

## Review Article

# Efficiency of Polymeric Membrane Graphene Oxide-TiO<sub>2</sub> for Removal of Azo Dye

Elahe Dadvar,<sup>1</sup> Roshanak Rezaei Kalantary,<sup>2</sup> Homayon Ahmad Panahi,<sup>3</sup> and Majid Peyravi<sup>4</sup>

<sup>1</sup>Department of Environmental Engineering, Faculty of Environment and Energy, Islamic Azad University, Science and Research Branch, Tehran, Iran

<sup>2</sup>Department of Environmental Health Engineering, School of Public Health, Iran University of Medical Sciences, P.O. Box 15875-4199, Tehran, Iran

<sup>3</sup>Chemistry Department, Islamic Azad University, Central Tehran Branch, Tehran, Iran

<sup>4</sup>Nanotechnology Research Institute, Chemical Engineering Department, Babol University of Technology, Babol, Iran

Correspondence should be addressed to Roshanak Rezaei Kalantary; rezaei.r@iums.ac.ir

Received 22 April 2016; Revised 11 August 2016; Accepted 14 September 2016; Published 27 February 2017

Academic Editor: Zuhui Zhang

Copyright © 2016 Elahe Dadvar et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Achieving the desired standard of drinking water quality has been one of the concerns across water treatment plants in the developing countries. Processes such as grid chamber, coagulation, sedimentation, clarification, filtration, and disinfection are typically used in water purification plants. Among these methods, unit filtration which employs polymers is one of the new technologies. There have been many studies about the use of semiconductive TiO<sub>2</sub> with graphene oxide (GO) on the base of different polymeric membranes for the removal of azo dyes, especially methylene blue (MB). Polymeric GO-TiO<sub>2</sub> membranes have high photocatalytic, antifouling property and permeate the flux removal of organic pollutants. The aim of this study was to investigate the characteristics of different polymeric membranes such as anionic perfluorinated polymer (Nafion), cellulose acetate, polycarbonate (PC), polysulfone fluoride (PSF), and polyvinylidene fluoride (PVDF). The result of this study showed that the GO-TiO<sub>2</sub> membrane can be used in the field of water treatment and will be used for the removal of polycyclic aromatic hydrocarbons (PAHs) from wastewater.

## 1. Introduction

With the development of heavy industries in recent decades, obtaining healthy drinking water has become a global concern [1]. Organic substances, industrial dyes, microorganisms, and heavy metals (heavy metals include cobalt, cadmium, mercury, chromium, and lead) are among the water pollutants [2–7]. In recent decades, there has been increasing interest in the use of clean water [8–10]. With high efficiency and low energy consumption, filtration is one of the most appropriate technologies for decreasing pollution [11–15]. The formation of a good membrane is an important and practical step toward increasing the efficiency of water treatment; this film could be made from materials such as polymer, fiber, ceramic, and carbon nanotubes [16–19].

In recent decades, ceramic and polymeric membranes have been increasingly used due to their strong mechanical

properties, chemical stability, high efficiency in minimizing pollutants, high photocatalytic power, and odor reduction ability [20, 21]. The photocatalytic process of separating organic pollutants from the membrane, under visible light and UV radiation, can occur without any energy or chemical consumption. This process is especially important for the removal of different types of environmental pollutants [22]. The photocatalytic process of isolating organic pollutants from membrane, under visible light and UV radiation, can demonstrate higher efficiency [23]. Titanium dioxide is one of the important semiconductors, having properties such as low toxicity, low cost, and highly efficient removal of pollutants [21, 24, 25].

TiO<sub>2</sub> has the ability to degrade organic materials (organic dye, oil, and toxic pollutants) into H<sub>2</sub>O and CO<sub>2</sub> [24, 25]. As a semiconductor, nanoparticles of anatase titanium dioxide have higher photocatalytic power than rutile and brookite

crystals and exhibit absorption at 390 nm when exposed to UV radiation [26]. The present study includes a review of the semiconductive properties of TiO<sub>2</sub> semiconductor and its photocatalytic power. Different methods, such as doping and surface chemical modification, were used to increase the photocatalytic power of TiO<sub>2</sub> [27]. It is worth mentioning that, in different industries, such as the textile industry, TiO<sub>2</sub> graphene membranes are increasingly used to improve the efficiency of water treatment.

In recent decades, there have been many reports on the mechanical and chemical properties of graphene (G) and graphene oxide (GO) [28]. In studies concerning water treatment and purification, nanostructured carbon has been used in the form of carbon nanotube and graphene. These structures have high absorption capacity and the ability to absorb organic materials in aqueous solutions [29]. After studies on the absorption of organic aromatic pollutants by graphene, carbon nanotube, and granular activated carbon, Onu et al. discovered that graphene possessed higher efficiency in the absorption of natural organic materials.

The presence of natural organic matter (NOM) reduced the absorption of synthetic organic compound (SOC) in carbon nanotube, granular activated carbon, and, finally, graphene [30]. After comparing the absorption of methylene blue and atrazine pollutants by super fine powdered activated carbon (SPAC), carbon nanotubes (CNTs), and graphene, Ellerie et al. found that SPAC had the highest efficiency, while multiwalled carbon nanotube (MWCNT) was the least efficient in absorbing pollutants [31].

Compared to membranes without absorbents, the direct use of absorbents in membrane structure improves the efficiency of absorbed pollutants. GO consists of graphene sheets having functional groups (R-O-H, epoxy, COOH, and C=O). Therefore, the GO-TiO<sub>2</sub> nanocomposite, under UV radiation and visible light, has the capability of photocatalytic degradation, high absorption capacity, and the capability of being more exposed to water pollutants as a result of its huge surface area of 2360 m<sup>2</sup>/gr [32]. Liu et al. studied the nanorod of TiO<sub>2</sub> on the surface of graphene oxide sheets interface water and toluene. They produced a high efficiency nanorod (GO-TiO<sub>2</sub> NRCs) composite. The TiO<sub>2</sub> nanorod was stabilized with oleic acid, low temperature, and hydrolysis approach. The photocatalytic activity (GO-TiO<sub>2</sub> NRCs) desired in the degradation of methylene blue (MB) under UV radiation was higher than GO-25 and the other original TiO<sub>2</sub> nanorod states [33].

Rao et al. reported efficient removal of 4-chlorophene, 2,4-dichlorophene, and 2,4,6-trichlorophene by ZrO<sub>2</sub> graphene composite and, herein, removal efficiency of 4-chlorophene was by far better than the others, and the absorbability decreased with the increase in pH [34].

According to the report of Zhang et al., TiO<sub>2</sub> nanowire membrane was able to remove TOC and HA pollution with a removal efficiency of 93.6 and 100%, respectively. This membrane was able to degrade organic materials and produce CO<sub>2</sub> [35].

Mele et al. carried out a characterization of polycrystalline bare TiO<sub>2</sub> for the degradation of 4-nitrophenol (4-NP) in aqueous suspension using TRMC, EPR, and XPS. The

TABLE I: The structural properties of TiO<sub>2</sub> crystals [43–45].

Properties	Rutile	Anatase	Brookite
Crystal structure	Tetragonal	Tetragonal	Orthorhombic
Lattice constant (Å)	$a = 4.5936$ $c = 2.9587$	$a = 3.784$ $c = 9.515$	$a = 9.184$ $b = 5.447$ $c = 5.154$
Space group	p4 <sub>2</sub> /mnm	I4 <sub>1</sub> /amd	pbca
Molecule (cell)	2	2	4
Volume/molecule (Å <sup>3</sup> )	31/2160	34.061	32/172
Density (g cm <sup>-3</sup> )	4.13	3.79	3.99
Ti-O band length (Å)	1.949 (4)	1.937 (4)	1.87–2.04
O-Ti-O band	81.2° 90.0°	77.7° 92.6°	77.0°–105°

results of this study showed that propylene impregnated on the surface of TiO<sub>2</sub> improved the photocatalytic properties compared to bare TiO<sub>2</sub> [35].

Afzal et al. synthesized anatase TiO<sub>2</sub>/TCPP (meso-tetra(4-carboxyphenyl)porphyrin) coated with cotton. TiO<sub>2</sub>/TCPP coated with cotton for the purpose of making comparison with bare TiO<sub>2</sub> was found to be better. There was complete degradation of methylene blue in 110 min and removal of coffee and red wine in 16 h by visible light [36].

There are many studies regarding the TiO<sub>2</sub> semiconductor and its photocatalytic features in removing pollutants, especially industrial dyes and heavy metals; however, to date, there has been no comprehensive study regarding the photocatalytic features, flow permeability, and antifouling property. Fouling resistance in GO-TiO<sub>2</sub> membrane, with regard to various polymer bases, has been used in this article.

**1.1. Titanium Dioxide.** Titanium(IV) oxide is the oxide of titanium, with a molecular weight of 79.87 g/mol and chemical formula of TiO<sub>2</sub>. When used as a pigment, it is called white titanium or pigment white. Titanium dioxide is used in industries as a mineral pigment. It occurs in nature in three forms: brookite, rutile, and anatase. White titanium dioxide is 200 to 300 nm in diameter and has a particular geometric form and structure. Table 1 shows the properties of different kinds of titanium. The first production of TiO<sub>2</sub> was manufactured in Norway, USA, and Germany in 1918 [39–42].

**1.2. Photocatalysts.** For several years in industrialized countries, photocatalysts have been used for the removal of pollutants which are not removed by bioprocesses. Most photocatalysts are semiconductor solid oxides which, under radiation, are activated with sufficient energy [47]. Chlorophyll in plants acts in a similar manner to photocatalysts. When compared with photosynthesis in which chlorophyll absorbs sunlight and produces oxygen and glucose by water and carbon dioxide, in the process of photocatalysis, organic materials are converted into water and carbon dioxide in the presence of light, water, and catalyst (Figure 1) [48].

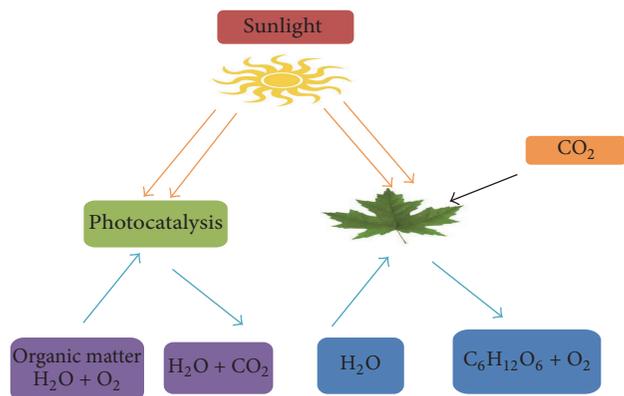


FIGURE 1: Comparison between the actions of a catalyst and chlorophyll.

TABLE 2: Band gap energy for some common semiconductor materials [46].

Semiconductors	Band gap energy (eV)
Diamond	5.4
CdS	2.42
ZnS	3.6
ZnO	3.436
TiO <sub>2</sub>	3.03
CdS	2.582
SnO <sub>2</sub>	3.54
CdSe	1.7
WO <sub>3</sub>	2.76
Si	1.17
Ge	0.744
Fe <sub>2</sub> O <sub>3</sub>	2.3
PbS	0.286
PbSe	0.165
ZrO <sub>2</sub>	3.87
Cu <sub>2</sub> O	2.172

**1.3. TiO<sub>2</sub> Photocatalytic Degradation Mechanism.** One of the important properties of TiO<sub>2</sub> solid and inorganic nanomaterials is the photocatalytic activity. In many cases, this feature is used for antibacterial surfaces. Also, the photocatalytic activity of TiO<sub>2</sub> has been applied in a wide range of metal oxides and their sulfides [49, 50] including ZnO [51], WO<sub>3</sub> [52], WS<sub>2</sub> [53], Fe<sub>2</sub>O<sub>3</sub> [54], V<sub>2</sub>O<sub>5</sub> [55], CeO<sub>2</sub> [56], CdS [57], and ZnS [58]. The band gap energy values for some common semiconductor materials are presented in Table 2 [46].

TiO<sub>2</sub> was found to be the best semiconductor because of its chemical stability and nontoxicity. Also, it is cost-effective and has an excellent photocatalytic activity in the presence of UV irradiation [59–62].

One of the commercial uses of TiO<sub>2</sub> is P<sub>25</sub>, which is often used as a photocatalytic material. It consists of 70 to 80% anatase and 20 to 30% rutile, with specific surface area of 50 m<sup>2</sup>/g. There exists an energy gap between the valence band

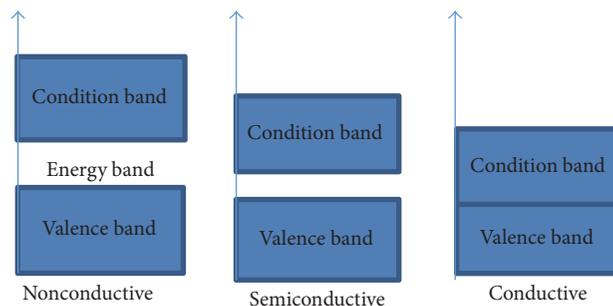
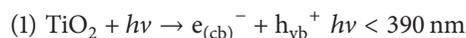


FIGURE 2: Energy gap in semiconductive, nonconductive, and conductive material.

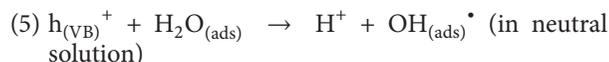
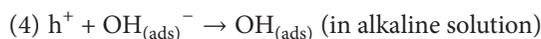
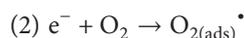
and the conduction band in semiconductors (Figure 2). Contrary to nonconductors, it is small; therefore, after radiation of light to the photocatalysts of semiconductors, photons with energy equal to or higher than the gap energy are absorbed, and electrons can be excited from the valence band to the conduction band.

After receiving solar energy (photons), semiconductors gain more energy than usual, and, as a result, electrons travel from the valence band to the conduction band and create holes in the valence band ( $h_{vb}^+$ ) (Figure 3).

TiO<sub>2</sub> produces this energy by receiving sunlight or UV radiation and acts as an important photocatalyst [63]. Moreover, the use of TiO<sub>2</sub> nanomaterials as a photocatalyst for the removal of pollutants has attracted much attention due to its physical and chemical properties, high efficiency, low cost, and low toxicity.



$h^+$  is suitable for producing OH<sup>•</sup> hydroxyl radicals on the surface of TiO<sub>2</sub> and also allows excitation of electrons from the valence band to the conduction band [51] and excitation of conduction band electrons to reduce the oxygen molecule.



Anatase and rutile are the two main types of TiO<sub>2</sub> with energies of 3.2 and 3.1 eV, respectively, showing that the photocatalytic activity of anatase is much greater than that of rutile [64, 65].

The photocatalytic power of TiO<sub>2</sub> is dependent not only on the energy band but also on the surface characteristics. The presence of a high surface area in each mass increases the photocatalytic power. The degradation of azo dye, especially methylene blue, by TiO<sub>2</sub> film, depends on the surface of the photocatalyst. This film could be either in anatase crystal form, having different thicknesses and surfaces, or in low pressure and chemical deposition, from which vapor is produced [66].

TiO<sub>2</sub> nanomaterials can be used for the photocatalytic cleaning of different types of organic compounds, such as

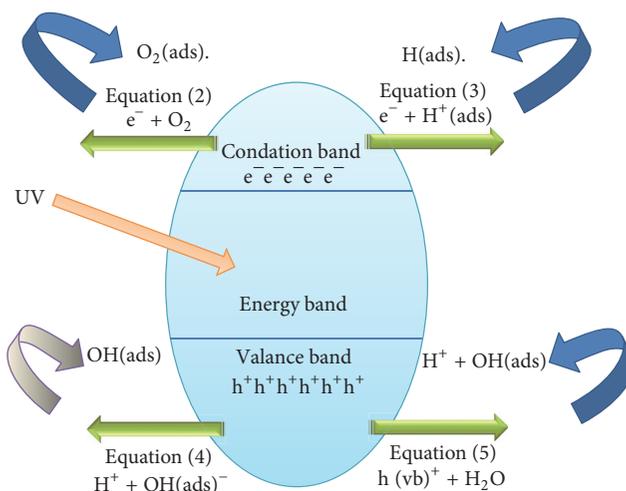


FIGURE 3: The mechanism of photocatalysis on  $\text{TiO}_2$  nanomaterials [37].

chlorinated hydrocarbons (like organic dye, insecticides, surfactants,  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{C}_2\text{HCl}_3$ , and phenol), decreasing heavy metals such as  $\text{Pt}^{4+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Au}^{3+}$ ,  $\text{Rh}^{3+}$ , and  $\text{Cr}^{3+}$ , and are also capable of the high efficiency removal of bacteria and viruses [65–69].

The pH of the solution has a great influence on the degradation of dye and  $\text{TiO}_2$  surface charge. The surface of  $\text{TiO}_2$  is positively charged in acidic pH and negatively charged in alkaline condition. The anionic dyes have strong adsorption in acidic pH while the cationic dyes have weak adsorption in alkaline pH [70, 71].

## 2. Background of Azo Dye

Dyes of textile industries and other kinds of dyes are dangerous to humans and the environment. During coloring, 1 to 20% of dyes are expelled from the wastewater of textile industries [72–75].

The discharge of wastewater from textile industries into the environment is regarded as a major source of pollution and main cause of eutrophication in rivers and lakes. Also, the oxidation, hydrolysis, and chemical activities in the discharged wastewater cause potential dangers [76–78].

The application of old processes (such as absorption, activated carbon, ultrafiltration, reverse osmosis, coagulation, and ion exchange) for the removal of dyes shows high efficiency. The transmission of organic materials from water to other phases, regeneration of absorbents and wastewater pretreatment, is quite expensive [79–82].

Due to high levels of aromatic compounds in dyes and their stability, the biological treatment takes a longer time and the crystals produced are not suitable for degradation [83–86]. Chlorination and ozonation are practical for the removal of some kinds of dyes. Both methods are expensive since they consume chemical materials, consume power, have low efficiency and limitations in the removal of carbon, and are not suitable for degradation [87–90].

In recent decades, advanced oxidation processes (AOPs) have become widespread. This process is based on the

production of super active species like hydroxyl ( $\cdot\text{OH}$ ), which is capable of oxidizing a wide range of materials, but its action is nonselective. Fenton and photo-Fenton, photocatalytic activities [91–95],  $\text{UV}/\text{H}_2\text{O}_2$  [96, 97], and modified photocatalytic activity of  $\text{TiO}_2$  [98–101] are some of the advanced oxidation processes (AOPs). In AOPs, the use of  $\text{TiO}_2$  as a photocatalyst has been recognized as a suitable technology [102–107].

Finally, the use of  $\text{TiO}_2$  as a photocatalyst under visible light has attracted much attention because it is economical. The use of a photocatalyst in the presence of sunlight can help in reducing dyes, especially methylene blue and methyl orange, and also their mineralization [108–110]. Many studies have considered the use of the desired photocatalyst for cleaning of textile industrial wastewater [111–114].

**2.1. Azo Dye.** The main problem of pollution in textile industries is water pollution. Methylene blue and methyl orange are among the commonly used dye compounds in the industry, and they are often known as azo dyes because they contain the functional group  $\text{R}-\text{N}=\text{N}-\text{R}$ , in which  $\text{N}=\text{N}$  is known as azo. The structures of methyl orange and methylene blue compounds are shown in Figure 4. Azo dyes are divided into three groups: mono, di, and tri, and this classification is dependent on the number of azo groups. R and R' can be aryl and alkyl groups, and as we know it is quite difficult to break down benzene ring; hence, the simplest benzene ring is  $\text{C}_6\text{H}_5$  in the aryl group.

Studies have shown that the presence of UV radiation helps  $\text{TiO}_2$  in removing organic dyes [50, 51].

## 3. Strategies for Improved Power of $\text{TiO}_2$

**3.1. Doping.** Doping titanium dioxide with metal elements such as Cr, Co, Cu, V, Mo, V, Ag, Au, Pt, Nb, and Ru and nonmetal elements such as C, N, S, P, I, F, and B increases the charge transfer reaction and thermal stability of the photocatalyst [27]. For example, X. Z. Li and F. B. Li reported the photodegradation of methylene blue in aqueous solutions

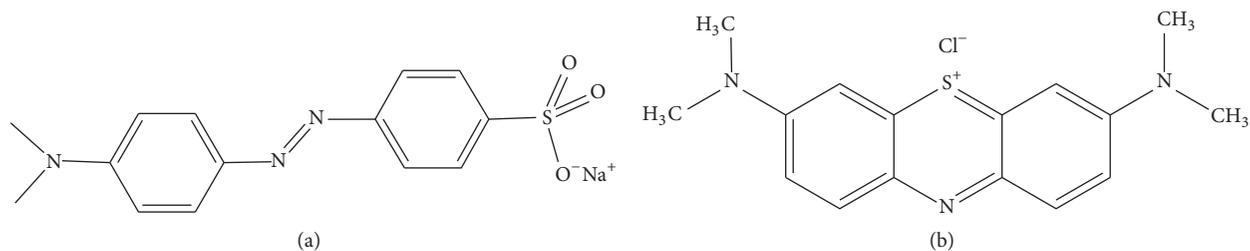


FIGURE 4: Structure of (a) methyl orange and (b) methylene blue.

under visible light over  $AU^{3+}$  with modified  $TiO_2$  power [115].

**3.2. Surface Chemical Modification.** Surface chemical modification is essential for increasing the efficiency of photocatalysts, thus preventing the recombination charge (electron and hole ( $h^+$ )) and their further separation, which is performed through two methods: sensitization and coupling. Sensitization, where different groups have used narrow band gap semiconductors to enhance optical absorption properties of  $TiO_2$  nanoparticles in the visible light region, can be used to sensitize  $TiO_2$  materials. Coupling different semiconductors with different energy systems provides another way to improve charge-carrier separation.

**3.2.1. Synthesis of Types of GO- $TiO_2$  Membrane.** The use of graphene, especially in the water treatment industry, has increased significantly in recent years due to its perfect mechanical and electrical features as well as high surface area. In the water treatment industry, graphene has been so useful in the removal of organic pollution, bacteria, heavy metals, and dyes, especially azo dyes [116], MB dyes and MO dyes [117, 118]. These dyes are produced, as mentioned before, in textile factories and have to be closely monitored to have standard concentration before being released into the environment [116]. In recent years, the synthesis of GO- $TiO_2$  membrane for the reduction of dye pollutants, especially azo dyes, has been studied in different cases in the water treatment industry to improve  $TiO_2$ .

The GO- $TiO_2$  membrane can be placed on any texture or on any membrane surface of the water filter. The photocatalytic process is an introduction to membrane properties, such as hydrophilicity, water penetration, and degradation of pollutants, and, as a result, there is a decrease in the odor produced from degradation of organic materials [117].

Studies were performed to achieve two major objectives: (1) studying the absorption ability of the membrane without considering the photocatalytic properties [118] and (2) studying the levels of degradation of organic dyes under UV radiation and considering the photocatalytic properties of the membrane [34, 117–119].

The GO- $TiO_2$  sheet can be placed on the following:

- (1) Anionic perfluorinated polymer (Nafion) [120]
- (2) Cellulose acetate [118]

(3) Polycarbonate (PC) [117]

(4) Polysulfone fluoride (PSF) [116]

(5) Polyvinylidene fluoride (PVDF) [120]

The polymeric membranes possess excellent chemical resistance, thermal stability, and good membrane formation [121, 122].

The photocatalytic effects of the produced membrane on the removal of organic dyes, especially for removed RB [117], MB [116], and MO dyes [117], which are considered as aromatic compounds, have been studied.

A comparison of hybrid membranes and standard nanomembranes showed that hybrid membranes act 5 times faster than standard nanomembranes in removing pollution [123]. Also, the energy consumption of hybrid membranes is half that of standard nanomembranes. Due to their mechanical and chemical features, these filters have stable photocatalytic activity in the presence of UV radiation [124, 125]. It is worth mentioning that GO is synthesized from natural graphite through Hommer' methods, similar to previous studies [126]. The  $TiO_2$  microsphere was synthesized by the reported method, with some modifications [127–129].

The LbL (layer-by-layer) method has the ability to form a hybrid membrane. This experiment used a gold coated sensor to determine the mass of  $TiO_2$  and GO during the LbL procedure. The sensor was coated with a base polymer membrane. The sensor was put in a desiccator for drying, after which it was put in DI water. A fixed concentration on the surface of the sensor was at  $0\text{ ng/cm}^2$  after 15 min, and the DI water was replaced with  $TiO_2$  solution.  $TiO_2$  nanoparticles were adsorbed on the base polymer and, after 2 h, the mass of the nanoparticle slowed down and became stabilized. After that,  $TiO_2$  solution was replaced with DI water for the removal of packed nanoparticles. Next, the  $TiO_2$  coated sensor was soaked in the GO solution [130].

According to Athanasekou et al., the reduced graphene oxide- $TiO_2$  (GO- $TiO_2$ ) was synthesized with GO suspension. GO was prepared according to previous studies, similar to the Hommer method, using LPD (liquid phase deposition) method at room temperature. Among all the membranes, GO- $TiO_2$  was the best membrane for removing MO under UV, and GO-Ti0 was the best membrane for removing MB. The hybrid membrane when compared with nanofiltration was better for the removal of pollutants and energy consumption [131].

**3.2.2. Reaction Schemes for Surface Modification GO-TiO<sub>2</sub>.** By forming Ti-O band between Ti<sup>4+</sup> or functional group membrane and hydrogen band, TiO<sub>2</sub> nanomaterials are placed on the surface of the base membrane between TiO<sub>2</sub> groups and the functional group [132]. In the next phase, GO is placed on TiO<sub>2</sub> layers via Ti-O band or the band between hydrogen and Ti<sup>4+</sup> and carboxyl groups of GO, and, eventually, GO reduced and bonded to TiO<sub>2</sub> by ethanol under UV radiation [133, 134]. One of the advantages of the GO-TiO<sub>2</sub> membrane is flexibility and great force in passing flow; the resistance to GO-TiO<sub>2</sub> is obvious after drying GO-TiO<sub>2</sub> and the absence of cracks on the membrane. TiO<sub>2</sub> alone is not highly efficient in removing organic materials and pollutants [135, 136].

## 4. GO-TiO<sub>2</sub> Membrane

Membranes are typically made of inorganic (ceramic) materials and a polymeric membrane. Membrane separation is basically on three principles: adsorption, sieving, and electrostatics as shown in Figure 5 [38]. The pore size determines the different membrane types: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Among the membrane processes, UF with polymeric membrane has the efficiency of removing contaminants such as organic pollutants, heavy metal, suspended solid, and different dyes. The polymeric membrane graphene oxide-TiO<sub>2</sub> is significantly efficient in the removal of organic pollutants and dye from solution. It has specific characteristics which completely explain some special traits.

### 4.1. Analysis of the GO-TiO<sub>2</sub> Membrane

- (i) Membrane analysis through transmission electron microscopy (TEM) and EDX shows the location of TiO<sub>2</sub> anatase crystal particles on the surface of GO [137, 138].
- (ii) The amount of TiO<sub>2</sub> on the surface of GO sheets is determined by thermogravimetric analysis (TGA) [139].
- (iii) The amounts of Ti and GO have been studied in the following researches through CS and XPS analysis [140–143].
- (iv) The absorption capacity of the GO-TiO<sub>2</sub> membrane is determined when different dye solutions are used in water [144, 145].

**4.1.1. Porosity of Membrane.** Atomic force microscopy (AFM) can record the roughness and surface morphology of polymeric membranes. The overall porosity of a membrane can be calculated using the gravimetric method as presented in [146]

$$\varepsilon = \frac{W_1 - W_2}{A \times L \times d_w}, \quad (1)$$

where  $W_1$  and  $W_2$  are the wet and dry weights of the membrane,  $A$  is the effective area of the membrane (m<sup>2</sup>),  $L$  is the membrane thickness (m), and  $d_w$  is the water of density 0.998 g/cm<sup>3</sup>. Using pure water flux, the porosity of the

membrane and the mean pore radius of the membrane ( $r_m$ ) can be calculated using the Guerout–Elford–Ferry equation:

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon) \times 8\eta LQ}{\varepsilon \times A \times \Delta P}}, \quad (2)$$

where  $\eta$  is the water viscosity ( $8.9 \times 10^{-4}$  pas),  $\Delta P$  is the operation pressure (3 MPa),  $Q$  is the permeated pure water amount (m<sup>3</sup>/s),  $L$  is the membrane thickness (m), and  $A$  is the surface area (m<sup>2</sup>) [146, 147].

Atomic force microscopy, field emission scanning electron microscopy, and the Guerout–Elford–Ferry equation applied for pure water permeation rate were used for determination of average pore size. The pore size calculated from the method of Guerout–Elford–Ferry was the highest, and, based on the make-ready sample (FESEM), the pore size calculated was the least in size [148].

**4.2. GO-TiO<sub>2</sub> Photocatalytic Membrane for Dye Removal.** Photocatalytic properties of TiO<sub>2</sub> nanoparticles under UV radiation for removal of dye occur according to the following reactions [149]. In the photocatalytic oxidation, TiO<sub>2</sub> has to be irradiated and excited in near-UV energy to induce charge separation. On the other hand, dyes rather than TiO<sub>2</sub> are excited by visible light followed by electron injection onto the TiO<sub>2</sub> conduction band, which leads to photosensitized oxidation. Subsequently, this is followed by electron injection from the excited dye molecule onto the conduction band of the TiO<sub>2</sub> particles, whereas the dye is converted to the cationic dye radicals (Dye<sup>•+</sup>) that undergo degradation to yield products:

- (6) dye<sub>ads</sub> +  $h\nu$  → dye<sub>ads</sub><sup>\*</sup> excitation
- (7) dye<sub>ads</sub><sup>\*</sup> → dye<sub>ads</sub><sup>•+</sup> + TiO<sub>2</sub>(e<sub>cb</sub><sup>-</sup>) electron injection
- (8) dye<sub>ads</sub><sup>•+</sup> + TiO<sub>2</sub>(e<sub>cb</sub><sup>-</sup>) → dye<sub>ads</sub> recombination
- (9) dye<sub>ads</sub><sup>•+</sup> → degradation
- (10) O<sub>2</sub> + TiO<sub>2</sub>(e<sub>cb</sub><sup>-</sup>) → O<sub>2</sub> (electron scavenging)

Anatase crystals which form mesosphere TiO<sub>2</sub> can have high mass transfer flux and photocatalytic activity [150–152]. The mesosphere structure of GO-TiO<sub>2</sub> has a huge surface area which forms numerous channels for passing water flow and photocatalysts for photocatalytic degradation [153, 154]. It is absolutely obvious that a membrane with high cross flow, removal efficiency, and low cost is suitable for filtration. GO sheets increase the filtration efficiency [154].

According to studies performed in different researches, GO-TiO<sub>2</sub> on a base membrane and under UV radiation shows great photocatalytic power in degrading organic materials. Membrane pretreatment, using ethanol and UV radiation, helps in increasing the degradation of MB [117].

The photocatalytic properties of porphyrin TiO<sub>2</sub> and graphene TiO<sub>2</sub> under visible light and UV radiation have been studied. Porphyrin graphene TiO<sub>2</sub> shows 35% higher efficiency than pure TiO<sub>2</sub> [155].

GO-TiO<sub>2</sub> is used for the degradation of RhB and AO<sub>7</sub> dyes under UV radiation within 20 to 30 min. In the absence of UV radiation, GO-TiO<sub>2</sub> membrane shows low efficiency,

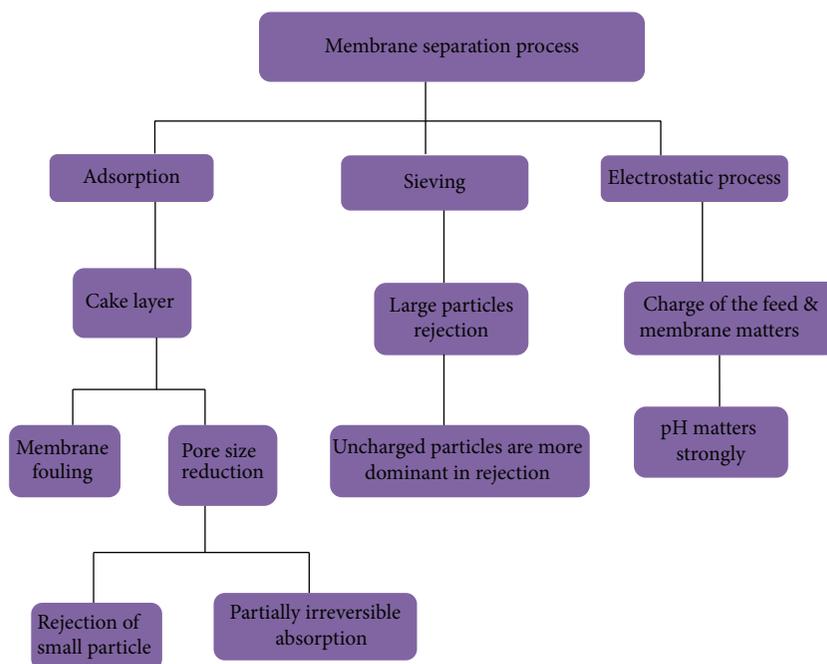


FIGURE 5: Schematic representing the basic principles involved in membrane separation [38].

lower than 15%, in the degradation of RhB and AO<sub>7</sub> dyes. The presence of UV radiation increases removal efficiency by 50% [118].

The presence of photocatalysts on a membrane prevents the accumulation of organic materials and macromolecules and therefore allows higher flow to pass through the membrane. Absorption of MO in darkness has minimal effects on the Nafion-GO SULF membrane, but under UV radiation the initial concentration is reduced by 90% [28, 118]. Pores size depends on the amount of GO-TiO<sub>2</sub> which is placed on the base membrane. GO-10 membrane (membrane having 10 nm pores) shows higher removal efficiency of dyes than other membranes [156].

The application of the method of liquid phase deposition (LPD) for synthesis of GO-TiO<sub>2</sub> composites and their stabilization on the integrated membranes is suitable for the removal of industrial dyes. Membranes with 1 m length and 30 monoliths consume less energy than nanomembranes [156].

**4.3. Permeation Flux through GO-TiO<sub>2</sub> Membrane.** Filtration tests on GO-TiO<sub>2</sub> membrane with 5%-5 mL/min flow rate, 0.6 nm constant membrane thickness, and 30 mg/L concentration cobalt ion show that the lesser the flow which is passed through, the more the cobalt removed. As the initial concentration of cobalt ion increases from 1 to 9 mg/L, the removal efficiency decreases from 89 to 21%. The high absorption capacity of nanosheets of graphene oxide ammonium for the removal of cobalt could be related to the ammonium functional groups. These absorbents are able to remove 30 mg/L concentration of cobalt ions in 5 min with 90% efficiency [119].

The presence of sulfonic functional group, along with graphene on Nafion membrane, allows more water to pass through it [28, 38, 118–157]. The movement of proton on Nafion membrane can help in separating ion compounds from the water molecule. These effects have been studied by adding the sulfonic functional group to the surface membrane of Nafion [38, 109–158].

The thickness of GO-TiO<sub>2</sub> membrane could be changed easily by changing the GO-TiO<sub>2</sub> mass which is placed on the base. Membrane thickness affects the flow passing through the membrane, meaning that a decrease in membrane thickness allows higher flow to pass through the membrane and decreases the removal efficiency [118].

**4.4. Fouling Resistant Membrane.** The total fouling resistance of the polymeric membrane ( $R_T$ ) is calculated from  $r_r$  and  $r_{ir}$ .  $r_r$  is a reversible fouling ratio which describes the fouling caused by concentration polarization, and  $r_{ir}$  is an irreversible fouling ratio which describes the fouling caused by adsorption or deposition of protein molecules on the membrane surface.

$$r_r = \frac{J_{W2} - J_P}{J_{W1}} \quad (3)$$

$$r_{ir} = \frac{J_{W1} - J_{W2}}{J_{W1}}$$

$R_T$  is the sum of  $r_r$  and  $r_{ir}$ , and  $J_{W1}$  is the permeation water flux (kg/m<sup>2</sup>h):

$$J_{W1} = \frac{M}{At}, \quad (4)$$

where  $M$  is the weight of collected permeation flux,  $A$  is the membrane effective area,  $t$  is the permeation time,  $J_{W2}$  is the water flux cleaned membrane, and  $J_P$  is the flux of the BSA solution [144]. Hence,

$$R_T = \left(1 - \frac{J_P}{J_{W1}}\right) \times 100. \quad (5)$$

Under special pressure, after the pure water test, the BSA solutions are immediately replaced in the filtration cell for 90 min [159].

**4.5. Antifouling Property of GO-TiO<sub>2</sub> Membrane.** Since the cost of cleaning normal membranes is too high and, over time, they produce odors because of the accumulation of organic materials, the application of GO-TiO<sub>2</sub> membrane in the water treatment industry seems to have become more widespread. Humic acid as a standard pollutant formed from natural organic materials and carcinogen disinfectants has been studied [160].

In the first phases of filtration, the accumulation of humic acid on the surface of membrane and closing of the pores are really obvious after 30 min [161]. After 2 h, with 7 L/m<sup>2</sup>·h flow rate, a layer of odorous HA cake becomes noticeable [162]. UV radiation reduces the produced odor significantly [118]. The reason is the degradation of humic acid and production of CO<sub>2</sub> and H<sub>2</sub>O under UV radiation; in this state, there is no reduction in the flow which passed through the membrane.

## 5. Future Work

GO-TiO<sub>2</sub> membrane, because of its significant applications such as high photocatalytic and antifouling property, flux permeation, and removal of organic pollutants, can be potentially used in the degradation of polycyclic aromatic hydrocarbon (PAH) as a low cost membrane in the future.

## 6. Conclusion

This study was carried out on the characteristics of different polymeric membranes of GO-TiO<sub>2</sub>. According to previous studies, this membrane has lots of advantages like the capability of passing flow. Graphene oxide has a number of covalent attached oxygen containing groups such as epoxy, carbonyl, and carboxyl. The existence of these groups makes membrane possess good hydrophilicity. Another good property of this membrane is the existence of photocatalytic TiO<sub>2</sub> semiconductor, which can help in the degradation of the cake layer of the organic material and the reduction of odor. The object is very economical to reduce cost of washing membrane compared to the usual form. Fouling of this membrane because of GO-TiO<sub>2</sub> photocatalytic properties is also reduced from other forms of membranes. This result shows that the GO-TiO<sub>2</sub> polymer membrane could make considerable improvement in the field of water treatment and could have significant effects on the filtration efficiency.

## Competing Interests

The authors declare that they have no competing interests.

## References

- [1] M. Elimelech and W. A. Phillip, "The future of seawater desalination: energy, technology, and the environment," *Science*, vol. 333, no. 6043, pp. 712–717, 2011.
- [2] M. A. Shannon, P. W. Bohn, M. Elimelech, J. G. Georgiadis, B. J. Marias, and A. M. Mayes, "Science and technology for water purification in the coming decades," *Nature*, vol. 452, no. 7185, pp. 301–310, 2008.
- [3] S. Kaur, R. Gopal, W. J. Ng, S. Ramakrishna, and T. Matsuura, "Next-generation fibrous media for water treatment," *MRS Bulletin*, vol. 33, no. 1, pp. 21–26, 2008.
- [4] Z. Wu and D. Zhao, "Ordered mesoporous materials as adsorbents," *Chemical Communications*, vol. 47, no. 12, pp. 3332–3338, 2011.
- [5] S. E. Bailey, T. J. Olin, R. M. Bricka, and D. D. Adrian, "A review of potentially low-cost sorbents for heavy metals," *Water Research*, vol. 33, no. 11, pp. 2469–2479, 1999.
- [6] A. Netzer and D. E. Hughes, "Adsorption of copper, lead and cobalt by activated carbon," *Water Research*, vol. 18, no. 8, pp. 927–933, 1984.
- [7] C. Gómez-Lahoz, F. Garcia-Herruzo, J. M. Rodriguez-Maroto, and J. J. Rodriguez, "Cobalt(II) removal from water by chemical reduction with sodium borohydride," *Water Research*, vol. 27, no. 6, pp. 985–992, 1993.
- [8] M. M. Pendergast and E. M. V. Hoek, "A review of water treatment membrane nanotechnologies," *Energy and Environmental Science*, vol. 4, no. 6, pp. 1946–1971, 2011.
- [9] H.-W. Liang, X. Cao, W.-J. Zhang et al., "Robust and highly efficient free-standing carbonaceous nanofiber membranes for water purification," *Advanced Functional Materials*, vol. 21, no. 20, pp. 3851–3858, 2011.
- [10] Y. Liu, Z. Wu, X. Chen, Z. Shao, H. Wang, and D. Zhao, "A hierarchical adsorption material by incorporating mesoporous carbon into macroporous chitosan membranes," *Journal of Materials Chemistry*, vol. 22, no. 24, pp. 11908–11911, 2012.
- [11] J. Cadotte, R. Forester, M. Kim, R. Petersen, and T. Stocker, "Nanofiltration membranes broaden the use of membrane separation technology," *Desalination*, vol. 70, no. 1–3, pp. 77–88, 1988.
- [12] E. A. Jackson and M. A. Hillmyer, "Nanoporous membranes derived from block copolymers: from drug delivery to water filtration," *ACS Nano*, vol. 4, no. 7, pp. 3548–3553, 2010.
- [13] H. P. Dijkstra, G. P. M. van Klink, and G. van Koten, "The use of ultra- and nanofiltration techniques in homogeneous catalyst recycling," *Accounts of Chemical Research*, vol. 35, no. 9, pp. 798–810, 2002.
- [14] C. Stoquart, P. Servais, P. R. Bérubé, and B. Barbeau, "Hybrid membrane processes using activated carbon treatment for drinking water: a review," *Journal of Membrane Science*, vol. 411–412, pp. 1–12, 2012.
- [15] P. Wang, J. Ma, F. Shi, Y. Ma, Z. Wang, and X. Zhao, "Behaviors and effects of differing dimensional nanomaterials in water filtration membranes through the classical phase inversion process: a review," *Industrial and Engineering Chemistry Research*, vol. 52, no. 31, pp. 10355–10363, 2013.
- [16] B. W. Stanton, J. J. Harris, M. D. Miller, and M. L. Bruening, "Ultrathin, multilayered polyelectrolyte films as nanofiltration membranes," *Langmuir*, vol. 19, no. 17, pp. 7038–7042, 2003.
- [17] S. El-Safty, A. Shahat, M. R. Awual, and M. Mekawy, "Large three-dimensional mesoporous pores tailoring silica nanotubes

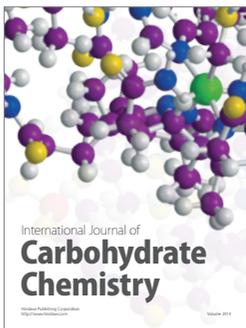
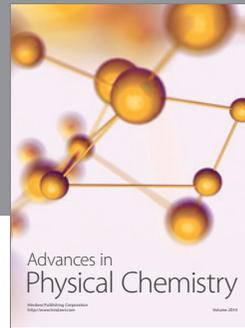
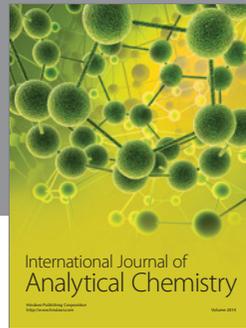
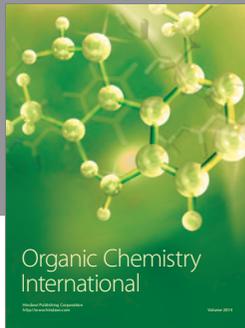
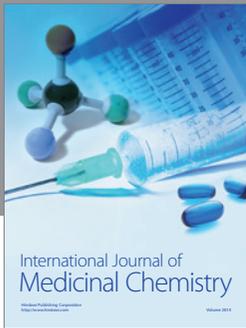
- as membrane filters: nanofiltration and permeation flux of proteins," *Journal of Materials Chemistry*, vol. 21, no. 15, pp. 5593–5603, 2011.
- [18] B. Zhao, L. Zhang, X.-Y. Wang et al., "Research progress in nanofiltration membrane based on carbon nanotubes," *New Carbon Materials*, vol. 26, no. 5, pp. 321–327, 2011.
- [19] J. Sekulić, J. E. Ten Elshof, and D. H. A. Blank, "A microporous titania membrane for nanofiltration and pervaporation," *Advanced Materials*, vol. 16, no. 17, pp. 1546–1550, 2004.
- [20] B. Van Der Bruggen, C. Vandecasteele, T. Van Gestel, W. Doyen, and R. Leysen, "A review of pressure-driven membrane processes in wastewater treatment and drinking water production," *Environmental Progress*, vol. 22, no. 1, pp. 46–56, 2003.
- [21] X. Zhang, T. Zhang, J. Ng, and D. D. Sun, "High-performance multifunctional TiO<sub>2</sub> nanowire ultrafiltration membrane with a hierarchical layer structure for water treatment," *Advanced Functional Materials*, vol. 19, no. 23, pp. 3731–3736, 2009.
- [22] M. N. Chong, B. Jin, C. W. K. Chow, and C. Saint, "Recent developments in photocatalytic water treatment technology: a review," *Water Research*, vol. 44, no. 10, pp. 2997–3027, 2010.
- [23] J. Grzechulska-Damszel, M. Tomaszewska, and A. W. Morawski, "Integration of photocatalysis with membrane processes for purification of water contaminated with organic dyes," *Desalination*, vol. 241, no. 1–3, pp. 118–126, 2009.
- [24] G. L. Liu, C. Han, M. Pelaez et al., "Enhanced visible light photocatalytic activity of C-N-codoped TiO<sub>2</sub> films for the degradation of microcystin-LR," *Journal of Molecular Catalysis A: Chemical*, vol. 372, pp. 58–65, 2013.
- [25] G. L. Liu, C. Han, M. Pelaez et al., "Synthesis, characterization and photocatalytic evaluation of visible light activated C-doped TiO<sub>2</sub> nanoparticles," *Nanotechnology*, vol. 23, no. 29, Article ID 294003, 2012.
- [26] X. Zhang, A. J. Du, P. Lee, D. D. Sun, and J. O. Leckie, "TiO<sub>2</sub> nanowire membrane for concurrent filtration and photocatalytic oxidation of humic acid in water," *Journal of Membrane Science*, vol. 313, no. 1–2, pp. 44–51, 2008.
- [27] R. M. Mohamed, D. L. McKinney, and W. M. Sigmund, "Enhanced nanocatalysts," *Materials Science and Engineering: R: Reports*, vol. 73, no. 1, pp. 1–13, 2012.
- [28] T.-F. Yeh, J. Cihlář, C.-Y. Chang, C. Cheng, and H. Teng, "Roles of graphene oxide in photocatalytic water splitting," *Materials Today*, vol. 16, no. 3, pp. 78–84, 2013.
- [29] G. P. Rao, C. Lu, and F. Su, "Sorption of divalent metal ions from aqueous solution by carbon nanotubes: a review," *Separation and Purification Technology*, vol. 58, no. 1, pp. 224–231, 2007.
- [30] A. G. Onu, W. Qil, Z. Yan, and K. Tan, "Adsorption of aromatic organic contaminants by graphene nanosheets: comparison with carbon nanotubes and activated carbon," *Water Research*, vol. 47, no. 4, pp. 1648–1654, 2013.
- [31] J. R. Ellerie, O. G. Apul, T. Karanfil, and D. A. Ladner, "Comparing graphene, carbon nanotubes, and superfine powdered activated carbon as adsorptive coating materials for microfiltration membranes," *Journal of Hazardous Materials*, vol. 261, pp. 91–98, 2013.
- [32] A. W. H. Mau, C. B. Huang, N. Kakuta et al., "Hydrogen photo-production by Nafion/cadmium sulfide/platinum films in water/sulfide ion solutions," *Journal of the American Chemical Society*, vol. 106, no. 65, pp. 37–42, 1984.
- [33] J. Liu, H. Bai, Y. Wang, Z. Liu, X. Zhang, and D. D. Sun, "Self-assembling TiO<sub>2</sub> nanorods on large graphene oxide sheets at a two-phase interface and their anti-recombination in photocatalytic applications," *Advanced Functional Materials*, vol. 20, no. 23, pp. 4175–4181, 2010.
- [34] R. A. K. Rao, S. Singh, B. R. Singh, W. Khan, and A. H. Naqvi, "Synthesis and characterization of surface modified graphene-zirconium oxide nanocomposite and its possible use for the removal of chlorophenol from aqueous solution," *Journal of Environmental Chemical Engineering*, vol. 2, no. 1, pp. 199–210, 2014.
- [35] G. Mele, R. D. Sole, G. Vasapollo et al., "TRMC, XPS, and EPR characterizations of polycrystalline TiO<sub>2</sub> porphyrin impregnated powders and their catalytic activity for 4-nitrophenol photodegradation in aqueous suspension," *The Journal of Physical Chemistry B*, vol. 109, no. 25, pp. 12347–12352, 2005.
- [36] S. Afzal, W. A. Daoud, and S. J. Langford, "Self-cleaning cotton by porphyrin-sensitized visible-light photocatalysis," *Journal of Materials Chemistry*, vol. 22, no. 9, pp. 4083–4088, 2012.
- [37] A. R. Khataee and M. B. Kasiri, "Photocatalytic degradation of organic dyes in the presence of nanostructured titanium dioxide: influence of the chemical structure of dyes," *Journal of Molecular Catalysis A: Chemical*, vol. 328, no. 1–2, pp. 8–26, 2010.
- [38] M. Padaki, R. Surya Murali, M. S. Abdullah et al., "Membrane technology enhancement in oil-water separation. A review," *Desalination*, vol. 357, pp. 197–207, 2015.
- [39] Kirk-Othmer, *Encyclopaedia of Chemical Technology*, vol. 19, Wiley-Inter Science Publication, 4th edition, 1996.
- [40] H. Takeda and O. Ishitani, "Development of efficient photocatalytic systems for CO<sub>2</sub> reduction using mononuclear and multinuclear metal complexes based on mechanistic studies," *Coordination Chemistry Reviews*, vol. 254, no. 3–4, pp. 346–354, 2010.
- [41] R. Zallen and M. P. Moret, "The optical absorption edge of brookite TiO<sub>2</sub>," *Solid State Communications*, vol. 137, no. 3, pp. 154–157, 2006.
- [42] X. Chen, "Titanium dioxide nanomaterials and their energy applications," *Chinese Journal of Catalysis*, vol. 30, no. 8, pp. 839–851, 2009.
- [43] D. T. Chomer and K. Herrington, "The structures of anatase and rutile," *Journal of the American Chemical Society*, vol. 77, no. 18, pp. 4708–4709, 1955.
- [44] V. W. H. Baur, "Atomabstände und bindungswinkel im brookite, TiO<sub>2</sub>," *Acta Crystallographica*, vol. 14, no. 3, pp. 214–216, 1961.
- [45] S.-D. Mo and W. Y. Ching, "Electronic and optical properties of three phases of titanium dioxide: rutile, anatase, and brookite," *Physical Review B*, vol. 51, no. 19, pp. 13023–13032, 1995.
- [46] R. Richards, *Surface and Nanomolecular Catalysis*, CRC Press/Taylor & Francis Group, 2006.
- [47] M. Zhang, G. Sheng, J. Fu, T. An, X. Wang, and X. Hu, "Novel preparation of nanosized ZnO-SnO<sub>2</sub> with high photocatalytic activity by homogeneous co-precipitation method," *Materials Letters*, vol. 59, no. 28, pp. 3641–3644, 2005.
- [48] M. Soltaninezhad and A. Aminifar, "Study nanostructures of semiconductor zinc oxide (ZnO) as a photocatalyst for the degradation of organic pollutants," *International Journal of Nano Dimension*, vol. 2, no. 2, pp. 137–145, 2011.
- [49] A. Mills and S. Le Hunte, "An overview of semiconductor photocatalysis," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 108, no. 1, pp. 1–35, 1997.
- [50] N. Daneshvar, D. Salari, and A. R. Khataee, "Photocatalytic degradation of azo dye acid red 14 in water: investigation of the effect of operational parameters," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 157, no. 1, pp. 111–116, 2003.

- [51] N. Daneshvar, D. Salari, and A. R. Khataee, "Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO<sub>2</sub>," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 162, no. 2-3, pp. 317-322, 2004.
- [52] X. F. Cheng, W. H. Leng, D. P. Liu, J. Q. Zhang, and C. N. Cao, "Enhanced photoelectrocatalytic performance of Zn-doped WO<sub>3</sub> photocatalysts for nitrite ions degradation under visible light," *Chemosphere*, vol. 68, no. 10, pp. 1976-1984, 2007.
- [53] D. Jing and L. Guo, "WS<sub>2</sub> sensitized mesoporous TiO<sub>2</sub> for efficient photocatalytic hydrogen production from water under visible light irradiation," *Catalysis Communications*, vol. 8, no. 5, pp. 795-799, 2007.
- [54] J. Bandara, U. Klehm, and J. Kiwi, "Raschig rings-Fe<sub>2</sub>O<sub>3</sub> composite photocatalyst activate in the degradation of 4-chlorophenol and Orange II under daylight irradiation," *Applied Catalysis B: Environmental*, vol. 76, no. 1-2, pp. 73-81, 2007.
- [55] K. Teramura, T. Tanaka, M. Kani, T. Hosokawa, and T. Funabiki, "Selective photo-oxidation of neat cyclohexane in the liquid phase over V<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub>," *Journal of Molecular Catalysis A: Chemical*, vol. 208, no. 1-2, pp. 299-305, 2004.
- [56] Y. Zhai, S. Zhang, and H. Pang, "Preparation, characterization and photocatalytic activity of CeO<sub>2</sub> nanocrystalline using ammonium bicarbonate as precipitant," *Materials Letters*, vol. 61, no. 8-9, pp. 1863-1866, 2007.
- [57] K. G. Kanade, J.-O. Baeg, U. P. Mulik, D. P. Amalnerkar, and B. B. Kale, "Nano-CdS by polymer-inorganic solid-state reaction: visible light pristine photocatalyst for hydrogen generation," *Materials Research Bulletin*, vol. 41, no. 12, pp. 2219-2225, 2006.
- [58] C. L. Torres-Martínez, R. Kho, O. I. Mian, and R. K. Mehra, "Efficient photocatalytic degradation of environmental pollutants with mass-produced ZnS nanocrystals," *Journal of Colloid and Interface Science*, vol. 240, no. 2, pp. 525-532, 2001.
- [59] M. R. Hoffmann, S. T. Martin, W. Y. Choi, and D. W. Bahnemann, "Environmental applications of semiconductor photocatalysis," *Chemical Reviews*, vol. 95, no. 1, pp. 69-96, 1995.
- [60] A. L. Linsebigler, G. Q. Lu, and J. T. Yates, "Photocatalysis on TiO<sub>2</sub> surfaces: principles, mechanisms, and selected results," *Chemical Reviews*, vol. 95, no. 3, pp. 735-758, 1995.
- [61] O. Zahraa, S. Maire, F. Evenou et al., "Treatment of wastewater dyeing agent by photocatalytic process in solar reactor," *International Journal of Photoenergy*, vol. 2006, Article ID 46961, 9 pages, 2006.
- [62] A. Fujishima, T. N. Rao, and D. A. Tryk, "Titanium dioxide photocatalysis," *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, vol. 1, no. 1, pp. 1-21, 2000.
- [63] N. Daneshvar, D. Salari, A. Niaei, M. H. Rasoulifard, and A. R. Khataee, "Immobilization of TiO<sub>2</sub> nanopowder on glass beads for the photocatalytic decolorization of an azo dye C.I. Direct Red 23," *Journal of Environmental Science and Health, Part A: Toxic*, vol. 40, no. 8, pp. 1605-1617, 2005.
- [64] V. Loddo, G. Marci, C. Martín, L. Palmisano, V. Rives, and A. Sclafani, "Preparation and characterisation of TiO<sub>2</sub> (anatase) supported on TiO<sub>2</sub> (rutile) catalysts employed for 4-nitrophenol photodegradation in aqueous medium and comparison with TiO<sub>2</sub> (anatase) supported on Al<sub>2</sub>O<sub>3</sub>," *Applied Catalysis B: Environmental*, vol. 20, no. 1, pp. 29-45, 1999.
- [65] S. Bakardjieva, J. Šubrt, V. Štengl, M. J. Dianez, and M. J. Sayagues, "Photoactivity of anatase-rutile TiO<sub>2</sub> nanocrystalline mixtures obtained by heat treatment of homogeneously precipitated anatase," *Applied Catalysis B: Environmental*, vol. 58, no. 3-4, pp. 193-202, 2005.
- [66] S.-C. Jung, S.-J. Kim, N. Imaishi, and Y.-I. Cho, "Effect of TiO<sub>2</sub> thin film thickness and specific surface area by low-pressure metal-organic chemical vapor deposition on photocatalytic activities," *Applied Catalysis B: Environmental*, vol. 55, no. 4, pp. 253-257, 2005.
- [67] X. Wang, J. C. Yu, P. Liu, X. Wang, W. Su, and X. Fu, "Probing of photocatalytic surface sites on SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub> solid acids by in situ FT-IR spectroscopy and pyridine adsorption," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 179, no. 3, pp. 339-347, 2006.
- [68] M. Zheng, M. Gu, Y. Jin, and G. Jin, "Preparation, structure and properties of TiO<sub>2</sub>-PVP hybrid films," *Materials Science and Engineering: B*, vol. 77, no. 1, pp. 55-59, 2000.
- [69] K. Tennakone and K. G. U. Wijayantha, "Heavy-metal extraction from aqueous medium with an immobilized TiO<sub>2</sub> photocatalyst and a solid sacrificial agent," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 113, no. 1, pp. 89-92, 1998.
- [70] M. N. Pons, A. Alinsafi, F. Evenou et al., "Treatment of textile industry wastewater by supported photocatalysis," *Dyes and Pigments*, vol. 74, no. 2, pp. 439-445, 2007.
- [71] N. Keller, G. Rebmann, E. Barraud, O. Zahraa, and V. Keller, "Macroscopic carbon nanofibers for use as photocatalyst support," *Catalysis Today*, vol. 101, no. 3-4, pp. 323-329, 2005.
- [72] H. Zollinger, Ed., *Color Chemistry: Synthesis, Properties and Applications of Organic Dyes and Pigments*, VCH, 2nd edition, 1991.
- [73] E. J. Weber and V. C. Stickney, "Hydrolysis kinetics of reactive blue 19-vinyl sulfone," *Water Research*, vol. 27, no. 1, pp. 63-67, 1993.
- [74] C. Ràfols and D. Barceló, "Determination of mono- and disulphonated azo dyes by liquid chromatography-atmospheric pressure ionization mass spectrometry," *Journal of Chromatography A*, vol. 777, no. 1, pp. 177-192, 1997.
- [75] A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, and J.-M. Herrmann, "Photocatalytic degradation pathway of methylene blue in water," *Applied Catalysis B: Environmental*, vol. 31, no. 2, pp. 145-157, 2001.
- [76] U. Pagga and D. Brown, "The degradation of dyestuffs: part II behaviour of dyestuffs in aerobic biodegradation tests," *Chemosphere*, vol. 15, no. 4, pp. 479-491, 1986.
- [77] A. B. Prevot, C. Baiocchi, M. C. Brussino et al., "Photocatalytic degradation of acid blue 80 in aqueous solutions containing TiO<sub>2</sub> suspensions," *Environmental Science and Technology*, vol. 35, no. 5, pp. 971-976, 2001.
- [78] M. Saquib and M. Muneer, "TiO<sub>2</sub>-mediated photocatalytic degradation of a triphenylmethane dye (gentian violet), in aqueous suspensions," *Dyes and Pigments*, vol. 56, no. 1, pp. 37-49, 2003.
- [79] W. Z. Tang and H. An, "UV/TiO<sub>2</sub> photocatalytic oxidation of commercial dyes in aqueous solutions," *Chemosphere*, vol. 31, no. 9, pp. 4157-4170, 1995.
- [80] V. Meshko, L. Markovska, M. Mincheva, and A. E. Rodrigues, "Adsorption of basic dyes on granular activated carbon and natural zeolite," *Water Research*, vol. 35, no. 14, pp. 3357-3366, 2001.
- [81] W. S. Kuo and P. H. Ho, "Solar photocatalytic decolorization of methylene blue in water," *Chemosphere*, vol. 45, no. 1, pp. 77-83, 2001.
- [82] C. Galindo, P. Jacques, and A. Kalt, "Photooxidation of the phenylazonaphthol AO20 on TiO<sub>2</sub>: kinetic and mechanistic investigations," *Chemosphere*, vol. 45, no. 6-7, pp. 997-1005, 2001.

- [83] S. S. Patil and V. M. Shinde, "Biodegradation studies of aniline and nitrobenzene in aniline plant wastewater by gas chromatography," *Environmental Science and Technology*, vol. 22, no. 10, pp. 1160–1165, 1988.
- [84] A. T. Moore, A. Vira, and S. Fogel, "Biodegradation of trans-1,2-dichloroethylene by methane-utilizing bacteria in an aquifer simulator," *Environmental Science and Technology*, vol. 23, no. 4, pp. 403–406, 1989.
- [85] V. M. Correia, T. Stephenson, and S. J. Judd, "Characterization of textile wastewaters—a review," *Environmental Technology*, vol. 15, no. 10, pp. 917–929, 1994.
- [86] I. Arslan and I. A. Balcioglu, "Degradation of commercial reactive dyestuffs by heterogenous and homogenous advanced oxidation processes: a comparative study," *Dyes and Pigments*, vol. 43, no. 2, pp. 95–108, 1999.
- [87] S. H. Lin and C. M. Lin, "Treatment of textile waste effluents by Ozonation and chemical coagulation," *Water Research*, vol. 27, no. 12, pp. 1743–1748, 1993.
- [88] S. H. Lin and W. Y. Liu, "Continuous treatment of textile water by ozonation and coagulation," *Journal of Environmental Engineering*, vol. 120, no. 2, pp. 437–446, 1994.
- [89] F. Strickland and S. Perkins, "Decolorization of continuous dyeing wastewater by ozonation," *Textile Chemist & Colorist*, vol. 27, no. 5, pp. 11–15, 1995.
- [90] P. Aranyosi, Z. Csepregi, I. Rusznák, L. Töke, and A. Víg, "The light stability of azo dyes and azo dyeings. III. The effect of artificial perspiration on the light stability of reactive and non-reactive derivatives of two selected azo chromophores in aqueous solution," *Dyes and Pigments*, vol. 37, no. 1, pp. 33–45, 1998.
- [91] W. G. Kuo, "Decolorizing dye wastewater with Fenton's reagent," *Water Research*, vol. 26, no. 7, pp. 881–886, 1992.
- [92] E. Balanosky, J. Fernadez, J. Kiwi, and A. Lopez, "Degradation of membrane concentrates of the textile industry by fenton like reactions in iron-free solutions at biocompatible pH values (pH  $\approx$  7 – 8)," *Water Science & Technology*, vol. 40, no. 4-5, pp. 417–424, 1999.
- [93] W. Feng, D. Nansheng, and Z. Yuegang, "Discoloration of dye solutions induced by solar photolysis of ferrioxalate in aqueous solutions," *Chemosphere*, vol. 39, no. 12, pp. 2079–2085, 1999.
- [94] C. Morrison, J. Bandara, and J. Kiwi, "Sun light induced decolouration/degradation of non-biodegradation Orange dye by advanced Oxidation technologies in homogenous and heterogeneous media," *Journal of Advanced Oxidation Technologies*, vol. 1, no. 2, pp. 160–169, 1996.
- [95] S.-F. Kang, C.-H. Liao, and S.-T. Po, "Decolorization of textile wastewater by photo-fenton oxidation technology," *Chemosphere*, vol. 41, no. 8, pp. 1287–1294, 2000.
- [96] I. Arslan, I. A. Balcioglu, and T. Tuhkanen, "Advanced oxidation of synthetic dyehouse effluent by  $O_3$ ,  $H_2O_2/O_3$  and  $H_2O_2/UV$  processes," *Environmental Technology*, vol. 20, no. 9, pp. 921–931, 1999.
- [97] N. H. Ince and D. T. Gönenç, "Treatability of a textile azo dye by UV/ $H_2O_2$ ," *Environmental Technology*, vol. 18, no. 2, pp. 179–185, 1997.
- [98] K. Vinodgopal and P. V. Kamat, "Combine electrochemistry with photocatalysis," *CHEMTECH*, vol. 26, no. 4, pp. 18–22, 1996.
- [99] C. Lizama, M. C. Yeber, J. Freer, J. Baeza, and H. D. Mansilla, "Reactive dyes decolouration by  $TiO_2$  photo-assisted catalysis," *Water Science and Technology*, vol. 44, no. 5, pp. 197–203, 2001.
- [100] F. Zhang, J. Zhao, T. Shen, H. Hidaka, E. Pelizzetti, and N. Serpone, " $TiO_2$ -assisted photodegradation of dye pollutants II. Adsorption and degradation kinetics of eosin in  $TiO_2$  dispersions under visible light irradiation," *Applied Catalysis B: Environmental*, vol. 15, no. 1-2, pp. 147–156, 1998.
- [101] P. Qu, J. Zhao, T. Shen, and H. Hidaka, " $TiO_2$ -assisted photodegradation of dyes: a study of two competitive primary processes in the degradation of RB in an aqueous  $TiO_2$  colloidal solution," *Journal of Molecular Catalysis A: Chemical*, vol. 129, no. 2-3, pp. 257–268, 1998.
- [102] G. Liu, T. Wu, J. Zhao, H. Hidaka, and N. Serpone, "Photoassisted degradation of dye pollutants. 8. Irreversible degradation of alizarin red under visible light radiation in air-equilibrated aqueous  $TiO_2$  dispersions," *Environmental Science and Technology*, vol. 33, no. 12, pp. 2081–2087, 1999.
- [103] J. Zhao, T. Wu, K. Wu, K. Oikawa, H. Hidaka, and N. Serpone, "Photoassisted degradation of dye pollutants. 3. Degradation of the cationic dye rhodamine B in aqueous anionic surfactant/ $TiO_2$  dispersions under visible light irradiation: evidence for the need of substrate adsorption on  $TiO_2$  particles," *Environmental Science and Technology*, vol. 32, no. 16, pp. 2394–2400, 1998.
- [104] M. R. Hoffmann, S. T. Martin, W. Choi, and D. W. Bahnemann, "Environmental applications of semiconductor photocatalysis," *Chemical Reviews*, vol. 95, no. 1, pp. 69–96, 1995.
- [105] I. K. Konstantinou and T. A. Albanis, "Photocatalytic transformation of pesticides in aqueous titanium dioxide suspensions using artificial and solar light: intermediates and degradation pathways," *Applied Catalysis B: Environmental*, vol. 42, no. 4, pp. 319–335, 2003.
- [106] A. L. Linsebigler, G. Lu, and J. T. Yates, "Photocatalysis on  $TiO_2$  surfaces: principles, mechanisms, and selected results," *Chemical Reviews*, vol. 95, no. 3, pp. 735–758, 1995.
- [107] P. Reeves, R. Ohlhausen, D. Sloan et al., "Photocatalytic destruction of organic dyes in aqueous  $TiO_2$  suspensions using concentrated simulated and natural solar energy," *Solar Energy*, vol. 48, no. 6, pp. 413–420, 1992.
- [108] X. Z. Li and M. Zhang, "Decolorization and biodegradability of dyeing wastewater treated by a  $TiO_2$ -sensitized photo-oxidation process," *Water Science and Technology*, vol. 34, no. 9, pp. 49–55, 1996.
- [109] Y. Wang, "Solar photocatalytic degradation of eight commercial dyes in  $TiO_2$  suspension," *Water Research*, vol. 34, no. 3, pp. 990–994, 2000.
- [110] S. Sakthivel, B. Neppolian, M. V. Shankar, B. Arabindoo, M. Palanichamy, and V. Murugesan, "Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and  $TiO_2$ ," *Solar Energy Materials and Solar Cells*, vol. 77, no. 1, pp. 65–82, 2003.
- [111] V. Augugliaro, C. Baiocchi, A. B. Prevot et al., "Azo-dyes photocatalytic degradation in aqueous suspension of  $TiO_2$  under solar irradiation," *Chemosphere*, vol. 49, no. 10, pp. 1223–1230, 2002.
- [112] M. Styliadi, D. I. Kondarides, and X. E. Verykios, "Pathways of solar light-induced photocatalytic degradation of azo dyes in aqueous  $TiO_2$  suspensions," *Applied Catalysis B: Environmental*, vol. 40, no. 4, pp. 271–286, 2003.
- [113] S. Gomes de Moraes, R. Sanches Freire, and N. Durán, "Degradation and toxicity reduction of textile effluent by combined photocatalytic and ozonation processes," *Chemosphere*, vol. 40, no. 4, pp. 369–373, 2000.

- [114] I. A. Balcioglu and I. Arslan, "Treatment of textile waste water by heterogenous photocatalytic oxidation processes," *Environmental Technology*, vol. 18, no. 10, pp. 1053–1059, 1997.
- [115] X. Z. Li and F. B. Li, "Study of Au/Au<sup>3+</sup>-TiO<sub>2</sub> photocatalysts toward visible photooxidation for water and wastewater treatment," *Environmental Science and Technology*, vol. 35, no. 11, pp. 2381–2387, 2001.
- [116] H. Zollinger, *Properties of Organic Dyes and Pigments in Color Chemistry*, VCH Publishers, New York, NY, USA, 1978.
- [117] B. Kraeutler and A. J. Bard, "Heterogeneous photocatalytic decomposition of saturated carboxylic acids on titanium dioxide powder. Decarboxylative route to alkanes," *Journal of the American Chemical Society*, vol. 100, no. 19, pp. 5985–5992, 1978.
- [118] W. Dunn, K. Wilboun, F. Fan, and A. Brad, "Heterogeneous photocatalytic oxidation of hydrocarbons on platinumized TiO<sub>2</sub> powders," *The Journal of Physical Chemistry A*, vol. 84, no. 32, pp. 7–10, 1980.
- [119] Y. Gao, M. Hu, and B. Mi, "Membrane surface modification with TiO<sub>2</sub>-graphene oxide for enhanced photocatalytic performance," *Journal of Membrane Science*, vol. 455, pp. 349–356, 2014.
- [120] C. Xu, A. Cui, Y. Xu, and X. Fu, "Graphene oxide-TiO<sub>2</sub> composite filtration membranes and their potential application for water purification," *Carbon*, vol. 62, pp. 465–471, 2013.
- [121] A. L. Ahmad, M. A. Majid, and B. S. Ooi, "Functionalized PSf/SiO<sub>2</sub> nanocomposite membrane for oil-in-water emulsion separation," *Desalination*, vol. 268, no. 1–3, pp. 266–269, 2011.
- [122] Z. Wang, H. Yu, J. Xia et al., "Novel GO-blended PVDF ultrafiltration membranes," *Desalination*, vol. 299, pp. 50–54, 2012.
- [123] C. P. Athanasekou, G. E. Romanos, F. K. Katsaros, K. Kordatos, V. Likodimos, and P. Falaras, "Very efficient composite titania membranes in hybrid ultrafiltration/photocatalysis water treatment processes," *Journal of Membrane Science*, vol. 392–393, pp. 192–203, 2012.
- [124] Y. S. Lin, "Microporous and dense inorganic membranes: current status and prospective," *Separation and Purification Technology*, vol. 25, no. 1–3, pp. 39–55, 2001.
- [125] L. G. A. van de Water and T. Maschmeyer, "Mesoporous membranes—a brief overview of recent developments," *Topics in Catalysis*, vol. 29, no. 1–2, pp. 67–77, 2004.
- [126] W. S. Hummers and R. E. Offeman, "Preparation of graphitic oxide," *Journal of the Preparation of Graphitic Oxide, American Chemical Society*, vol. 80, no. 6, p. 1339, 1958.
- [127] P. Gao, J. Liu, S. Lee, T. Zhang, and D. D. Sun, "High quality graphene oxide-CdS-Pt nanocomposites for efficient photocatalytic hydrogen evolution," *Journal of Materials Chemistry*, vol. 22, no. 5, pp. 2292–2298, 2012.
- [128] J. Liu, H. Jeong, K. Lee et al., "Reduction of functionalized graphite oxides by trioctylphosphine in non-polar organic solvents," *Carbon*, vol. 48, no. 8, pp. 2282–2289, 2010.
- [129] D. C. Marcano, D. V. Kosynkin, J. M. Berlin et al., "Improved synthesis of graphene oxide," *ACS Nano*, vol. 4, no. 8, pp. 4806–4814, 2010.
- [130] Y. Gao, M. Hu, and B. Mi, "Membrane surface modification with TiO<sub>2</sub>-graphene oxide for enhanced photocatalytic performance," *Journal of Membrane Science*, vol. 455, pp. 349–356, 2014.
- [131] C. P. Athanasekou, N. G. Moustakas, S. Morales-Torres et al., "Ceramic photocatalytic membranes for water filtration under UV and visible light," *Applied Catalysis B: Environmental*, vol. 178, pp. 12–19, 2015.
- [132] M.-L. Luo, J.-Q. Zhao, W. Tang, and C.-S. Pu, "Hydrophilic modification of poly (ether sulfone) ultrafiltration membrane surface by self-assembly of TiO<sub>2</sub> nanoparticles," *Applied Surface Science*, vol. 249, no. 1–4, pp. 76–84, 2005.
- [133] H.-B. Yao, L.-H. Wu, C.-H. Cui, H.-Y. Fang, and S.-H. Yu, "Direct fabrication of photoconductive patterns on LBL assembled graphene oxide/PDDA/titania hybrid films by photothermal and photocatalytic reduction," *Journal of Materials Chemistry*, vol. 20, no. 25, pp. 5190–5195, 2010.
- [134] G. Williams, B. Seger, and P. V. Kamt, "TiO<sub>2</sub>-graphene nanocomposites. UV-assisted photocatalytic reduction of graphene oxide," *ACS Nano*, vol. 2, no. 7, pp. 1487–1491, 2008.
- [135] S. Morales-Torres, L. M. Pastrana-Martínez, J. L. Figueiredo, J. L. Faria, and A. M. T. Silva, "Design of graphene-based TiO<sub>2</sub> photocatalysts—a review," *Environmental Science and Pollution Research*, vol. 19, no. 9, pp. 3676–3687, 2012.
- [136] X. B. Ke, H. Y. Zhu, X. P. Gao, J. W. Liu, and Z. F. Zheng, "High-performance ceramic membranes with a separation layer of metal oxide nanofibers," *Advanced Materials*, vol. 19, no. 6, pp. 785–790, 2007.
- [137] X. Chen and S. S. Mao, "Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications," *Chemical Reviews*, vol. 107, no. 7, pp. 2891–2959, 2007.
- [138] Y. Xu, H. Bai, G. Lu, C. Li, and G. Shi, "Flexible graphene films via the filtration of water-soluble noncovalent functionalized graphene sheets," *Journal of the American Chemical Society*, vol. 130, no. 18, pp. 5856–5857, 2008.
- [139] R. Bissessur, P. K. Y. Liu, W. White, and S. F. Scully, "Encapsulation of polyanilines into graphite oxide," *Langmuir*, vol. 22, no. 4, pp. 1729–1734, 2006.
- [140] C. Xu, Z. Chen, and X. Fu, "Graphene oxide-mediated formation of freestanding, thickness controllable metal oxide films," *Journal of Materials Chemistry*, vol. 21, no. 34, pp. 12889–12893, 2011.
- [141] H.-K. Jeong, P. L. Yun, R. J. W. E. Lahaye et al., "Evidence of graphitic AB stacking order of graphite oxides," *Journal of the American Chemical Society*, vol. 130, no. 4, pp. 1362–1366, 2008.
- [142] O. Akhavan, "Photocatalytic reduction of graphene oxides hybridized by ZnO nanoparticles in ethanol," *Carbon*, vol. 49, no. 1, pp. 11–18, 2011.
- [143] O. Akhavan and E. Ghaderi, "Photocatalytic reduction of graphene oxide nanosheets on TiO<sub>2</sub> thin film for photoinactivation of bacteria in solar light irradiation," *Journal of Physical Chemistry C*, vol. 113, no. 47, pp. 20214–20220, 2009.
- [144] J. Zhao, W. Ren, and H.-M. Cheng, "Graphene sponge for efficient and repeatable adsorption and desorption of water contaminations," *Journal of Materials Chemistry*, vol. 22, no. 38, pp. 20197–20202, 2012.
- [145] C. Chen, W. Cai, M. Long et al., "Synthesis of visible-light responsive graphene oxide/TiO<sub>2</sub> composites with p/n heterojunction," *ACS Nano*, vol. 4, no. 11, pp. 6425–6432, 2010.
- [146] J.-F. Li, Z.-L. Xu, H. Yang, L.-Y. Yu, and M. Liu, "Effect of TiO<sub>2</sub> nanoparticles on the surface morphology and performance of microporous PES membrane," *Applied Surface Science*, vol. 255, no. 9, pp. 4725–4732, 2009.
- [147] N. A. A. Hamid, A. F. Ismail, T. Matsuura et al., "Morphological and separation performance study of polysulfone/titanium dioxide (PSF/TiO<sub>2</sub>) ultrafiltration membranes for humic acid removal," *Desalination*, vol. 273, no. 1, pp. 85–92, 2011.
- [148] E. Yuliyati, A. F. Ismail, T. Matsuura, M. A. Kassim, and M. S. Abdullah, "Characterization of surface-modified porous PVDF

- hollow fibers for refinery wastewater treatment using microscopic observation,” *Desalination*, vol. 283, pp. 206–213, 2011.
- [149] H. Park and W. Choi, “Photocatalytic reactivities of nafion-coated TiO<sub>2</sub> for the degradation of charged organic compounds under UV or visible light,” *Journal of Physical Chemistry B*, vol. 109, no. 23, pp. 11667–11674, 2005.
- [150] J. S. Chen, C. Chen, J. Liu, R. Xu, S. Z. Qiao, and X. W. Lou, “Ellipsoidal hollow nanostructures assembled from anatase TiO<sub>2</sub> nanosheets as a magnetically separable photocatalyst,” *Chemical Communications*, vol. 47, no. 9, pp. 2631–2633, 2011.
- [151] H. B. Wu, H. H. Hng, and X. W. D. Lou, “Direct synthesis of anatase TiO<sub>2</sub> nanowires with enhanced photocatalytic activity,” *Advanced Materials*, vol. 24, no. 19, pp. 2567–2571, 2012.
- [152] P. Gao, J. Liu, T. Zhang, D. D. Sun, and W. Ng, “Hierarchical TiO<sub>2</sub>/CdS ‘spindle-like’ composite with high photodegradation and antibacterial capability under visible light irradiation,” *Journal of Hazardous Materials*, vol. 229–230, pp. 209–216, 2012.
- [153] J.-Y. Liao, B.-X. Lei, D.-B. Kuang, and C.-Y. Su, “Tri-functional hierarchical TiO<sub>2</sub> spheres consisting of anatase nanorods and nanoparticles for high efficiency dye-sensitized solar cells,” *Energy and Environmental Science*, vol. 4, no. 10, pp. 4079–4085, 2011.
- [154] T. Zhang, J. Liu, and D. D. Sun, “A novel strategy to fabricate inorganic nanofibrous membranes for water treatment: use of functionalized graphene oxide as a cross linker,” *RSC Advances*, vol. 2, no. 12, pp. 5134–5137, 2012.
- [155] C. Ruan, L. Zhang, Y. Qin et al., “Synthesis of porphyrin sensitized TiO<sub>2</sub>/graphene and its photocatalytic property under visible light,” *Materials Letters*, vol. 141, pp. 362–365, 2015.
- [156] C. P. Athanasekou, S. Morales-Torres, V. Likodimos et al., “Prototype composite membranes of partially reduced graphene oxide/TiO<sub>2</sub> for photocatalytic ultrafiltration water treatment under visible light,” *Applied Catalysis B: Environmental*, vol. 158–159, pp. 361–372, 2014.
- [157] C. Heitner-Wirguin, “Recent advances in perfluorinated ionomer membranes: structure, properties and applications,” *Journal of Membrane Science*, vol. 120, no. 1, pp. 1–33, 1996.
- [158] S. J. Sondheim, N. J. Bunce, M. E. Lemke, and C. A. Fyfe, “Acidity and catalytic activity of Nafion-H,” *Macromolecules*, vol. 19, no. 2, pp. 339–343, 1986.
- [159] N. Zhang, Y. Zhang, and Y.-J. Xu, “Recent progress on graphene-based photocatalysts: current status and future perspectives,” *Nanoscale*, vol. 4, no. 19, pp. 5792–5813, 2012.
- [160] J. Wiszniowski, D. Robert, J. Surmacz-Gorska, K. Miksch, and J.-V. Weber, “Photocatalytic decomposition of humic acids on TiO<sub>2</sub> part I: discussion of adsorption and mechanism,” *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 152, no. 1–3, pp. 267–273, 2002.
- [161] W. Yuan and A. L. Zydney, “Humic acid fouling during micro-filtration,” *Journal of Membrane Science*, vol. 157, no. 1, pp. 1–12, 1999.
- [162] A. W. Zularisam, A. F. Ismail, and R. Salim, “Behaviours of natural organic matter in membrane filtration for surface water treatment-a review,” *Desalination*, vol. 194, no. 1–3, pp. 211–231, 2006.



**Hindawi**

Submit your manuscripts at  
<https://www.hindawi.com>

