# Binary cooperative complementary nanoscale interfacial materials*

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*Abstract:* Binary cooperative complementary nanoscale interfacial materials, i.e, materials with two complementary properties on the nanoscale, are introduced as a new concept for the design of functional materials. The concept is based on the generation of nanostructures with mutually compensating properties on the surface of a solid. Under certain coordinating conditions, unexpected properties may often appear at these kinds of interfaces, creating a huge potential for applications and theoretical research. Recent research indicates that the binary cooperative complementary concept is extremely useful for the design and creation of nanoscale functional materials.

## INTRODUCTION

In the development of nanometer-scale materials, ever since the early 1980s, scientists began discovering ultra-small crystal grains. The important point is that small is not only beautiful but also eminently useful. Therefore, the virtues of working in the nanodomain are increasingly recognized by the scientific community, the technological world, and the popular press. These small groups of atoms go by several different names: nanoparticles, nanocrystals, atomic clusters, and quantum dots. Much recent research has gone into finding ways to make small and uniform-size clusters that possess unusual optical, electrical, magnetic, and mechanical properties [1].

This effort has already paid several commercial dividends, for example, ceramics and chemical catalysts with increased efficiency due to high surface-to-volume ratios. Moreover, advances with semiconducting nanoclusters are bringing several commercial applications into view as well. However, in order to develop new kinds of high-level functional materials, one should not only consider the properties of a single nanoparticle (e.g., high surface ratios, quantum confinement effect), but also the cooperative effect among nanostructures and the macroscopic properties of their organized states. In this report, we attempt to introduce a new concept for the design and creation of new types of interfacial materials, i.e., binary cooperative complementary nanoscale materials.

In fact, from ancient times in China, the binary cooperative complementary concept has been used as "yin" and "yang" to explain the phenomenon and catalog the materials of nature and the uni-

verse. This initial philosophical principle has had a great influence on classical and modern science. Following the development of science, people have realized that binary cooperative complementary character is a universal feature of the material world. For example, the constitution of the chemical elements and the universe, as well as the physical and chemical properties of materials, are all involved in this binary concept.

In the development of materials science, people have also used the binary cooperative complementary effect to create unique functional materials. So far, binary atomic materials (e.g., binary alloys) and binary molecular materials have been developed that demonstrate tremendous potential in both basic research and practical applications. Well-known examples of binary atomic materials exist, such as the combination of Fe and Cr, which creates a type of stainless steel (also, cobalt is added to iron to make cobalt steels, among the hardest alloys known). Furthermore, many other binary alloys show a number of unique properties [2]. Binary molecular, amphiphilic molecules, with both hydrophilic and hydrophobic groups on the same molecule, have been used in different fields, such as surfactants, in which a huge variety of industrial products have been developed. When electron donors and acceptors are incorporated into a single molecule, nonlinear optical materials can result. Also, binary molecular solids provide another good example. Through the synthesis of donor-acceptor complexes, organic conductors and even superconductors may be generated [3]. The quintessential functional binary molecules (multi-binary molecules) are DNA and RNA, which precisely control the heredity of all living things, animal and plant. Still many unknowns remain, waiting to be elucidated in further research. Above all, binary cooperative complementary atomic and molecular systems have shown us unique material words.

Here we extend this concept from the molecular level to the nanostructural level and introduce a new material system, i.e., binary nanoscale materials. Before going into this topic, we would first like to start from the binary interfacial material, since understanding interfacial materials is key to the design of high-level functional materials. The motivation to develop binary cooperative complementary nanoscale interfacial materials is the desire to create unique functional macroscopic properties. By applying the binary coordinating complementary concept on the nanoscale on a solid surface, we expect to generate nanostructures with mutually compensating properties, e.g., hydrophilic and hydrophobic; conducting and insulating; convex and concave; p-type and n-type; oxidizing and reducing; ferromagnetic and antiferromagnetic, and so on (as shown in Fig. 1). Whenever an interface (or a surface) is formed by the mixture of nanostructures with a pair of these mutually complementary properties, under certain cooperative conditions, unusual interfacial properties can be created, i.e., binary cooperative complementary nanoscale interfacial materials. Our recent results indicate that such a concept is useful for designing new types of interfacial materials. In the following sections we will introduce several examples for the unique character of binary cooperative complementary nanoscale interfacial materials.

## EXPERIMENTAL

These kinds of surfaces or interfaces can be generated by outside stimuli, e.g., light, electric fields, magnetic fields, heat, plasma etching, or chemical synthesis on the surface of the solid. The surface nanostructures were characterized by atomic force microscopy (AFM) in air (SPI300 Seiko Instruments) or in high vacuum (SPI300HV Seiko Instruments).

## RESULTS AND DISCUSSION

Recent research indicates that the binary cooperative complementary concept is truly useful for the design and creation of nanoscale functional interfacial materials [4–14]. Here, we will simply mention
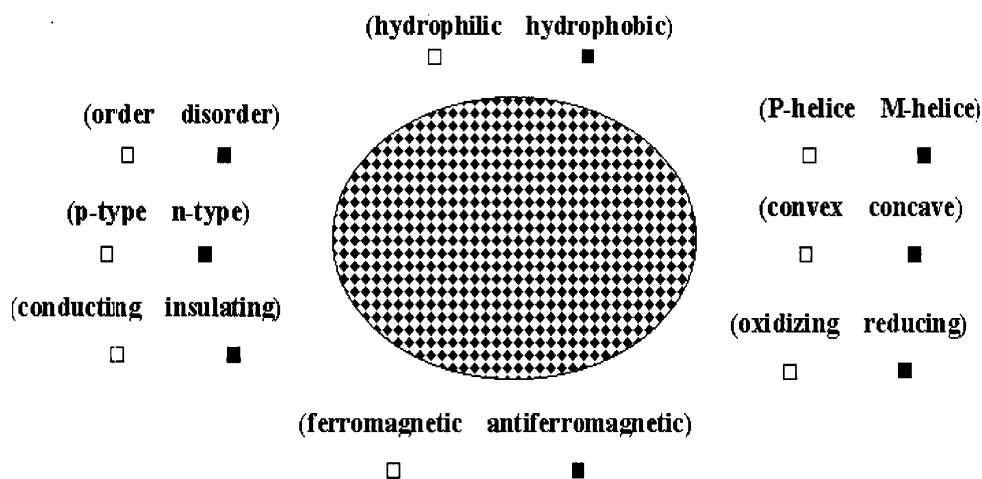
**Fig. 1** Several possibilities for binary cooperative complementary nanoscale interfacial materials are shown. Nanostructures with mutually complementary properties are presented by the squares in black and white.

these as follows.

## Super-amphiphilic surfaces (hydrophilic/hydrophobic binary cooperative complementary nanostructure)

Binary complementary hydrophilic and hydrophobic nanoscale structures on the surface of $TiO_2$ thin films and single crystals appear to create super-amphiphilic properties, with contact angles of 0° for both water and oil [4–7]. Figure 2 shows AFM images on the (110) face of rutile $TiO_2$ single crystals and suggests the binary $TiO_2$ surface can be induced by UV light illumination (Figs. 2a and 2b), heating at 300 °C (Fig. 2c), or argon ion sputtering (Fig. 2d), respectively. The key transformation involves loss of oxygen atoms from $Ti^{4+}$ sites to $Ti^{3+}$ sites, which can adsorb hydroxyl groups and thus produce hydrophilic regions. In all of the images, hydrophilic domains appear as rectangular shapes, aligned along the [001] direction of the (110) face which was confirmed by friction force microscopy (FFM) [6]. This unique amphiphilic $TiO_2$ surface character is ascribed to a composite of hydrophilic and hydrophobic (oleophilic) phases on the scale of several tens of nanometers, with the hydrophilic phases formed, for dissociative water adsorption. Microscopically, these areas may be hydrophilic and oleophilic; however macroscopically, the surface is highly amphiphilic. Furthermore, no visible water drops can form on the surface, and the material appears to have an antifogging property. The polycrystalline $TiO_2$ thin film, which has same character, can be coated on various substrates, e.g., glass, ceramics, plastics and metals. This highly amphiphilic surface has self-cleaning, antifogging properties [4–7]. Furthermore, this basic idea can be also used to design and synthesize other types of super-amphiphilic materials, e.g., super-amphiphilic polymers.

## High-efficiency catalysis (Re./Ox. sites binary cooperative complementary nanostructure)

Pt nanograins on the surface of $TiO_2$ thin films, i.e., a binary (with both oxidizing and reducing sites) coordinating complementary catalyst surface, can be created through synthesis processes [7]. Figures
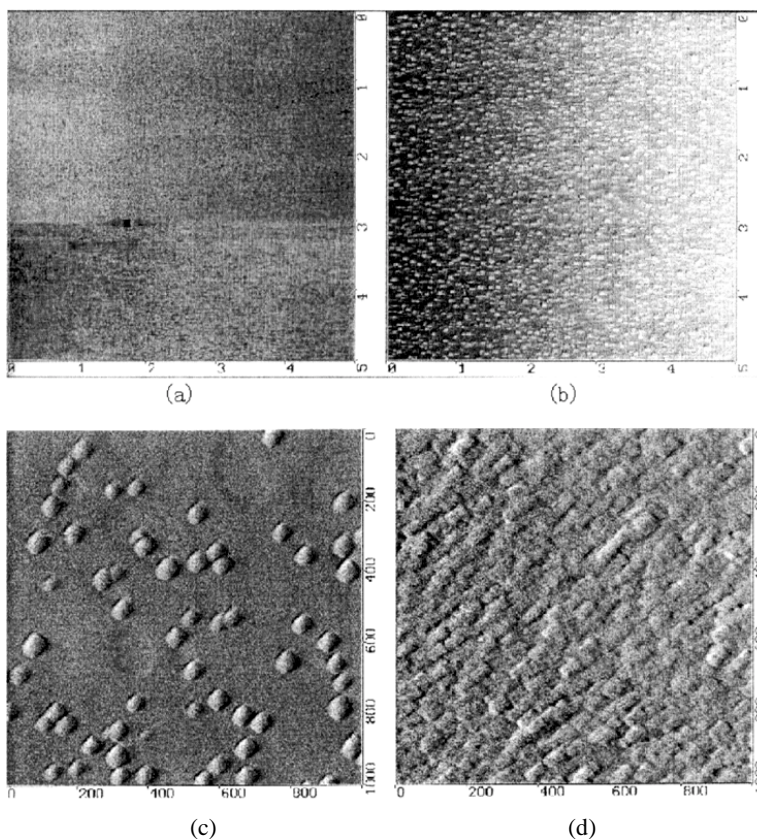
**Fig. 2** AFM images of TiO$_2$ (110) single crystal surface before (a) and after (b) UV illumination in 5000 × 5000 nm scale; after heating at 300 °C (c) and argon ion sputtering (d) treatments in 1000 × 1000 nm scale.

3a and 3b are AFM and FFM images of the Pt/TiO$_2$ surface. The AFM image shows nanograin structures of 20–30 nm size on the surface of the substrate. In the FFM image, the Pt nanograins appear darker than the surrounding TiO$_2$ surface. This is due to the difference in the friction factor property between Pt and TiO$_2$ contact surface. The initial Pt/TiO$_2$ electrochemical cell was designed for photo-electrochemical reactions in the liquid state, e.g., splitting water to produce H$_2$ and O$_2$ [8]. Here, we develop this old work into a new application. It was found that this binary complementary nanoscale surface was used to decompose ice at low temperatures. Figure 3c shows AFM images of an ice-coated (about 2 nm) Pt/TiO$_2$ substrate in N$_2$ atmosphere at –30 °C. After 1 h UV illumination with a power density of 0.1 mW/cm$^2$, the bare Pt/TiO$_2$ surface appears and indicates that the ice was decomposed completely as shown in Fig. 3d. The effect is useful for the prevention of icing on windows and electrical cables in winter. The important advantage of this technique is that the anti-icing process is carried out through a photo-electrochemical reaction, but not a physical heating process. The necessary reaction for removing ice blocks on the substrate is just the decomposition of single molecular layer of H$_2$O contacting with the substrate. Furthermore, this kind of structure can be also applied to other catalysis systems for various industrial applications.
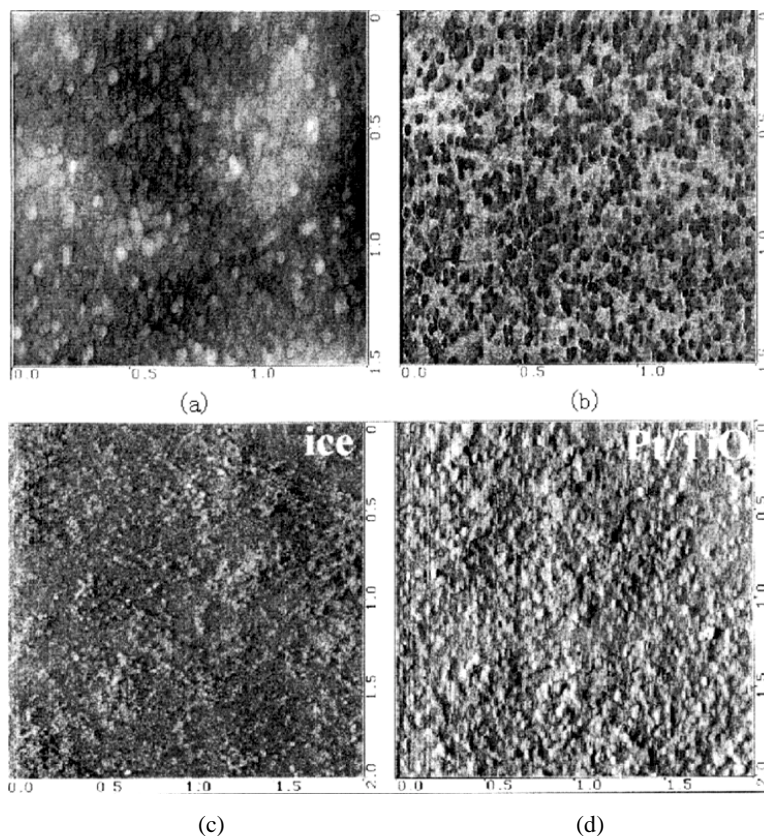
**Fig. 3** AFM image (a) and FFM image (b) of Pt nanoparticle on $TiO_2$ thin films in $1500 \times 1500$ nm. AFM images of ice-coated $Pt/TiO_2$ surface before (c) and after (d) UV illumination in $N_2$ atmosphere at $-30$ °C in 2000 nm $\times$ 2000 nm scale.

## Super-"amphiphobic" surface (convex and concave binary cooperative complementary surface)

Through a phase-separation process, polyporous with hydrophobic convex and hydrophilic concave surfaces are generated in copolymer film which appears as an "amphiphobic" surface (i.e., the surface appears to have both hydrophobic and oileophobic properties) [10]. It was known that the roughness can enhance the wettability of a surface. However, a pure hydrophilic or hydrophobic surface of polyporous (as shown in Fig. 4 top) may only enhance the hydrophilic or hydrophobic property of a solid surface, but "amphiphobic" behavior can not be created. Interestingly, as-grown copolymer films show an "amphiphobic" property. This unique property resulted from the special structure of the films. The AFM image of film is shown in Fig. 5a where polyporous structures are observed indicating a porous density of $3 \times 10^7/cm^2$. The FFM image of the same area (Fig. 5b) indicated that the wettability of the inside porous surface and out-surrounding surface are different, i.e., a hydrophilic inside surface and a hydrophobic outside surface. This contrast in the FFM image is due to the fact that a hydrophilic AFM tip ($Si_3N_4$) may generate a stronger friction force at the hydrophilic area than that of the hydrophobic area. This type of surface structure can be designed in two ways, i.e., hydrophilic (or hydrophobic) inside surface and a hydrophobic (or hydrophilic) outside surface, as shown in Fig. 4 bottom. This
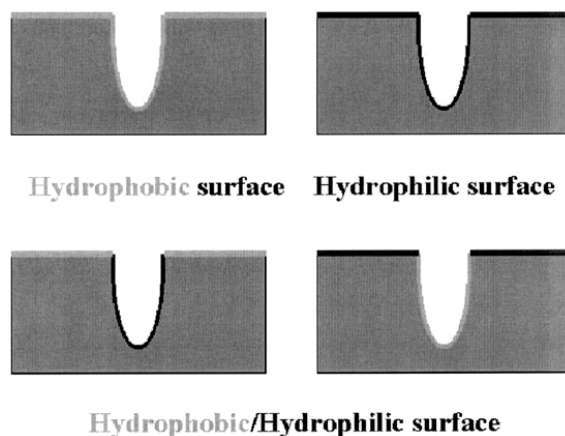
**Fig. 4** The schematic profiles of the polyporous in different structural designs (top) with pure hydrophilic surface in blue color or pure hydrophobic surface in yellow color, (bottom) with hydrophilic (or hydrophobic) inside surface and a hydrophobic (or hydrophilic) outside surface.
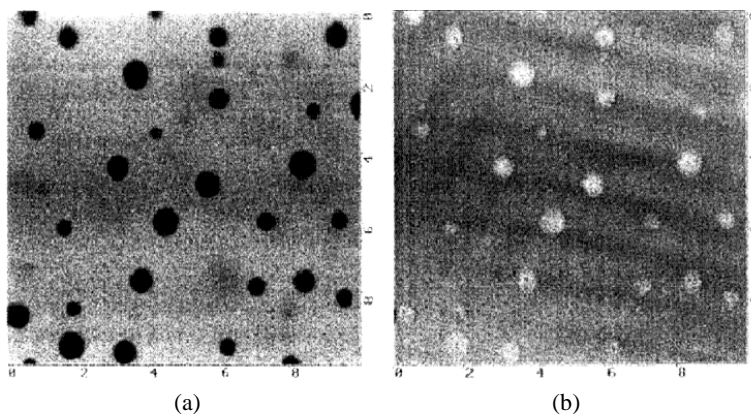


**Fig. 5** Image in (a) AFM mode and (b) FFM mode of surface structure of the copolymer film in 10 000 × 10 000 nm scale.

microscale structure may prevent liquid (both water and oil) from entering the porous (detailed discussion will be published in ref. 10), therefore the surface appears an "amphiphobic" property which may also provide a self-cleaning surface with wide application potential. Furthermore, this essential idea for controlling the wettability of a solid surface is also useful to the design of various special surfaces.

## Super-lattice surface structures (stable and metastable binary cooperative complementary structure)

Photoinduced surface phase transitions (surface reconstruction) generate binary (stable cubic phase and metastable hexagonal phase) nanostructures showing several different types of nanopatterns on the surfaces of $C_{60}$ single crystals [11,12]. $C_{60}$ solid may condense into both face-centered cubic (fcc) and hexagonal close-packed (hcp) phase at room temperature. The hcp phase is a metastable one, and cohesive energy difference between the hcp and fcc phases is as small as 0.9 kcal mol$^{-1}$. This provides a possibility
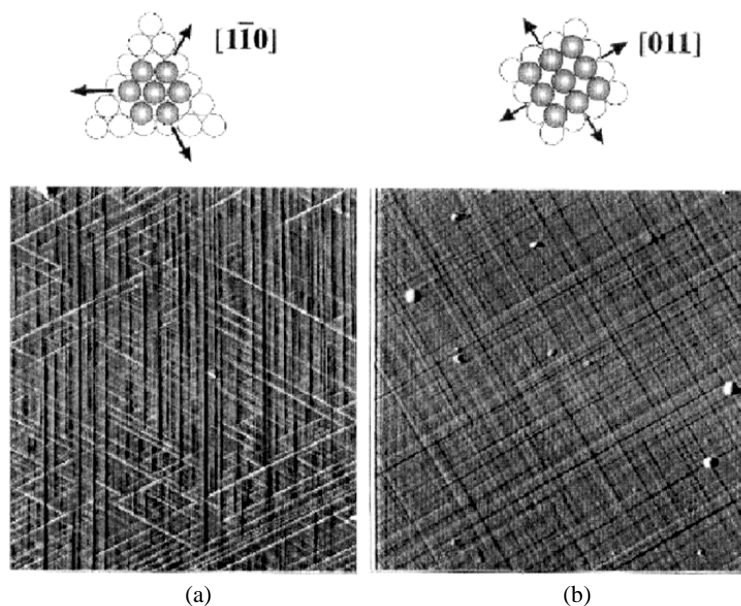
**Fig. 6** AFM images of (a) triangular and cubic nanopatterns in $10 \times 10$ μm scale, which were generated using unpolarized light illumination with an intensity of $1.8 \times 10^4$ photons nm$^{-2}$ on the surface of (111) and (100) surface of the $C_{60}$ single crystal. Above the images, two-layer molecular models of the collective molecular displacement directions are shown.

for the coexistence of the two phases on the same surface. Upon photon absorption in the 1.62–2.2 eV range, Frenkel excitons are generated from a strong exciton-lattice coupling in solid $C_{60}$. These excitons are found hopping between nearest neighbor molecules, that is, anisotropic hopping along the three equivalent [110] directions on the (111) surface or two equivalent [011] directions on (100) face. Under higher light intensity, collective molecular displacement is induced on the surface of the crystal, which results in a large-scale surface molecular rearrangement. On the (111) surface, the collective displacement is along the three [110] directions (top of Fig. 6) forming a triangular pattern. On the (100) surface, the displacement is along two equivalent [011] directions forming a cubic pattern. Photoinduced surface reconstruction can be understood as a general phenomenon, and may occur on a wide variety of molecular crystals.

## Optically controllable superconducting system (superconducting/normal-conducting phase binary cooperative complementary structure)

Binary nanostructures formed from superconducting and normal-conducting phases provide an optically controllable superconducting system [13–14]. The photoinduced modification of near-surface region of $K_3C_{60}$ samples generates very large enhancement of the diamagnetic shielding fraction value. Before illumination, only ~10 vol% of $K_3C_{60}$ quenched sample exhibited diamagnetism. However, after illumination, values close to 100% of shielding fraction value were obtained. Interestingly, the diamagnetic shielding fraction value was found to return to its original value upon heating, demonstrating that the transformation is reversible. By using Raman spectroscopy, this effect is addressed as photopolymerization and thermal depolymerization of $C_{60}$ molecules in the normal-conducting phase at grain boundaries of the superconducting phase. The nanodomain structures are directly observed by AFM as shown in Fig. 7a. The domains appear as spherical surface and 30 ~ 60 nm in size. Upon illumination in a wavelength range of 300–500 nm, an obvious shrinkage occurs near the domain boundaries, and produces a clear
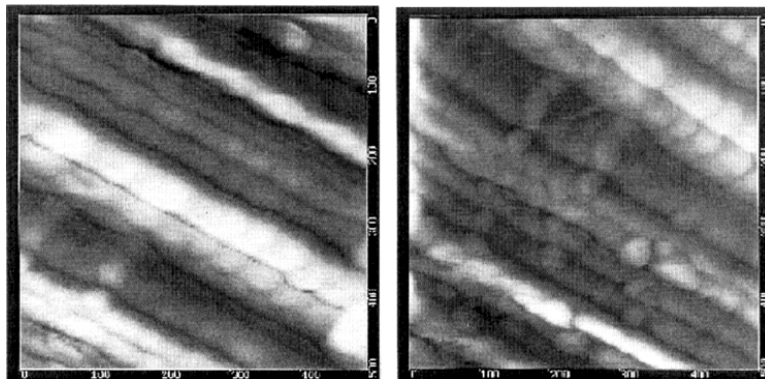
**Fig. 7** AFM images of $K_3C_{60}$ film with nanosized domain structures before (a) and after (b) UV illumination in a vacuum condition of $2 \times 10^{-7}$ torr (in $500 \times 500$ nm scale).

outline of the domain structures as shown in Fig. 7b. The obvious change upon illumination is in the domain boundaries. These results indicate that the electronic connection between the superconducting nanodomain structure may greatly influence the physical properties of the superconducting system.

The above results demonstrate the unique character of binary complementary nanoscale materials.

## CONCLUSIONS

In summary, binary cooperative complementary nanoscale interfacial materials are introduced as a new concept for the design of novel functional materials. This concept is based on the generation of nanostructures with a pair of mutually complementary properties on the same surface. Under the right conditions, these types of interfaces can exhibit unexpected properties, providing a huge potential for applications and theory. Of course, this concept is not limited to the surface but can also be extended to bulk materials, i.e., binary cooperative complementary nanoscale materials. We can predict that there is a multitude of functional materials waiting to be explored.

## ACKNOWLEDGMENT

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