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Chapter

# A Triphasic Superwetting Catalyst for Photocatalytic Wastewater Treatment

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## Abstract

The increasing organic contamination is mainly produced by the widespread industrial, agricultural, and household applications and has become a serious world-wide issue. Therefore, we need to develop sustainable and environmentally friendly technologies to reduce waste detrimental to the environment. A promising approach is known as heterogeneous photocatalysis, inspired by natural photosynthesis. For this purpose, the challenges raised to synthesize appropriate surface nano/micro-structured materials with long-term stability and mechanical durability for practical use. The traditional photocatalytic system is diphasic (dependent upon the solid-liquid phase), where the solid-liquid reaction interface depends upon the mass transfer. Especially, the low concentrations of oxygen in water and the slow diffusion rate limit the removal of electrons which decreases the photocatalytic reaction rates even if the presence of high light intensities. Therefore, the work aims to develop novel triphasic superwetting photocatalytic materials where the photocatalytic reaction is carried out at gas-liquid-solid joint interfaces. This triphasic contact line can allow oxygen from the air to this reaction interface and minimize electron-hole recombination even at high light intensities. Herein, we intend to discuss the importance of a novel superwetting triphasic nanoarrays catalyst that will be developed and implemented.

**Keywords:** heterogeneous photocatalysis, triphasic system, gas-liquid-solid joint interfaces

## 1. Introduction

Photocatalysis has wide applications in environmental, fuel production, and chemical synthesis [1, 2]. Photocatalytic materials that can convert photon energy to chemical energy are employed to split water to produce hydrogen and also produce highly reactive intermediates for chemical synthesis and reactive oxygen radicals for the degradation of organic pollutants [3]. Light absorption generates holes and electrons within the valence and conduction bands in heterogeneous photocatalysis. Those charges may migrate within the semiconductor particle and be trapped at surface sites. They'll also participate in the interfacial electron transfer processes involving the molecules of electron acceptor (A) and donor (D). within the photocatalytic organic degradation process, oxygen act as A and water as D, creating anion

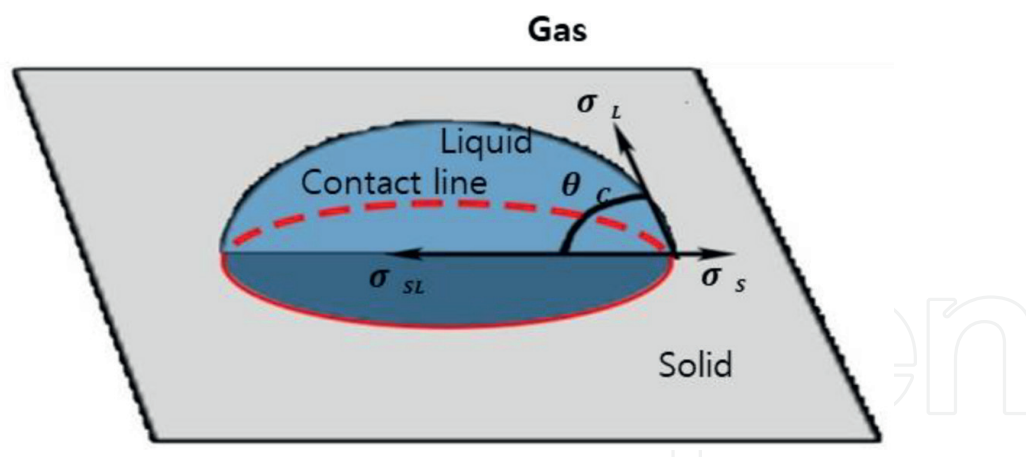
( $O_2^{\bullet-}$ ) and chemical group ( $OH^{\bullet}$ ) radicals. Those reactive radicals are liable for most of the oxidation of organic substances. Oxidation under these conditions is sometimes complete, giving  $H_2O$  and  $CO_2$  because of the final products.

The reactions can therefore be used in water, air, or surface purification. But, the recombination of photogenerated charge carriers competes with this photocatalytic degradation process, which is a critical factor in limiting the kinetics of photocatalysts and reaction rate. To overcome this limitation, numerous photocatalysts have been developed to enhance efficiency. The nanomaterials with large surface areas, abundant surface states, and specific morphologies have emerged as pioneering photocatalysts for the dye degradation process. The optimal structure-properties relationships are essential for efficient organic pollutant degradation [4]. Significantly, the hierarchical hetero-nanostructured materials called nanoarrays give rise to separating the photogenerated electron-hole pairs to improve the photocatalytic activity further [5]. To reduce the recombination of charge carriers, the photocatalyst surface need suitable and sufficient acceptors. Since these processes involve some complicated steps, but improvement of separation and transportation of photogenerated charge carriers are the main challenges to designing highly effective photocatalysts for practical applications. Another critical issue that induces the photocatalytic activity of a catalyst is the nature of its surface/interface chemistry. The surface energy and chemisorption properties are vital in transferring electrons and energy between substances at the interface. This process allows the overpotential of redox reactions on the photocatalyst surface, which reduces photo-corrosion. Previous studies have mainly focused on the reactivity of the catalyst. Moreover, the less diffusion rate of oxygen in water, limits the photocatalytic reactions even under high light intensity. In contrast to conventional double-phase photocatalytic systems, which consist of catalysts immersed in a bulk liquid phase, triple-phase catalytic systems by supporting catalysts at the gas-liquid boundaries have been developed and exhibited outstanding performance [6].

The wettability modification of a catalyst surface includes a vital role in improving the charge transfer ability. Superwetting behavior could be a unique wetting phenomenon that always depends upon the phases. Superwetable surfaces, like super-hydrophilic and superhydrophobic surfaces, exhibit unique transport dynamics and providing exceptional prospects for reinforcing chemical process efficiency. Therefore, these materials are dramatically different from traditional materials. Superwetting catalysts have enhanced catalytic activity when introducing an air layer between the catalyst and liquid. The charge carriers from reacting interface are very fast to radicals by oxygen, and enough oxygen within the air layer can effectively capture electrons and minimize the electron-hole recombination. Superwetting materials are commonly designed by controlling surface energy, chemical compositions, and geometric structures of solid surfaces. This chapter discussed the photocatalytic organic pollutants supported superwetting materials. The discussion mainly contains widely investigated photocatalytic reactions involving gas and water molecules as reactants and products for organic pollutant degradation.

## **2. Theoretical basis of wettability**

Contact angle (CA) assigned as  $\theta$ , which can give the quantitative measurement of wetting of a solid by a liquid. Therefore, it can be defined as the angle measured by a liquid where the liquid-gas interface meets at solid surface as shown in **Figure 1**.



**Figure 1.**  
 Schematic illustration of the triple-phase contact line.

## 2.1 Theoretical models

Wettability is an essential property of solid materials. When liquid droplet contacts a solid surface in air, a three-phase contact line is formed at the three-phase junction. The contact line expands outward up to the droplet reaches a static state. In a steady-state system, a three-phase contact line is contact because of an equilibrium tangential forces created by the interfacial and surface tensions. The wetting properties of the liquid on solid surface is measured by the CA such as when  $\theta < 90^\circ$ , the surface considered to be hydrophilic and when  $\theta > 90^\circ$ , the surface is hydrophobic. However, when the  $\theta > 150^\circ$ , the surfaces are highly hydrophobic and called superhydrophobic. Similarly, superhydrophilic surfaces have a  $\theta < 10^\circ$ .

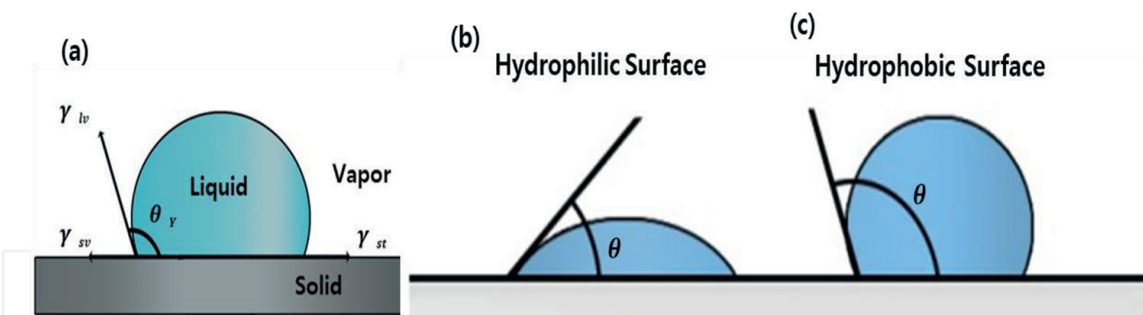
The Wetting properties of the solid surfaces is governed by the Young, Wenzel, and Cassie-Baxter equation. The young are derived by balancing the interfacial forces at a three-phase contact line Eq. (1).

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (1)$$

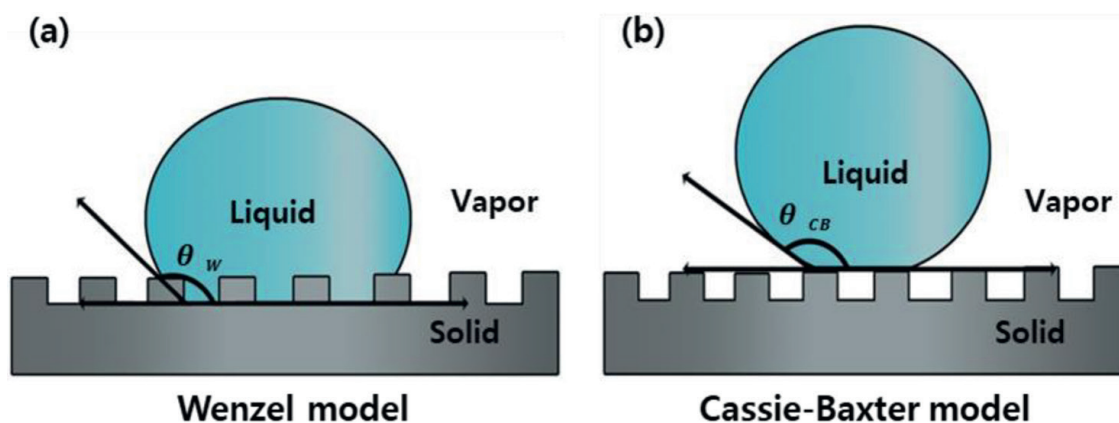
Here  $\theta$  is the CA of the liquid droplet,  $\gamma_{sv}$  (solid-gas)  $\gamma_{lv}$  (liquid-gas), and  $\gamma_{sl}$  (solid-liquid) interfacial force per unit length of the contact line which is surface tension. Moreover, the balance of angle formed by the liquid at the three-phase boundary is defined as young's contact angle (**Figure 2a**). According to the value of contact angle, the surface should be hydrophilic ( $\theta < 90^\circ$ ,  $\gamma_S > \gamma_{SL}$ ) and hydrophobic ( $\theta > 90^\circ$ ,  $\gamma_S < \gamma_{SL}$ ) (**Figure 2b** and **c**).

For the solid surface which has rough morphology, then Wenzel introduced the factor of surface roughness,  $r$ , into Young's equation after considering the influence of rough surface structure on wettability. Therefore, the definition is the actual surface area to the projected surface area is " $r$ ". In this case, the liquid fills the microstructure of the solid surface (**Figure 3a**). For a liquid droplet in the Wenzel state, the measured/apparent CA ( $\Theta_w$ ) can be expressed by the Wenzel equation Eq. (2) which can be expressed the surface roughness.

$$\cos \Theta_w = r \cdot \cos\theta \quad (2)$$



**Figure 2.** (a) The wetting regime for Young's model, measurement of contact angle for (b) hydrophilic and (c) hydrophobic surfaces.



**Figure 3.** Various states of droplets on a solid surface (a) Wenzel model, and (b) Cassie-Baxter model.

For hydrophobic surfaces, the roughness is very high and large  $r$  value. Sometimes, the liquid does not penetrate in to the roughness, so that the layer of trapped air between the solid surface and the liquid. In this case the contact interface between liquid and the solid surface consists of liquid-solid contact and liquid-air contact (**Figure 3b**) and expressed by Cassie equation Eq. (3)

$$\cos \theta_c = f_1 \cdot \cos \theta_1 + f_2 \cdot \cos \theta_2 \quad (3)$$

Where  $\theta_c$  is the CA,  $\theta_1, \theta_2$  are the CA of the liquid droplet on the solid and air phases and  $f_1, f_2$  are the area ratio of liquid-solid contact and the liquid-air contact, respectively. Again, for solid microstructure surface, if the liquid-solid contact area fraction is  $f$ , then liquid-air contact will be  $(1 - f)$ . So that, the Cassie equation will be Eq. (4):

$$\cos \theta_c = f \cos \theta_1 + (1 - f) \cos 180^\circ \quad (4)$$

According to wettability, superwetting materials are generally categorized into four types: superhydrophobic, superhydrophilic, superoleophilic, and superoleophobic states. Specially, the first two kinds of superwetting materials which can be used for oil/water separation. These superwetting materials are believed to be promising



materials for removing pollutants from water due to their superwetting property towards oils and water [7, 8].

## **2.2 Characterization of wettability**

### *2.2.1 Classification of wettability*

The most common measurements involving the static CA and the dynamic CA are utilized to know the surface property. The materials with specific wettability attain excessive attention owing to their outstanding performances for practical applications [9–11].

### *2.2.2 Static contact angle and dynamic contact angle*

During the measurement, the contact area between liquid and solid is not changed from outside, but the dynamic contact angle can produce during wetting (advancing angle) or de-wetting (receding angle). Besides water droplets, other organic liquids can be also used for testing the surface wettability. When oil on a solid substrate, it can be observed four fundamental states: oleophilic, oleophobic, superoleophilic, and superoleophobic.

### *2.2.3 Contact angle hysteresis*

Contact angle hysteresis (CAH) is an important physical phenomenon. Contact angle hysteresis reflects the activation energy required to move a droplet from one metastable state to another on a surface. CAH refers to the difference value between the advanced CA ( $\theta_{Adv}$ ) and the receding CA ( $\theta_{Rec}$ ). An analysis software usually measures  $\theta_{Adv}$  and  $\theta_{Rec}$  after a microscopy system reordered real-time images.

## **3. Importance of super wetting materials for photocatalysis**

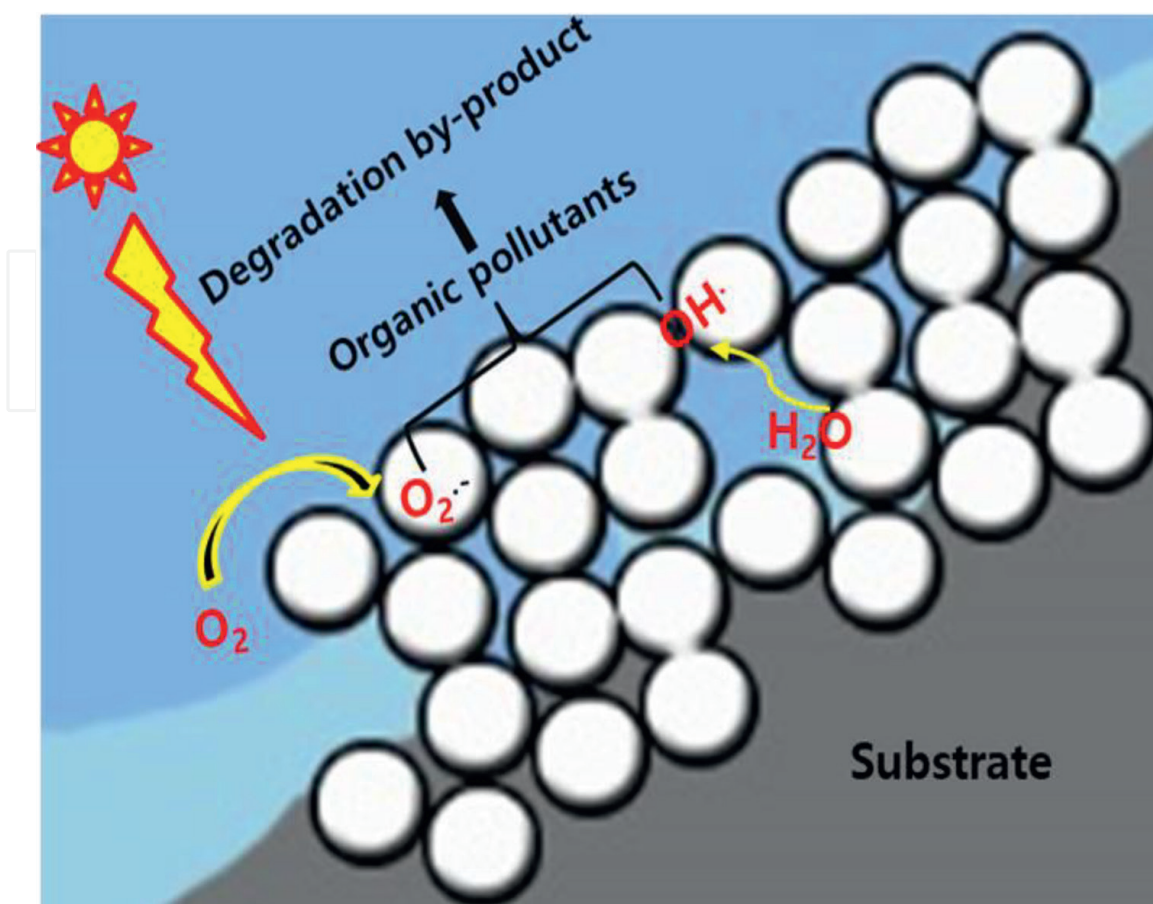
### **3.1 Triphase interfaces**

In the liquid phase, air pockets are stuck with the rough topological surface of the superhydrophobic substrate, forming a triphasic solid–liquid–air interface. For photocatalytic reactions, this triphasic contact line usually serves as an active area for interfacial reactions and provides a vital clue to surface behavior. The oxygen supply from the air reacts with photogenerated electrons from the surface of the photocatalyst, producing oxidative reactive oxygen species (ROS) such as superoxide radicals ( $O_2^{\bullet-}$ ) and hydroxide radicals ( $OH^{\bullet}$ ) and resulting in the degradation of organic pollutants (**Figure 4**). Especially, during organic pollutant degradation, the carbon bonds breaks the on the superhydrophobic surface and can show long-term stability. Practically, a superhydrophobic with long-term stability catalyst is required.

### **3.2 Photocatalysts based on different wettability**

#### *3.2.1 Superhydrophilic photocatalysts*

Inspired by the natural world's self-cleaning as well as the water-repellent properties of the lotus leaf, superwetting materials with unique wettability are believed to



**Figure 4.** Schematic representation of a triphasic nanoarray photocatalyst and the photocatalytic water purification process.

be promising materials for removing organic pollutants from water. Historically, the study of the superhydrophilicity of titanium dioxide ( $TiO_2$ ) films traces back to 1997. Before illumination by UV light, the contact angle of  $TiO_2$  surface was  $72^\circ$ . But after the UV illumination on the particular duration, the droplets completely spread on. This is due to creating numerous high-energy domains with hydrophilic/oleophilic properties on  $TiO_2$  surfaces. Moreover, the wetting properties of single  $TiO_2$  surfaces could be exchange between hydrophobicity and superhydrophilicity under the interchange of long-term dark storage and UV light irradiation.

After discovering its confirmed that, the  $TiO_2$  surface with superamphiphilic ability has unique wetting transition under UV light [12, 13]. Furthermore, Wang and co-workers reported a hydrophilic  $TiO_2$ -coated glass with effective photogeneration, displaying antifogging and self-cleaning induced by UV illumination [14]. Then, Fujishima et al. confirmed the nanostructure  $TiO_2/SiO_2$  films shows superwettability under UV irradiation. In the case, the upper part of  $TiO_2$  layer and the bottom part of porous  $SiO_2$  layer with a low refractive index providing platforms for self-cleaning and antifogging/reflection [15]. Also, Shang et al. fabricated visible active N-F doped  $TiO_2$  Nanotube and palladium oxide is decorated on the surface of the nano array [16]. Due to their superior photocatalytic property and particular nanoarray alignment, it gives promising self-cleaning applications. Since then, the superwetting approach has been frequently used for antifogging and self-cleaning applications. Jiang's group fabricated translucent and stable  $Ag@AgCl/g-C_3N_4/TiO_2$  ceramic films that showed superhydrophilicity and excellent photocatalytic activities for Rhodamine B degradation under visible and complete spectral irradiations. In this case, the water molecules

from air can occupy the oxygen vacancies of  $\text{TiO}_2$  of the composite and produce hydroxyl groups, which makes the  $\text{TiO}_2$  more hydrophilic. So, by mixing P25 with  $g\text{-C}_3\text{N}_4$  in a colloidal silica system, nano  $\text{TiO}_2$  particles can be dispersed and attached to the  $g\text{-C}_3\text{N}_4$  particles, leading to increased surface roughness and hydrophilicity of the film systems. In this case, the hydroxyl groups of P25 may interconnect with that of silica particles which helps to increase the bonding strength of graphitic carbon nitride composite film and silicate glass. Besides adding P25 into the film system, the catalytic efficiency is improved [17]. Then, the Zhang group studied the Polymer-based nanocomposites functionalization by organic moieties to make superhydrophilicity. Afterwards,  $\text{TiO}_2$  nanoparticles coated with hydroxyethyl acrylate (HEA) without any solvent formed high durable superhydrophilic catalyst [18]. Compared with the bare  $\text{TiO}_2$  films, the  $\text{TiO}_2$  nanotube array film has excellent photocatalytic efficiency in terms of methyl orange (MO) degradation is reported [19].

Chen and co-workers reported hydrophilic interface engineering of the hydrophilic  $\text{CoO}_x$  modified hydrophobic  $\text{Ta}_3\text{N}_5$ , which improves its water oxidation efficiency under visible light irradiation. Compared to the pristine  $\text{Ta}_3\text{N}_5$  surface,  $\text{CoO}_x$  deposited onto the  $\text{MgO-Ta}_3\text{N}_5$  surface showed a 23-fold improvement [20]. Similarly, core-shell  $\text{NaYF}_4\text{:Yb, Tm@TiO}_2$  NPS is fabricated for photocatalytic activities. Here, the hydrophilic layers of  $\text{TiO}_2$  were coated onto hydrophobic  $\text{NaYF}_4\text{:Yb}$  materials and the Tm nanoplates are partially exchanging with oleic acid ligands which shows hydrophobic in nature into cetyltrimethylammonium bromide (CTAB) surfactants which is amphiphilic character. The combination of  $\text{NaYF}_4\text{:Yb, Tm}$  (up conversion materials) with  $\text{TiO}_2$  (wide bandgap) with broad spectrum absorption changes the wettability of a solid surface to achieve high-quality interfaces in photocatalysts for smooth carrier migration [21].

### 3.2.2 Superhydrophobic photocatalysts

Superhydrophobic metal oxide like  $\text{ZnO}$  [22], exhibits advanced photocatalytic activity; however, during prolonged UV irradiation, superhydrophobicity changes into superhydrophilicity, resulting from the easy decompositions of low-surface-energy compositions under the stimulus of light. Consequently, a photocatalyst showing long-term superhydrophobicity was once considered not to exist. More generally, it is undoubtedly necessary to modify the surface of the catalyst with stable hydrophobic organics, which are chemically and directly bonded. Therefore, to achieve photocatalytically active hydrophobic materials, researchers have combined metal-oxide particles with hydrophobic polymers like Polydimethylsiloxane (PDMS) and polytetrafluoroethylene (PTFE) as composite mixtures [23–25]. Recently, metal oxides ( $\text{TiO}_2$ ) and nonwetting organic polymers, namely epoxy resin, followed by grafting 1H,1H,2H,2H-perfluorooctyltriethoxysilan (PFOS), we prepared an inorganic-organic superhydrophobic paint (IOS-PA) used for photocatalytic removal of three organic dyes, Nile red, methyl blue, and methyl orange [26]. PDMS, PTFE, and silicone nanofilaments have also been used to conduct long-term superhydrophobicity and photocatalysis on one surface [26–29]. Sheng and co-workers established a novel triphase photocatalytic system by creating a unique photocatalyst in which  $\text{TiO}_2$  nanoparticles (NPs) were immobilized on carbon fiber (CF) substrate treated by poly(tetrafluoroethylene) (PTFE) for water pollution remediation [30]. After immobilizing  $\text{TiO}_2$ , the surface of the materials are changed from superhydrophobic to hydrophilic. In the time of photocatalytic reactions, the  $\text{TiO}_2$  will be hydrophilic part while the substrate will be the superhydrophobic state which was connected with the atmosphere. Hence, the total system should



have an abundant triphasic contact area, which allowed a sufficient oxygen transport and the rapid generation of reactive oxygen species for organic pollutants degradation. Recently, a superhydrophobic (SHB) TiO<sub>2</sub> nanoarrays catalyst with low surface energy and rough surface microstructure was reported as a model photocatalyst. The soft surface energy and rough surface microstructures of the SHB nanoarrays give the photocatalytic system long-range hydrophobic in nature and helps to introduce the triphasic reaction interface [31]. Superhydrophobicity is an integral part of self-cleaning on a photocatalyst which showed the synergistic effect of strong water repellency and photocatalytic activity [28], where the rolling drops remove macroscopic particles and the photocatalytic degradation ensure by UV or solar light. In a superhydrophobic system's air-water-solid triphase joint interface [27, 32, 33], a continuous and steady gas channel is recognized, providing abundant gaseous reactants and the resulting quick gas transportations. This system overcomes the drawbacks of weak dissolved gas transfer and low solubility in liquid-solid diphasic reaction systems. Thus, photocatalytic activity efficiency and selectivity are sharply increased. Jinxiu groups reported about the oil-water mixture separation and photocatalytic degradation of quinoline blue, rhodamine B, methyl orange and methylene blue by using [Ni(DMG)<sub>2</sub>] hollow microtubes. The prepared [Ni(DMG)<sub>2</sub>] films act as superhydrophobicity and superoleophilicity and ascribed to the Cassie-Baxter model. Similarly, Ag/TiO<sub>2</sub>@PDMS coated cotton fabric which is low-cost effective, and recyclable separation material used for water purification to degrade methylene blue (MB) [34]. The effect of a grafted PDMS layer on wetting properties of TiO<sub>2</sub> for photocatalytic application is studied by Butt group [35]. The most effective dual-purpose ceria nanoparticle membrane is fabricated by facile spray-deposition method on stainless steel membrane for oil-water separation and photocatalytic degradation. The prepared membrane has superwetting properties which is efficient for oil/water separation. In this case the oil is passing through the stainless-steel membrane, whereas, high column of water is blocked. Furthermore, the CeO<sub>2</sub> coated membrane is utilized for the efficient degradation of a dye [36].

#### **4. Conclusions**

The present chapter fully addresses the main objectives of water purification by using a triple-phase catalyst. Under irradiation, charge carriers are formed on the surface of the photocatalyst, and the success of pollutant molecule degradation critically depends on the interaction between the surface and the target molecules. Therefore, the organic pollutant degradation efficiency strongly depends on the fabrication method as it drives the shape and size of the photocatalyst and its hydrophobic or hydrophilic characteristics. Compared with state-of-the-art diphasic photocatalytic systems, for which the limited concentration and diffusion rate of oxygen reduces the degradation efficiency, the novel triphasic photocatalytic system with superhydrophobic triphasic interface architecture will allow the rapid delivery of oxygen directly from the air to the reaction interface, thus minimizing electron-hole recombination and resulting in remarkably high efficiency. Recently, a solid surface's superwettability (especially underwater superoleophobicity) has attracted much attention owing to its importance for photocatalytic. Although this is new research, it is rapidly growing and promising in future research, which enormously extends the research field of superior wettability to the triphasic system. Therefore, the surface wettability of a photocatalyst film in the liquid-liquid-solid system should also be an exciting research focus shortly.

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