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1. Introduction

Ordered micro/nanostructured arrays have attracted much interest due to their important applications in microfluidic devices, optoelectronic devices, nanophotonics, field emitters, nanogenerators, sensors, nano-biotechnology, surface science, photocatalytic properties etc.\textsuperscript{3-11} The traditional routes to create periodic micro/nanostructured arrays are generally divided into two step. Microsized structure arrays are first fabricated by traditional lithographic techniques (e.g. photo-lithography, electron-beam lithography, ion beam lithography, x-ray lithography)\textsuperscript{12-15}, as well as soft lithography (e.g. the techniques of replica molding, microcontact printing, micromolding in capillaries)\textsuperscript{16-19}, the nanostructures are then modified on the microsized units in array,\textsuperscript{20} thus hierarchical micro/nanostructured arrays are finally achieved. However, they cannot be afforded due to the high costs and time-consuming in the most laboratories. Recently, the monolayered colloidal crystals (or called colloidal monolayers), ordered monolayer colloidal sphere arrays with hexagonal close-packed lattice structures on a certain substrate by self-assembly,\textsuperscript{21-35} can be used to prepare ordered structure arrays.\textsuperscript{36-41} It has proved that it is a flexible approach to fabricate the periodic micro or nanostructure arrays (e.g. nanoparticle arrays,\textsuperscript{42-49} nanopore arrays,\textsuperscript{50-59} hollow sphere arrays\textsuperscript{60-65}) based on colloidal monolayer templates by the different routes, solution/sol-dipping route, electrochemical deposition etc. Their properties are morphology and arrangement parameter dependent. Besides these periodic structure arrays, the colloidal monolayer template also can be used to prepare hierarchical micro/nanostructured arrays. For example, the hierarchical micro/nanostructured polystyrene (PS) sphere/CNTs composite arrays were obtained by wet chemical self assembling\textsuperscript{66-68}, hierarchical microsized PS sphere/silver nanoparticle composite arrays or microsized pore/silver nanoparticle arrays were made by thermal deposition of silver precursor\textsuperscript{69,70}, gold hierarchical micro/nanostructured particle arrays were created by electrochemical deposition based two step replication of colloidal monolayer template.\textsuperscript{71} However, these routes have been
developed by basically chemical reaction. They have some disadvantages of impurities on surface of arrays due to incompletely decomposition of precursors, residua of surfactants in self-assembling or electrochemical deposition. Additionally, it is quite difficult to achieve very uniform morphology of hierarchical micro/nanostructure arrays on a large-scale. Another route of colloidal monolayer template combining with physical deposition is expected to resolve these problems. In this chapter, we focus on introducing the recent work to create micro/nanostructured arrays based on colloidal templates with physical deposition (pulsed laser deposition (PLD) and sputtering). The parameters of microstructure or nanostructure can be tuned by periodicities of colloidal templates or experimental conditions of physical deposition. The applications of nanorod arrays with controllable morphology and arrangement parameters in self-cleaning surfaces, enhanced catalytic properties, field emitters etc. are also presented in following section.

2. Pulsed laser deposition assisted colloidal lithography

2.1 Method

A polystyrene (PS) colloidal monolayer was first fabricated on a substrate. The desired material was then deposited on this colloidal monolayer substrate by PLD at room temperature and oxygen was introduced into PLD chamber as the background gas. This periodic array has a special hierarchical micro/nanostructure array with a hexagonal-close-packed (hcp) arrangement, which originate from the pattern of colloidal monolayer. In this micro/nanostructure unit in array, the nanorod stands vertically on the microsized PS sphere tops, and nanobranches in each nanorod grow in a radiationlike manner, perpendicular to the PS sphere surface. The detailed experiments are described as following.

Fig. 1. Schematic illustration of PLD process.
Commercial monodispersed PS spheres dispersed in water with a certain size were purchased from companies. The PS colloidal monolayers were first fabricated on cleaned Si substrates by self-assembly using spin coating. The colloidal monolayer with its supporting substrate was placed in a deposition chamber of PLD, close to the target and at an off-axial position with respect to the target, as shown in Figure 1A laser beam with a 355 nm wavelength from a Q-switched Nd:YAG laser (Continuum, Precision 8000), operated at 10 Hz with 100 mJ/pulse and a pulse width of 7 ns was applied and focused on the target surface with a diameter of about 2 mm. The desired target, for example, rutile typed titanium dioxide was used for deposition. The substrate and target were rotated at 40 and 30 rpm, respectively. PLD was carried out at a base pressure of $2.66 \times 10^{-4}$ Pa and a background O$_2$ pressure of 6.7 Pa.

Fig. 2. Morphology of a sample obtained by PLD using a Si substrate with a PS colloidal monolayer coating (PS sphere size: 350 nm; deposition time: 70 min). (a) FESEM image from top view and (b) FE-SEM image of cross-section. (c) and (d) are high-resolution images observed from the side. (d) much higher magnification image of (c).

After deposition, the sample demonstrated a periodic hierarchical micro/nanorod array with an hcp arrangement, as reflected from Figure 2a. Each nanorod consists of two parts: a PS sphere at the bottom and a vertical nanorod on the top of the PS sphere (Figure 2b). The diameter of the nanocolumn was almost the same as that of the PS sphere, 350 nm, and its height was about 870 nm. The nanorod had a very rough structure on the surface and was composed of many nanobranches, according to the high-resolution images of the side view (Figure 2 c, d). TEM observation from the top of the nanorod arrays reflects that each nanorod consists of radiation-shaped nanobranches emanating from the center (Figure 3a).
Fig. 3. Corresponding TEM images of the sample in Figure 2. (a) Periodic nanorod array observed from the top. (b) Single nanorod observed from the side. The inset in (b) is the corresponding electron diffraction pattern.

Fig. 4. a, b: FE-SEM images of a CuO hierarchical micro/nanostructured array obtained by combining the PS colloidal monolayer and PLD process. (PS sphere size 350 nm, deposition time 2 h, ambient oxygen pressure during deposition 6.7 Pa). (a) top-view image; (b) section view. Scale bars in parts a and b indicate 500 nm. c, d: TEM images of a CuO hierarchical micro/nanostructured array: (c) TEM image from the top; (d) TEM image of several separated units from the periodic array and the corresponding selected area electron diffraction (SAED) pattern.
The TEM image of a single nanorod also clearly displays that the nanorod consists of a PS sphere at bottom and a nanocolumn on the sphere surface. The nanorod possesses nanobranch-structures, which grow almost vertically on the PS sphere surface (Figure 3b). The nanobranch-structures indicate that the nanorod has a hierarchical, porous structure and hence has a high surface area. The selected area electron diffraction (SAED) pattern shows that the deposited materials on PS sphere surfaces by PLD are amorphous. Besides TiO$_2$ amorphous hcp nanocolumn arrays, the presented strategy can be extended to the fabrication of similar amorphous structures of SnO$_2$, WO$_3$, C, and so forth, just by changing the corresponding target in the PLD process. Additionally, some materials, e.g. CuO, Fe$_2$O$_3$, ZnO are easily crystalline by PLD at room temperature. If the colloidal monolayer is applied as a template, the crystalline CuO, Fe$_2$O$_3$, ZnO etc. hierarchical micro/nanostructured arrays can also be obtained. Figure 4 shows the SEM and TEM image CuO crystalline hierarchical micro/nanostructured arrays using colloidal monolayers as templates by PLD. Each arrayed unit is composed of PS sphere at bottom and deposited materials at top. Deposited materials are well crystalline, they do not exhibit round shapes but radially aligned nanocolumns having tips with trigonal pyramidal shapes on the PS sphere. The deposited CuO nanostructures can be tuned by varying ambient gas pressures during the PLD process. Figure 5 shows the FE-SEM and TEM images of samples achieved by PLD under higher ambient gas pressures during the PLD process using the colloidal monolayers as substrates. When oxygen pressure increased from 6.7 to 26.7 Pa, the morphology did not appreciably change and exhibited similar hierarchical structures as before (Figure 5a). However, when the oxygen pressure increased to 53.3 Pa, the morphology completely changed and was very different from those at lower pressures. The nanocolumn tips on the PS sphere demonstrated imperfect trigonal pyramid shapes, and the tip sizes became much smaller (Figure 5b). According to the corresponding TEM image and SAED pattern (Figure 5c), we find that hierarchical micro-/nanostructures were still observed at such high oxygen pressure, but the crystallization of deposited aligned nanocolumns on the PS sphere becomes worse than that obtained at lower oxygen pressure. When the gas pressure increased to as high as 79.8 Pa, similar hierarchical micro-/nanostructured array was not obtained, and many aggregates of small particles were produced on the colloidal monolayer template (Figure 5d). The XRD spectra of the samples obtained under different oxygen pressures are shown in Figure 6. Strong preferential orientation growth along (002) was observed at the gas pressure of 26.7 Pa. Increasing oxygen pressure led to weakening of this preferential orientation and broadening of X-ray diffraction peaks. This result reflects that deposited materials gradually changed to small nanoparticles from aligned nanocolumn arrays and the particles became much smaller with increasing oxygen pressure during PLD, agreeing with FE-SEM images. When the oxygen pressure increased to very high value, 79.8 Pa, the deposited material completely consisted of small nanoparticles or the aggregates of small nanoparticles, and there was no preferential orientation growth. Because when the gas pressure increases to a high value, the plume is compressed into a smaller space in PLD process, and the possibility of collision among ions or atoms in plasma is greatly enhanced, further resulting in a kinetic energy decrease of ions or atoms, which leads to less crystallization and smaller nanoparticle formation.
Fig. 5. Images obtained by the different ambient oxygen pressures: (a, b, d) FE-SEM images of the samples obtained under ambient oxygen pressure of 26.7, 53.3, and 79.8 Pa, respectively; (c) TEM image of the sample obtained at 53.3 Pa and the corresponding SAED pattern of several units. Scale bars in (a), (b), and (d): 1 μm.

Fig. 6. XRD patterns of the samples obtained under different oxygen pressures.
Similar crystalline hierarchical micro-/nanostructured arrays of Fe$_2$O$_3$ and ZnO can be also created by the same route, as shown in Figure 7. Fe$_2$O$_3$ nanobelts or ZnO nanocolumns were well aligned on the PS sphere tops, like those of CuO. However, the Fe$_2$O$_3$ nanobelt or ZnO nanocolumn tops were not like those of CuO. The slight differences among CuO, Fe$_2$O$_3$, and ZnO fine nanostructures are determined mainly by their various chemical and physical properties: a crystal facet of the interface with different energies etc.

![Image of hierarchical micro-/nanostructured arrays of Fe$_2$O$_3$ and ZnO.](image)

Fig. 7. FE-SEM images of hierarchical micro-/nanostructured arrays of Fe$_2$O$_3$ and ZnO. (a, b) Fe$_2$O$_3$, oxygen pressure 6.7 Pa, deposition time 1.5 h; (c, d) ZnO. a and c: top views; b and d: side views (oxygen pressure 6.7 Pa and deposition 40 min). The inset in (b): the high magnification image of a single Fe$_2$O$_3$ hierarchical micro-/nanostructure.

In this strategy, the height of micro/nanostructured unit can be obviously controlled by varying deposition time during PLD process, the height will increase with increase of PLD time. From the Figure 8, it can be found that the unit height increases by increasing deposition time from 30 min to 60 min. However, if the deposition time is too long, to say, 180 min, the tops of micro/nanostructured units will aggregate with each other due to strong Van de Waals attraction among units in the deposition process, as shown in Figure 8 (c), (c') and (c''). Additionally, the top of micro/nanostructured unit gradually flattens from convex shape with increasing deposition time, resulting in a weakening shadow effect. Therefore, a continuous film might be formed at top of hierarchical micro/nanostructured array if further increasing deposition time after 180 min.
4.1 Wettability

Wettability is generally related to the surface morphologies, roughness and free energy of materials surface and it is evaluated by the water or oil contact angle. A special surface with self-cleaning effect is usually defined as a surface that has the ability to remove dirt or contaminants that are on it when water droplets slide along the surface. Self-cleaning is closely related to surface wettability\(^\text{90-94}\). The self-cleaning effect is normally attributed to superhydrophobicity (water contact angle (CA) exceeding 150\(^\circ\) and sliding angle (SA) less than 10\(^\circ\)) or superhydrophilicity (water CA less than 10\(^\circ\)) of the surface. For superhydrophobicity with a self-cleaning effect, contaminants adhere to the water droplet surface and are removed after the water droplet slides off the solid surface with a small tilted angle, due to large water CA and low surface free energy. For superhydrophilic surfaces, contaminants can easily be swept away by adding water droplets on them, due to very low water CA. Wettability can be enhanced by increasing surface roughness, according to Wenzel’s equation:\(^\text{95}\)

\[
\cos \theta_r = r \cos \theta
\]

where \(r\) is the roughness factor, defined as the ratio of total surface area to projected area on the horizontal plane; \(\theta_r\) is the CA of film with a rough surface; and \(\theta\) is the CA of film with a smooth surface. Obviously, increased roughness can enhance the hydrophobicity and/or hydrophilicity of hydrophobic and/or hydrophilic surfaces. The hierarchical micro/nanostructured arrays based on colloidal monolayers are actually rough films at the micro/nano-scale level. It is expected that such hierarchical micro/nanostructured arrays could induce surface superhydrophilicity or superhydrophobicity with a self-cleaning effect, due to their high roughness. Amorphous, porous hierarchical TiO\(_2\) micro/nanostructured arrays were prepared by PLD assisted colloidal lithography (Figure 3).\(^\text{73}\) These arrays exhibited strong superhydrophilicity. When a small water droplet was dropped on a hierarchical structured array, the droplet spread out rapidly on the surface and displayed a water CA of 0\(^\circ\) in 0.225 s (Figure 29). Additionally, this hierarchical array film exhibited superoleophilicity when a small oil droplet was placed on the nanorod surface and the oil CA became 0\(^\circ\) in 0.5 s (Figure 30). These results suggest that this amorphous hierarchical micro/nano-structured array had superamphiphilicity with 0\(^\circ\) of both water CA and oil CA. A TiO\(_2\) film with superamphiphilicity can generally be obtained by UV irradiation, due to hydroxyl ions generated by oxygen defects or dangling bonds on its surface, induced by photochemical processes\(^\text{96}\). However, the TiO\(_2\) hierarchical micro/nano-structured array film possessed superamphiphilicity without further UV irradiation. The ions (e.g., Ti\(^{4+}\), and O\(^{2-}\)) and electrons are released into the PLD chamber and some oxygen species are lost in the vacuum environment in PLD after a TiO\(_2\) target absorbs energy from laser irradiation by exceeding its threshold. Oxygen vacancies are produced in the deposited TiO\(_2\) during PLD, converting relevant Ti\(^{4+}\) sites to Ti\(^{3+}\) sites that are favorable for dissociative water adsorption. Therefore, these defect sites microscopically form hydrophilic domains on the TiO\(_2\) surface. However, the other parts surrounding the hydrophilic domain remain oleophilic on the surface. A composite TiO\(_2\) surface having hydrophilic and oleophilic domains on a microscopically distinguishable scale demonstrates macroscopic amphiphilicity on the TiO\(_2\) surface\(^\text{96}\). Additionally, a TiO\(_2\) nanoparticle film prepared by PLD without a PS colloidal monolayer exhibited a water CA of 15\(^\circ\) and an oil CA of 27\(^\circ\) (Figure 31). The roughness of the hcp TiO\(_2\) hierarchical micro/nano-structured array film

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was greatly increased compared with that of the nanoparticle TiO$_2$ film produced by PLD without using a colloidal monolayer. According to Wenzel’s equation, wettability is enhanced from amphiphilicity to superamphiphilicity. Therefore, the superamphiphilicity of the amorphous micro/nano-structured array originates from the combination of the amphiphilicity produced by PLD and the special rough structures of hcp hierarchical arrays.

Fig. 29. Time course of water-contacting behavior on the amorphous TiO$_2$ micro/nano-structured array film.
More importantly, this amorphous TiO$_2$ hierarchical array demonstrated very good photocatalytic activity for organic molecular degradation (e.g., effective decomposition of stearic acid under UV illumination). A combination of superamphiphilicity and photocatalytic activity can yield a self-cleaning surface. For instance, an oily liquid contaminant spreads out on a surface due to superoleophilicity, which is helpful in improving the photocatalytic efficiency under light illumination. An organic contaminant including oil gradually degrades under sunlight irradiation (sunlight contains some UV light). The self-cleaning effect can be realized after washing away contamination from the superhydrophilic surface.

Additionally, superhydrophobic surfaces with large water CA and small SA have a self-cleaning effect. For superhydrophobic film, the surface should be sufficiently rough and have a chemical coating with low free-energy materials in order to trap the air on the rough surface. In this case, the area fraction of a water droplet in contact with the sample surface is very small, which helps obtain a small SA. Hierarchical periodic micro/nanostructured arrays based on colloidal templates provide surfaces with regularly ordered and well-defined roughness. They may lead to enhancement from hydrophobicity to superhydrophobicity on the surface after modification with low free-energy materials. For instance, Co$_3$O$_4$ hierarchical, hncp micro/nano-rod arrays was created by PLD assisted colloidal lithography after annealing at 450 °C for 3 h (oxygen pressures: 93.1 Pa), as shown in Figure 32 a and b. Such surface was chemical modification with fluorosilane, a kind of low free energy material, it presented superhydrophobicity with water CA of 152.6° and a very small SA, indicating self-cleaning effect. It can be explained by Cassie and Baxter equation:

$$\cos \theta = f_1 \cos \theta_1 - f_2$$  

(2)

Here, $f_1$ and $f_2$ are the surface area fractions of the projecting solid and air ($f_1 + f_2 = 1$). The large fraction of air trapped in the nanorod arrays forms a cushion at the film–water interface that prevents the penetration of water droplets into the grooves. In this case, $\theta_1$ is
152.6° and θ is 18.8°, so a value for $f_1$ of 0.06 is calculated from eqn (2) (i.e. $f_2$ is 0.94), implying that only 6% of the observed contact area beneath a water droplet is in contact with the water droplet. High $f_2$ of 0.94 means that the air was well trapped into the groove among nanorod arrays and hence the water droplet kept a spherical shape.

Fig. 31. Water and oil CAs on a TiO$_2$ film on a silicon wafer prepared by PLD without using a PS colloidal monolayer. (a) Water CA: 15 degrees. (b) Oil (rapeseed) CA: 27 degrees.
Fig. 32. FE-SEM images of Co$_3$O$_4$ hierarchical micro/nano-rod arrays obtained by PLD assisted colloidal lithography after annealing at 450°C for 3 h (oxygen pressures: 93.1 Pa). (a) Top views; (b) Tilted at 45° (c) water CA after modification with low free energy materials.
4.2 Field emission

Field-emission (FE) properties have recently attracted so much attention due to great commercial interest in flat-panel displays and other microelectronic devices.\textsuperscript{101} Besides carbon nanotubes, semiconductors have also attracted great interest in field emitters owing to their good mechanical stability, low work function, and high electrical and thermal conductivities.\textsuperscript{102} FE properties are usually decided by the nature of the cathode materials as well as geometry and size of them. By well designing the geometry and size of cathode, for example, to introduce nanostructures on it, good FE performances have been achieved including faster turn-on time, compactness, and sustainability during the field emission compared to conventional bulky material forms. More importantly, researchers have found that cathodes composed of periodic regular arrays on the surface are very highly helpful for producing a low operating voltage and a stable current because of the elimination of the shield effect on densely packed 1D nanostructured arrays in field emission.

Periodic TiO$_2$ micro/nano-rod arrays with hncp arrangement can be synthesized by combining a colloidal monolayer template with pulsed laser deposition (PLD) followed by annealing in ambient air, as described before.\textsuperscript{86} By this route, the periodicity of such special nanorods can be easily tuned by changing the colloidal sphere size in the colloidal monolayer template. While a distance between neighboring nanorods can be controlled by varying the background gas pressure during the PLD process if periodicity is fixed for a nanorod array. The well tunable periodicity and distance between neighboring nanorods are very useful for investigating and optimizing their FE performance.\textsuperscript{86}

The periodic hncp TiO$_2$ nanorod array was fabricated by PLD using a colloidal monolayer template with 350nm PS spheres at 6.7 Pa O$_2$ for 60 min and subsequent annealing at 650 °C for 2 h in air (Figure 19). It demonstrated a low turn-on field of about 5.6 V μm$^{-1}$ (here the turn-on field was defined as the value of electric field when an emission current density was 4.5 nA cm$^{-2}$) according to the FE current density–applied electric field curve (J–E) at a working distance of 60 μm from the anode to the nanorod array serving as the cathode (Figure 33). This FE current–voltage characteristics can be expressed by a simplified Fowler–Nordheim (FN) equation and a field-enhancement factor, $\beta$ can be defined as $B\phi^{3/2}/\kappa$ according to the FN equation (here $\phi$: the work function of cathode material; $\kappa$: slope in FN plot).\textsuperscript{103} This hncp TiO$_2$ nanorod array showed a field-enhancement factor $\beta$ of 8.38×10$^2$. However, a TiO$_2$ nanorod array with top aggregation for several neighboring nanorods caused by longer deposition displayed a much higher turn-on field of 15.8 V μm$^{-1}$ and lower field-enhancement factor $\beta$ of 3.34×10$^2$ (Figure 34). This result indicates that the good FE properties of a periodic TiO$_2$ hncp nanorod array are mainly attributable to the aligned and periodic hncp nanorod morphology.

When a periodicity of hncp nanorod array increased from 350 nm to 750nm and 1 μm by choosing the colloidal monolayers with different PS sphere sizes during the PLD at the same background gas pressure as before and followed by the same annealing, as presented in Figure 35. The field-enhancement factor decreased with increasing periodicity of the hncp nanorod array (Figure 36a). This is mainly attributed to a decreasing number density of nanorods with an increase in the hncp array periodicity. When the periodicity of the hncp nanorod array was increased from 350 to 750 nm, the turn-on field also increased from 5.6 to 13.0 Vμm$^{-1}$. When a periodicity further increased to 1 μm, the turn-on field remained about 13.0 Vμm$^{-1}$. It is evident that the hncp nanorod array with the smallest periodicity of 350nm exhibited the best FE properties in this investigation.
Fig. 33. FE properties of periodic hncp nanorod array by PLD using a colloidal monolayer template with 350nm PS spheres in O₂ at a pressure of 6.7 Pa for 60 min and subsequent annealing in air. a) FE current density–electric field (J–E) curves measured for an hncp TiO₂ nanorod array at an anode–cathode distance of 60 μm. b) Corresponding Fowler–Nordheim (FN) plot.
Fig. 34. Top aggregation of a TiO$_2$ nanorod array obtained PLD assisted colloidal lithography with a longer PLD time (80 min) and subsequent annealing. a) FE-SEM image; b) FE J-E curves measured at an anode-cathode distance of 60 mm for a top-aggregated TiO$_2$ nanorod array; c) Corresponding FN plot.
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Fig. 35. FE-SEM images of hncp nanorod arrays with different periodicities: 750nm for (a) and (b); 1μm for (c) and (d). PLD was performed in 6.7 Pa of oxygen for 130 min. (a) and (c) are observed from the top, (b) and (d) are observed with a tilt angle of 45°.

While a distance between neighboring nanorods can be tuned by changing the background gas pressure during the PLD process if periodicity is fixed to 350 nm for a nanorod array (Figure 22). With increasing this distance of neighboring ones, the field-enhancement factor increased and the turn-on field decreased (Figure 36a). The sample with a small nanorod distance of 20 nm exhibited a relatively low field-enhancement factor of 5.04×10^2 and a high turn-on field of 9.7 V μm^-1. When the nanorod distance increased to 50 nm, the FE properties showed enhanced performance with a high field-enhancement factor of 8.38 ×10^2 and a low turn-on field of 5.6 Vμm^-1. When the nanorod distance further increased to 110 nm, the best FE properties with a field-enhancement factor of 9.39 ×10^2 and a turn-on field of 5.3 Vμm^-1 were obtained. (Figure 36b) The above results suggest that optimized FE properties can be achieved by increasing the nanorod distance by controlling the experimental parameters. The increased field-enhancement factor β with the increase of nanorod distance can easily be understood as follows if the periodicity of hncp nanorod array is fixed. The field enhancement factor β is generally related to geometry of an emitter and can be expressed as β=h/r, where h is the height and r is the curvature radius of an emitting center. With an increase in the nanorod distance, the effective diameter of an individual nanorod and a curvature radius r would decrease (Figure 37), resulting in an increase of β according to the above relationship.
Fig. 36. (a) Field-enhancement factor $\beta$ changing with increasing periodicity of an hncp nanorod array, (b) Change in field-enhancement factor and turn-on field with varying neighboring nanorod distance in an hncp array.
4.3 Enhanced catalytic properties
The hierarchical micro/nanostructured arrays possess a large specific surface area and hence they might have important application in catalytic fields. For instance, the hcp amorphous TiO$_2$ micro/nanostructured array on a colloidal monolayer obtained by PLD assisted colloidal lithography demonstrated an enhanced photocatalytic activity (Figure 2). Its photocatalytic performance was estimated based on the decomposition of organic molecules, stearic acid under UV illumination by monitoring the FT-IR spectra. The frequencies of 2919 and 2849 cm$^{-1}$ reflect the methylene group asymmetric ($\nu_{\text{asymmetric}}$) and symmetric ($\nu_{\text{symmetric}}$) stretching modes of stearic acid. These values for the methylene group stretching mode are close to those of a crystalline alkane and are typically taken as evidence of the formation of a dense, well-ordered, self-assembled monolayer of stearic acid on the oxide surface. Therefore, the photodegradation of stearic acid can be monitor by observing density of these two frequencies. With increasing the UV irradiation time, the vibrational bands of the methylene group gradually decreased and almost completely disappeared after 25 min, as shown in Figure 38a. The decrease in C-H vibrational bands reflects that the stearic acid is gradually photodegraded by such TiO$_2$ hierarchical micro/nanostructured array films under UV irradiation. Figure 38b shows that degradation curves of a stearic acid film on a silicon wafer, an amorphous TiO$_2$ film by PLD without using a colloidal monolayer, an hcp amorphous TiO$_2$ hierarchical micro/nano-rod array on the colloidal monolayer, and an anatase TiO$_2$ rod array (obtained by annealing hcp amorphous TiO$_2$ hierarchical micro/nano-rod array on the colloidal monolayer at 650 °C for 2 h. These results indicate that TiO$_2$ exhibited efficient degradation for stearic acid and that the hcp amorphous TiO$_2$ hierarchical micro/nano-rod array on a colloidal monolayer demonstrated the best performance compared to the amorphous film and the anatase rod array. Anatase is usually deemed to be more photocatalytically active than the rutile and
Fig. 38. (a) Photocatalytic activity of an hcp amorphous TiO$_2$ micro/nano-rod array with a PS colloidal monolayer. (b) Photocatalytic activity evaluation of different substrates based on the absorbance ratio $A/A_0$ as a function of UV irradiation time. $A$ and $A_0$ are the absorbance after the UV irradiation and that from the initial surface, respectively.
amorphous TiO$_2$. However, besides the crystal phase, other factors, including the specific surface area, crystal composition, and material microstructures, also significantly affect the catalytic performance of TiO$_2$.\textsuperscript{109-111} In this case, an amorphous hcp hierarchical micro/nano-rod array has porous structures and possesses a much higher specific surface area than that of an anatase rod array, which contributes to better photocatalytic properties. These results suggest that the surface area of TiO$_2$ is preferable to its crystal structure for enhancing photocatalytic activity. Additionally, a periodic structured array of amorphous TiO$_2$ can enhance photocatalytic activity better than an amorphous TiO$_2$ thin film produced by PLD without using a colloidal monolayer. This may be ascribed to special hierarchical structures composed of radiation-shaped nanobranches emanating from a center point on the PS sphere.\textsuperscript{112} The combination of superamphiphilicity and photocatalytic activity is helpful in realizing a self-cleaning surface.

Fig. 39. Isomerization equilibrium of ethyl acetoacetate between the two kinds of isomers, keto and enol.

Additionally, hierarchical alumina micro/nanostructured arrays demonstrate very excellent catalytic properties for some organic reactions. For example, as we know, ethyl acetoacetate has two kinds of isomers, keto and enol, because of the acidic hydrogen on the active methylene. The corresponding isomerization equilibrium can be depicted in Figure 39. Under common conditions, the keto isomer is more stable than the enol isomer. By the using hierarchical alumina micro/nanostructured arrays as catalyst, keto isomer might be efficiently converted into the enol isomer. The isomerization can be commonly detected by on-line gas chromatography (GC) or on-line high-performance liquid chromatography (HPLC). Such technique is complicated and, most importantly, not cost-effective. An effective alternative is monitoring the UV-vis spectrum of reaction process. In the keto isomer configuration, there are only two isolated carbonyl groups, with an R absorption band having a quite small $\varepsilon$ value in the UV-vis spectrum. For the enol isomer, there is a conjugation system between alkene and carbonyl group, with a K absorption band having a high $\varepsilon$ value at around 244 nm in the UV-vis spectrum. This difference makes it convenient to analyze the content and the isomerization process using the UV-vis spectrum. Therefore, the catalytic activity of the hncp alumina was estimated based on the isomerization of ethyl acetoacetate by monitoring the UV-vis absorption spectrum (Figure 40A). The absorption at 244 nm indicates absorption of the conjugation system in the enol isomer as stated above. In the isomerization process, the absorption peak at 244 nm gradually increased and almost completely saturated after 40 min. The increase in absorption at 244 nm indicates that the proportion of enol isomer gradually increased, demonstrating the transition of the keto isomer to the enol isomer and verifying successful isomerization in the presence of hncp alumina. The corresponding control experiments were performed in order to confirm the
Fig. 40. (A) Catalytic activity of hncp Al$_2$O$_3$. (B) Catalytic activity evaluation of different substrates based on the absorbance ratio A/A$_0$ as a function of reaction time. A and A$_0$ are the absorbance after a given reaction time and that from the initial solution.

catalytic performance of the hncp alumina for such isomerization. Figure. 40B presents the isomerization process of ethyl acetoacetate in the presence of a silicon wafer and alumina film (by sputtering without using a colloidal monolayer) under the same deposition condition. These results indicate that the hncp alumina exhibited efficient catalytic activity
for the isomerization of ethyl acetoacetate. γ-Alumina is generally deemed to be catalytically active. However, besides the crystal phase, other factors, including the specific surface area, crystal composition, material microstructures, and the absence of exotic species from the remnant starting materials, also significantly affect the catalytic performance. In this case, the special hierarchical structures of the amorphous hncp alumina array have porous structures and possess a much higher specific surface area than the dense alumina film, which, together with the pure compositions, contributes to better catalytic properties.

5. Conclusions and remarks

The physical deposition assisted colloidal lithography has proven to be a facile, inexpensive, versatile route to construct hierarchical micro/nanostructured arrays with controlled morphologies, sizes, periodicities. The morphologies of these hierarchical micro/nanostructured arrays can be tuned by controlling the experimental conditions, including deposition time, background gas pressure in the vacuum chamber, periodicity of colloidal monolayer template etc. Compared with chemical routes, the physical deposition are more suitable for preparing high quality micro/nanostructured arrays with uniform morphologies. These special structures possess morphology- or size-dependent properties, such as superamphiphilicity, superhydrophobicity, photocatalytic activity, field emission etc., which have important applications in devices, microfluidic devices, field emitters, solar cells etc. Compared to development of fabrication strategies of micro/nanostructured arrays, investigation of morphology- or parameter- properties and micro/nanodevices dependent on them is not so much. The more micro/nanodevices based on these structures will be hoped, and it might be realized under researchers’ efforts in the future.

6. Acknowledgements

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7. References


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The term Lithography encompasses a range of contemporary technologies for micro and nano scale fabrication. Originally driven by the evolution of the semiconductor industry, lithography has grown from its optical origins to demonstrate increasingly fine resolution and to permeate fields as diverse as photonics and biology. Today, greater flexibility and affordability are demanded from lithography more than ever before. Diverse needs across many disciplines have produced a multitude of innovative new lithography techniques. This book, which is the final instalment in a series of three, provides a compelling overview of some of the recent advances in lithography, as recounted by the researchers themselves. Topics discussed include nanoimprinting for plasmonic biosensing, soft lithography for neurobiology and stem cell differentiation, colloidal substrates for two-tier self-assembled nanostructures, tuneable diffractive elements using photochromic polymers, and extreme-UV lithography.

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