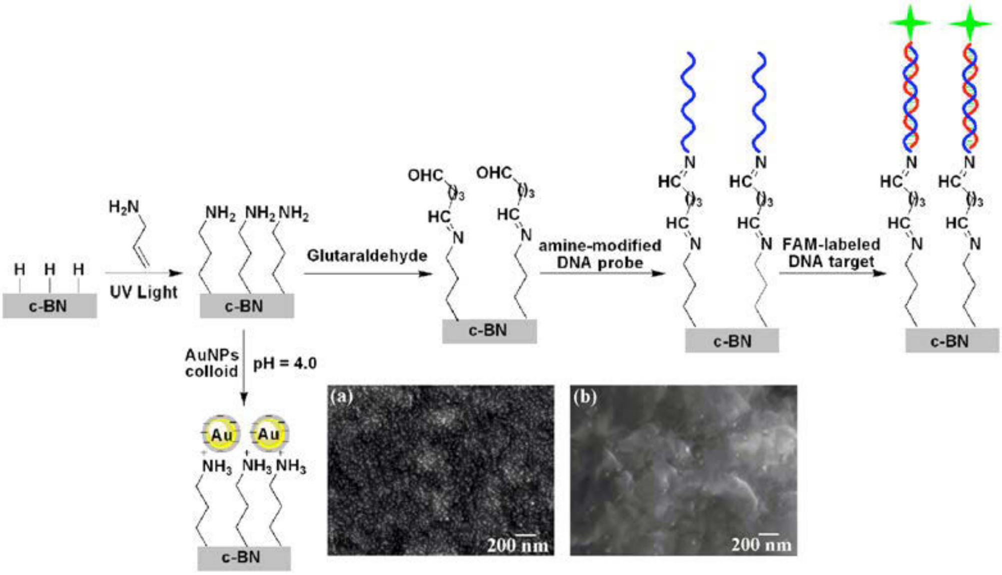


**Fig. 2** Illustration of photochemical modification of cBN film, subsequent immobilization of AuNPs or attachment of amine-modified DNA probes and hybridization with FAMlabeled DNA targets. Inset: SEM surface images of (a) amine-terminated and (b) hydrogenterminated cBN films with AuNPs immobilized on the surfaces.

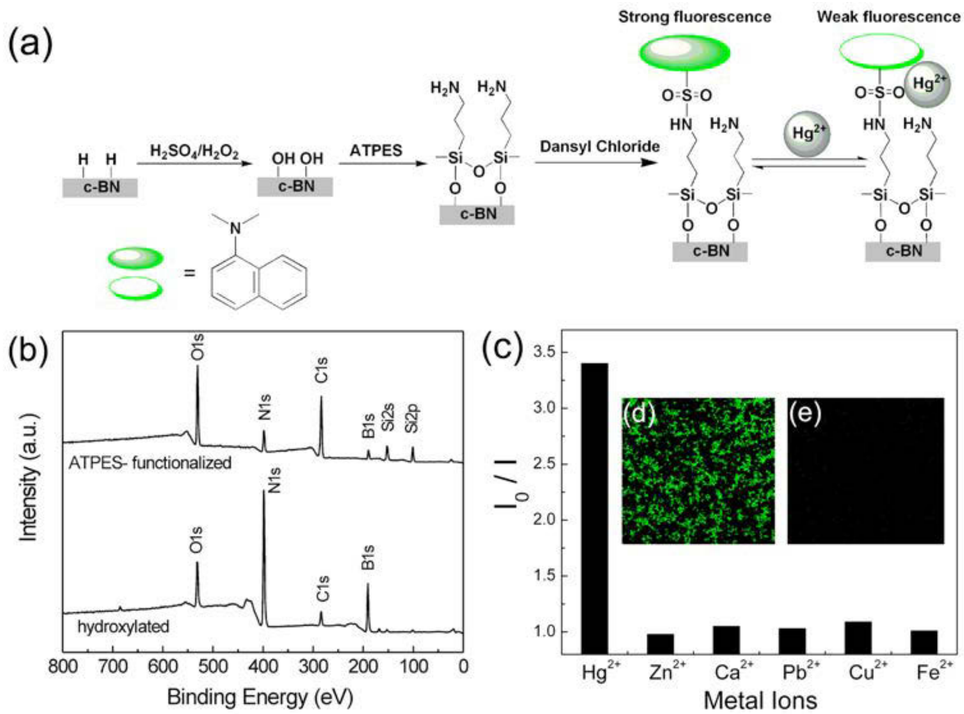


**Fig. 3** (a) Illustration of the process to immobilize dansyl chloride on cBN surfaces. (b) XPS survey spectra of hydroxylated and ATPES- functionalized cBN surfaces. (c) The fluorescence intensity quenching ratio ($I_0/I$) of dansyl chloride-functionalized cBN film sensors upon addition of different metal cations in ethanol solutions at a constant concentration of $10^{-3}$ M. Inset: Fluorescence images of the dansyl chloride-functionalized cBN film sensor (d) in ethanol and (e) in the presence of $10^{-3}$ M $Hg^{2+}$ in ethanol for 15 min.