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Editorial

Fabrication of Metallic Micro-/Nano-Composite Materials for Environmental Applications

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Micro-/nano-structured materials refer to functional materials with excellent chemical and physical properties at the level of micro-/nano-size, which have played an important role in a wide range of applications for addressing environmental problems. For example, hollow micro-/nano-structured materials with a high specific surface area can improve the energy conversion efficiency of various types batteries with the growing clean energy needs [1]. Moreover, micro-/nano-structures can also produce high-performance electrochemical sensors for environmental pollution [2–4], and metallic semiconductor micro-/nano-materials are used as catalysts to degrade organic pollutants in water [5]. In particular, metallic micro-/nano- materials and their composites show great potential in oil/water separation and catalytic degradation of water resources due to tunable interfacial energy and electron-hole recombination mechanisms.

Membrane separation [6,7], as a traditional and efficient means, is the most common method in wastewater treatment. The characteristics of semi-permeability and permeability of the membrane are used to separate mixtures [8]. Unlike separating solid–liquid mixtures, the pore size of the semi-permeable membrane for oil/water separation needs to reach the micro-/nano-size level. In addition, efficient separation of oil/water mixtures can be achieved when the difference in the wettability of two phases on the membrane is utilized [9,10]. The preferred materials that are inherently hydrophobic have certain limitations, whereas the surface modification of membranes suitable for separation may be a better option. In the selection of membrane materials, the most popular property is hydrophobic/hydrophilic materials. In terms of physical characteristics, the metallic film has a certain stiffness and flexibility, which can be shaped into a specific shape while ensuring the wear resistance of the film. Due to its mechanical strength and flexibility, metallic membrane attracts intense attention by performing surface modification [11] to obtain a hydrophobic or oleophobic surface, which is an extension of the active selectivity of the membrane surface [12]. The metallic film has the advantages of green, high efficiency and effective circulation. At the same time, it also has good biological compatibility, excellent antibacterial activity, high natural abundance, low cost and the existence of a variety of cost-effective synthesis routes, making the metallic film a good application in oil/water separation [13].

At present, the most popular method is to modify the wettability of the material surface by introducing the Wenzel or Cassie–Baxter model, integrating the morphology of the nanomaterials and the micro-/nano-particles. To change the surface wetting property,

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there are generally two strategies to obtain super-hydrophobic surfaces [14], namely, (1) to fabricate secondary structures on the surface of the material [15,16], and (2) to reduce the interfacial energy of the material [17]. The fabrication of oil/water separation membranes is generally relied on constructing a surface with superhydrophobicity or superoleophobicity. In the case of low interfacial energy, liquid molecules will form liquid beads on the surface and could not penetrate into the micropores of the membrane due to the interfacial tension. According to Wenzel model, the construction of micro-/nano-structures on the surface of hydrophobic materials will further enhance their hydrophobicity. Therefore, to construct superhydrophobic membrane surface, it is usually necessary to fabricate a hierarchical micro-/nano-structure on the surface of the material and modify it with low interfacial energy substances to reduce the surface energy. The commonly used processing methods include electrochemical deposition, laser processing, electrochemical dissolution, anodic oxidation, hydrothermal method, physical/chemical vapor deposition, sol–gel method, template method, etc. Along with the fast development of new technologies, hybrid processing methods have also been developed, such as laser-chemical water bath [18], laser-electrochemical deposition [19] lithography electrochemical deposition [20], and other methods. Because increasing the surface roughness of hydrophobic materials can increase the water contact angle [21], coarsening hydrophobic surfaces is the most direct method. Furthermore, as for hydrophilic materials, obtaining a rough surface first and then modifying the surface is also a common method to obtain a superhydrophobic surface [22]. Micro-/nano-particles can meet the above requirements and realize the separation of oil and water.

Micro-/nano-textured multi-functional filters have been extensively studied in water purification and wastewater treatment. To further advance these applications, there is an urgent desire to develop easy-to-use, low-cost, and high-throughput methods for the preparation of multifunctional membranes filters with ultra-wettability and catalytic activities. Filters incorporating nanocatalysts have not only the advantage of high catalytic efficiency, but also alleviate membrane fouling by forming a hydration layer consisting of water molecules constrained by surface micro-/nano- micro-/nano-structures. On this occasion, the highly rigid demand for various functional materials oriented towards carbon neutrality and environmental sustainability has inspired the exploration of innovative fabrication strategies based on laser-assisted processing and chemical synthesis to synthesize heterogeneous catalytic metal nanocomposites. Micro-/nano-scale hierarchical structure and elemental changes generated by laser surface treatment and chemical synthesis have been widely used to produce surface wettability required for membranes [23] for water purification, most typically by photocatalytic methods [24,25]. The most significant advantage of photocatalysis is to utilize natural sunlight as the energy source for organic water pollutants degradation [26]. Semiconducting catalyst like metal oxide provides a good choice to avoid secondary pollution. Due to the discontinuous energy band of semiconductor catalyst, the electrons on the valence band are excited to transition to the conduction band, and the valence band produces holes, when receiving energy radiation greater than or equal to the band gap [27]. Photogenerated holes have strong electron acquisition ability and strong oxidation, which can seize electrons in adsorbed substances or solvents on the surface of semiconductor particles, producing highly reactive free radicals to oxidize organic pollutants in the system, and produce water or carbon dioxide [28]. Titanium dioxide (TiO_2) has been widely studied due to its abundant availability, photostability and catalytic efficiency under ultraviolet (UV) irradiation [29]. Meanwhile, zinc oxide (ZnO) is also a representative catalytic material. The researchers prepared a modified PVDF membrane casting solution by adding TiO_2 [30]. In addition, tin oxide [31], zirconia [32] and metal sulfide [33] are good photocatalysts. The unique organization of nanostructured materials will affect several catalytic properties, such as selectivity, sensitivity and catalytic efficiency [34]. Metal nanoparticles such as ZrO_2 show excellent electrical, magnetic, optical and other physical properties compared with other types of materials [35]. In catalytic reactions, single metallic nanoparticles are important catalytic centers with high interfacial energy, which may lead to agglomeration and deactivation during the preparation process and catalytic reaction, affecting catalytic activity and selectivity. This phenomenon would reduce service life [36,37]. In order to improve the performance of metallic nano-catalyst, other components could be introduced to synthesize composite catalysts [38]. On the other hand, through the introduction of other components, the stability and dispersion of metal nanoparticles can be optimized due to the existence of electronic effects and anchoring effects. On the other hand, there is a strong interaction between the components in the metallic nanocomposite catalyst, which can further improve the catalytic activity due to the formation of p-n heterostructure at the interfaces, further reducing the electron-hole recombination rate, which makes it have light catalytic/piezoelectric/piezoelectric photocatalytic photoelectric performance improvements.

In recent years, piezoelectric catalysis has attracted increasing attention. There is no absolute static state of the world. It is of great practical significance to design catalysts that can collect discrete energy such as fluid mechanical energy to form electric fields [39]. The driving force of piezoelectric catalysis comes from charge separation caused by the deformation in the presence of external mechanical energy. The external mechanical energy used in piezoelectric catalysis includes ultrasonic cavitation, vortex-induced shearing force, and physical bending [40]. If the strained induced potential in piezoelectric materials is higher than 3V (versus standard hydrogen electrode (SHE)), the charge carriers in the piezoelectric materials can then participate in the reduction or oxidation reactions [41]. The induced charge carriers can easily trap oxygen/water to generate reactive oxygen species (ROS) for degrading organic pollutants in water [42]. Unlike photocatalysis, piezoelectric catalysis can be used to treat water pollution under no light conditions. It is of great practical significance to design catalysts that can collect discrete energy such as fluid mechanical energy to form electric fields [39]. Small mechanical vibration is used to generate charges on the surface of piezoelectric materials, and then reactive groups such as hydroxide and superoxide anion are generated to achieve catalysis [43]. The ubiquitous mechanical energy such as noise and vibration in the environment is effectively utilized to reduce energy consumption. Lin et al. studied piezoelectric $Pb(Zr_{0.58}Ti_{0.48})O_3$ fibers to decompose 7 dye molecules under ultrasonic vibration [44]. Hong et al. reported the efficient mechanical vibration-induced decomposition and water decomposition of lime 7 solutions using piezoelectric nano/micromaterials under ultrasonic vibration [45]. Wu and colleagues used piezoelectric MoS_2 to achieve an ultra-high decomposition ratio of rhodamine B (RhB) solution induced by mechanical vibration and MoS_2 nanoflowers [42,46].The origin of the piezoelectric effect, from the application of an external mechanical force, was demonstrated in a previous study. When external mechanical energy is applied, a strain-induced potential is generated, which results in bending or deforming dendrites of the catalytic crystal. The strain-induced electric potential can be used to perform reduction and oxidation reactions by transferring charge to organic molecules adsorbed on the surface [46].

Nowadays, the rational deposition and growth of nanostructured catalyst coatings on micro/nano filters are employed to achieve efficient, reliable and synergistic multifunctional composites. Novel composite bi-functional membrane preparation techniques can be divided into two categories: membrane material modification and membrane surface modification. Based on raw materials, the membrane surface modification, methods can be roughly divided into the blending method, surface coating method and bottom-up synthesis method [47]. Another factor affecting the composite properties is the interaction surface between the host matrix and the particles. Composite materials can be defined as a combination of two or more materials that perform better than individual components used alone [48]. Composite materials have unlimited possibilities in meeting many emerging industrial requirements, including extreme mechanical, electrical, magnetic, optical, and thermal properties that monolithic materials cannot meet [49]. Composite materials consist of a matrix material called matrix, which has low performance but low cost, reinforced with other materials in the form of continuous fibers, short fibers or particles with mechanical physical or chemical properties. Under the current demand for green manufacturing, the method of using laser-assisted processing combined with chemical synthesis technology has become a direction worth exploring. Yuan et al. detailed how iron films were ablated using laser interference followed by the growth of carbon nanotubes via iron-catalyzed chemical vapor deposition. Laser energy was used to modify the iron surface at a preset position, generating iron oxide with catalytic performance at a fixed position and then growing to obtain the desired surface morphology [3]. Moreover, reactive laser ablation (RLAL) was used to reduce titanium/silver ions, and nanoparticles in the solution. NIDOME et al., also used lasers to deposit gold particles in colloidal solutions onto thin films as chemical catalytic sites [47]. Zhang et al. prepared an electrospinning film embedded with gold particles [50], and the mold has two properties of oil-water separation and catalysis. As for photocatalytic degradation, based on the principle of achieving superoleophobic/superhydrophilic behavior by changing the dispersion and polar components of the surface tension [51], although the embedded photocatalytic separation film shows excellent photocatalyst stability, the photocatalytic efficiency is reduced. In other studies, Li et al. reported PVDF membranes modified by the atomic layer deposition method and 3D TiO_2. The ZnO photocatalyst was coated on the surface of the membrane and the pore wall. The results show that the modified film has good photocatalytic activity and stable reusability during the degradation of methylene blue. Compared with other methods for preparing modified membranes, the layer-by-layer (LbL) method is not only easy to prepare and rich in material storage, but also can control the composition and structure of the membrane at the molecular level, tuning the thickness of the separation layer by adjusting the number and time of the deposited layers. This special issue aims to provide a forum for researchers to share current research findings on multifunctional metallic composite nanomaterials and promote further research into functional composite fabrication to provide inspiration for environmental applications of the next generation of multifunctional composite manufacturing, including experimental modeling and theoretical calculations.

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