Photoinduced Wetting Kinetics of Water on Immersed Nanoporous Titania Surfaces with Application to Oil-Water Separation

by

Divya Panchanathan

Submitted to the Department of Mechanical Engineering in partial fulfillment of the requirements for the degree of Master of Science

at the

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Abstract

We study the self-cleaning ability of titania surfaces in oil-water environments for fouling recovery in oil-water separation applications. A number of previous studies have shown that meshes and porous structures can be used to separate oil/water mixtures through careful control of surface energy and preferential wettability, however these structured surfaces are prone to fouling by oil and dirt. The photocatalytic and hydrophilic nature of titania coatings can be exploited to ensure preferential wetting of water over oil under ultraviolet (UV) irradiation and this provides a mechanism for recovery of fouling. Titania nanoporous surfaces were prepared by depositing TiO$_2$ nanoparticles onto flat substrates using Layer-by-Layer (LBL) assembly, and were then impregnated with oil to simulate typical fouling conditions experienced in oil-water separation applications. The resulting hydrophobic surfaces were irradiated with UV light in an oil-water environment to photocatalytically decompose the organic pollutants and restore hydrophilicity. The kinetics of this conversion from hydrophobicity to hydrophilicity were studied in situ under various UV intensities using goniometric measurements and a simple adsorption-photocatalysis model is proposed to describe the observed data.

Thesis Supervisor: Gareth H. McKinley
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Title: Professor of Mechanical Engineering
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<th>Meaning</th>
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<tr>
<td>( \theta_y )</td>
<td>Young’s contact angle</td>
</tr>
<tr>
<td>( \gamma_{\alpha,\beta} )</td>
<td>Interfacial tension of ‘( \alpha )’ and ‘( \beta )’ phases (( \alpha ) and ( \beta ) are defined in the subscripts section)</td>
</tr>
<tr>
<td>( \theta_{\alpha,\beta} )</td>
<td>Contact angle of a drop of ‘( \alpha )’ in an environment of ‘( \beta )’</td>
</tr>
<tr>
<td>( f_{\alpha,\beta} )</td>
<td>Interfacial area between phases ‘( \alpha )’ and ‘( \beta )’</td>
</tr>
<tr>
<td>( S_{\alpha,\beta} )</td>
<td>Spreading coefficient of phase ‘( \alpha )’ on ‘( \beta )’</td>
</tr>
<tr>
<td>( e^- )</td>
<td>Electron</td>
</tr>
<tr>
<td>( h^+ )</td>
<td>Hole</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>LBL</td>
<td>Layer-by-layer</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>( \lambda_\alpha )</td>
<td>Attenuation coefficient in phase ( \alpha )</td>
</tr>
<tr>
<td>( r )</td>
<td>Roughness</td>
</tr>
<tr>
<td>( S )</td>
<td>Uncontaminated titania surface</td>
</tr>
<tr>
<td>( C )</td>
<td>Contaminant</td>
</tr>
<tr>
<td>( P )</td>
<td>Photocatalysis products</td>
</tr>
<tr>
<td>( c_s )</td>
<td>Concentration of uncontaminated sites</td>
</tr>
<tr>
<td>( c_c )</td>
<td>Concentration of contaminated sites</td>
</tr>
<tr>
<td>( f_s )</td>
<td>Fraction of uncontaminated sites</td>
</tr>
<tr>
<td>( f_c )</td>
<td>Fraction of contaminated sites</td>
</tr>
<tr>
<td>( k_c )</td>
<td>Rate constant for adsorption of contaminant</td>
</tr>
<tr>
<td>( k_{-c} )</td>
<td>Rate constant for desorption of contaminant</td>
</tr>
<tr>
<td>( k_p )</td>
<td>Rate constant for photocatalysis for contaminant</td>
</tr>
<tr>
<td>Subscript</td>
<td>Meaning</td>
</tr>
<tr>
<td>-----------</td>
<td>---------</td>
</tr>
<tr>
<td>$a$</td>
<td>Air</td>
</tr>
<tr>
<td>$s$</td>
<td>Solid</td>
</tr>
<tr>
<td>$l$</td>
<td>Liquid</td>
</tr>
<tr>
<td>$v$</td>
<td>Vapor</td>
</tr>
<tr>
<td>$w$</td>
<td>Water</td>
</tr>
<tr>
<td>$o$</td>
<td>Oil</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

Production, transportation and utilization of petroleum and its products have led to unwanted release of oil into the environment causing pollution of fresh and marine waters. Although accidental oil spills are the ones which generate a lot of attention due to immediate and concentrated impact on the environment, they account for only 10% of all the oil that enters the ocean. The other sources are from motor oil run-offs from non-tank vessels, storm water run-offs from paved urban areas, untreated industrial waste streams and natural sources [7]. Figure 1-1 shows the relative contribution of each of these sources towards oil pollution and Figure 1-2 shows the various types of sources in each of the categories. The major reasons for lack of control over oil release are the lack of affordable and accessible technologies for treating effluents to meet environmental standards. This work is focused on designing coatings for membranes with photocatalytic cleaning ability for oil-water separation. This has potential to reduce costs incurred from membrane cleaning and replacement due to oil fouling.

This chapter introduces the need for self-cleaning membrane technologies and explains why titania is a suitable material for the same. Chapter 2 gives an overview of titania properties and illustrates the need to study the photocatalytic wetting properties of titania in an oil-water environment. Experimental procedures are described in detail in Chapter 3 and the results of this study are presented in Chapter 4. The final chapter summarizes the conclusions of this study and presents opportunities for
future work.

1.1 Need for Oil-Water Separation

The current world crude oil production is about 4,200 megatonne per year [1] and it is predicted to be on the rise for the next two decades [2]. As oil supply and demand continues to increase with time, the necessity for treatment of waste produced during production, transportation and utilization of petroleum and its products is also increasing. One of the major steps in the treatment of this wastewater is oil-water separation. The following passages elaborate on the different sources of waste streams and the need for oil-water separation in each of these.

'Produced water' is the largest wastewater stream in oil and gas production. This refers to the mixture of water, residual oil and other dissolved components which come out along with bulk oil stream during oil extraction. The produced water production is estimated to be about 71 billion bbl per year from all over the world with the U.S.A alone contributing 30% of the total [20]. The ratio of water to oil in produced water increases with the age of the oil well and the current water-oil ratio hovers
### Table 1-2: Average annual releases (1990-1999) of petroleum by source (in kilotonnes)

<table>
<thead>
<tr>
<th>Source</th>
<th>North America</th>
<th>Worldwide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Seeps</td>
<td>160</td>
<td>80</td>
</tr>
<tr>
<td>Extraction of Petroleum</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plots</td>
<td>3.0</td>
<td>2.3</td>
</tr>
<tr>
<td>Atmospheric deposition</td>
<td>0.16</td>
<td>0.15</td>
</tr>
<tr>
<td>Produced waters</td>
<td>0.12</td>
<td>0.07</td>
</tr>
<tr>
<td>Transportaion of Petroleum</td>
<td>2.7</td>
<td>2.1</td>
</tr>
<tr>
<td>Pipeline spills</td>
<td>9.1</td>
<td>7.4</td>
</tr>
<tr>
<td>Tank vessel spills</td>
<td>1.9</td>
<td>1.7</td>
</tr>
<tr>
<td>Operational discharges (cargo washings)</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>Coastal facility spills</td>
<td>1.9</td>
<td>1.7</td>
</tr>
<tr>
<td>Atmospheric deposition</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Consumption of Petroleum</td>
<td>84</td>
<td>19</td>
</tr>
<tr>
<td>Land-based (river and runoff)</td>
<td>54</td>
<td>2.6</td>
</tr>
<tr>
<td>Recreational marine vessels</td>
<td>5.6</td>
<td>2.2</td>
</tr>
<tr>
<td>Spills (non-tank vessels)</td>
<td>1.2</td>
<td>1.1</td>
</tr>
<tr>
<td>Operational discharges (vessels ≥100 GT)</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>Operational discharges (vessels&lt;100 GT)</td>
<td>0.12</td>
<td>0.03</td>
</tr>
<tr>
<td>Atmospheric deposition</td>
<td>21</td>
<td>9.1</td>
</tr>
<tr>
<td>Jettisoned aircraft fuel</td>
<td>1.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Total</td>
<td>260</td>
<td>110</td>
</tr>
</tbody>
</table>

- Numbers are reported to no more than two significant figures.
- "Regions" refers to 17 zones or regions of North American waters for which estimates were prepared. These are discussed later in this chapter.
- "Cargo washing is not allowed in U.S. waters, but is not restricted in international waters. Thus, it was assumed that this practice does not occur frequently in U.S. waters (see Chapter 3 and Appendix E)." Source: [1](#).
- "Estimated loads of less than 10 tonnes per year reported as "trace."" Source: [1](#).
- "Worldwide populations of recreational vessels were not available (see Chapter 3 and Appendix F)." Source: [1](#).
- "Insufficient data were available to develop estimates for this class of vessels (see Chapter 3 and Appendix E)." Source: [1](#).
around 2:1 to 3:1 worldwide. Most of the produced water is currently re-injected back into underground formations, re-used for secondary recovery or discharged into the environment. The general legislation for oil levels in discharged produced water is around 40 ppm but the stringency is increasing over time with increase in technological advances [39]. Thus, there is a lot of effort going into produced water purification to re-use this water for domestic and agricultural purposes in areas with water scarcity and to prevent environmental pollution by direct disposal of these waters.

Apart from produced water, there are oil spill accidents which cause huge release of oil into the oceans during transportation of oil. Some of the major (greater than 5000 Tonnes) oil spills in the past 5 years include Gulf of Mexico(2010), Xingang Port oil spill (Yellow Sea, China), ExxonMobil(Nigeria, 2010) and Bonga Field(Nigeria) and most of the times, these spills take months to clean up. Currently used biological and chemical mitigation measures have known to cause harm to the environment. Hence there a need for more environment friendly measures to take care of accidents.

It is important to note that human activities are not the only causes of oil release in the oceans [7]. Natural seeps of oil into the marine waters from highly pressurized seafloor rock account for about 40% of the total oil released into the ocean and typically, there are natural evolved bacteria which eat away the hydrocarbons in the environment. However in case of oil spills, the flora and fauna of the surroundings are adversely affected because they are usually not adapted to digest the oil. Hence, it is essential to find ways to clean man-made water pollution.

1.2 Need for Membrane Separation

Current oil-water separation technologies can be classified into three categories based on the size and nature of oil content being treated. The separation technologies listed below are focused on treating produced water but are not limited to it [22, 39, 20].

1. **Primary treatment**

Primary treatment aims at separation of bulk oil content from water by using gravitational and centrifugal forces. These include plate separators, hydro-
cyclones and centrifuges.

2. Secondary treatment
Secondary treatment aims at conditioning the produced water for re-injection, overboard discharge or further complex treatment. These include gas flotation, coalescence, disk stack centrifuges.

3. Tertiary treatment
Tertiary treatment is the final stage of treatment which is aimed at achieving high quality separation and elimination of soluble organics as well. The type of tertiary treatment selected depends on the type of wastewater and size of particles to be removed. This includes adsorption (modified zeolites, activated carbon, activated alumina, organoclays), media filtration (nutshell), macro-porous polymer extraction technology, membrane filtration, thermal oxidation, chemical oxidation, biological aerated filters etc.

A combination of the above methods can be used to create more efficient systems and save process costs. Figure 1-3 summarizes the advantages and limitations of the various technologies available for produced water treatment. While there are many techniques available to remove bulk oil and micron-sized oil droplets from water, there is still a need for cheap and efficient methods to remove dispersed oil (especially sub-micron sized drops) from water (See Table 1.1). Many of the chemical and biological methods use toxic chemicals, need high installation space, cause secondary pollution and incur high costs of treatment. Membrane filtration can eliminate many of these disadvantages as discussed below.

Membrane filtration includes microfiltration (MF) which uses pore sizes ranging from 0.1-3 μm and ultrafiltration (UF) which uses 0.01-0.1 μm. UF is a more effective method for removing residual oil content when compared to MF as it can remove nano-sized droplets as well (See Figure 1-4). Typical recovery using UF/MF ranges from 85-95 % and flux rates range from 2-100 gallons per day per square foot [34]. They have lighter weight and smaller space requirements compared to other technologies. Being a barrier technology, the treated water is less susceptible to contamination from
<table>
<thead>
<tr>
<th>Treatment</th>
<th>Description</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Waste stream</th>
<th>Oil and gas produced water applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrugated plate separator</td>
<td>Separation of free oil from water under gravity effects enhanced by flocculation on the surface of corrugated plates</td>
<td>No energy required, cheaper, effective for bulk oil removal and suspended solid removal, with no moving parts, this technology is robust and resistant to breakdowns in the field</td>
<td>Inefficient for free oil particles, requirement of high retention time, maintenance</td>
<td>Suspended particles slurry at the bottom of the separator</td>
<td>Oil recovery from emulsions or water with high oil content prior to discharge. Produced water from water-driven reservoirs and water flood production are most likely feed stocks. Water may contain oil and grease in excess of 1000 mg/L.</td>
</tr>
<tr>
<td>Centrifuge</td>
<td>Separation of free oil from water under centrifugal force generated by spinning the centrifuge cylinder</td>
<td>Efficient removal of smaller oil particles and suspended solids, lesser retention time high-throughput</td>
<td>Energy requirement for spinning, high maintenance cost</td>
<td>Suspended particles slurry at pretreatment waste</td>
<td></td>
</tr>
<tr>
<td>Hydroclone</td>
<td>Free oil separation under centrifugal force generated by pressured tangential input of influent stream</td>
<td>Compact modules, higher efficiency and throughput for smaller oil particles</td>
<td>Energy requirement to pretreat inlet, no solid separation, fouling</td>
<td>Skimm off volume, lumps of oil</td>
<td></td>
</tr>
<tr>
<td>Gas flotation</td>
<td>Oil particles attach to induced gas bubbles and float to the surface</td>
<td>No moving parts, higher efficiency due to coalescence, easy operation, robust and durable</td>
<td>Generation of large amount of air, retention time for separation, skimm volume</td>
<td>Use of solvent, extract handling, regeneration of solvent</td>
<td>Oil removal from water with low oil and grease content (&lt;1000 mg/L) or removal of trace quantities of oil and grease prior to membrane processing. Oil reservoirs and thermogenic natural gas reservoirs usually contain trace amounts of liquid hydrocarbons.</td>
</tr>
<tr>
<td>Extraction</td>
<td>Removal of free or dissolved oil soluble in lighter hydrocarbon solvent</td>
<td>Easy operation, efficient for primary treatment of soluble constituents</td>
<td>High retention time, less efficient at higher feed concentration</td>
<td>Solids precipitated in slurry form</td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>Porous media adsorbs contaminants from the influent stream</td>
<td>Compact packed bed modules, cheaper, efficient</td>
<td>Chemical addition, pre-treatment necessary</td>
<td>Used adsorbent media, regeneration waste</td>
<td>These technologies typically require less power and less pretreatment than membrane technologies. Suitable produced waters will have TDS values between 10,000 and 1000 mg/L. Some of the treatments remove oil and grease contaminants and some of them require oil and grease contaminants to be treated before these operations.</td>
</tr>
<tr>
<td>Ion-exchange</td>
<td>Addition of time to remove carbonates, bicarbonate, etc. hardness</td>
<td>Cheaper, accessible, can be modified</td>
<td>Used chemical and precipitated water</td>
<td>Used chemical and precipitated water</td>
<td></td>
</tr>
<tr>
<td>Rapid spray evaporation</td>
<td>Dissolved salts or minerals are ionized and removed by exchanging ions with ion-exchangers</td>
<td>Low energy required, possible continuous regeneration of resin, efficient, mobile treatment possible</td>
<td>Chemical addition, post-treatment necessary</td>
<td>Regeneration chemicals</td>
<td></td>
</tr>
<tr>
<td>Freeze-thaw evaporation</td>
<td>Injecting water at high velocity in heated air evaporates the water which can be condensed to obtain treated water</td>
<td>High quality treated water, higher conversion efficiency</td>
<td>Pre- and post-treatment required for high efficiency, produce efficient concentrate</td>
<td>Waste in sludge form at the end of evaporation</td>
<td></td>
</tr>
<tr>
<td>Microfiltration</td>
<td>Utilize natural temperature-cycles to freeze water into crystals from contaminated water and thaw crystals to produce pure water</td>
<td>No energy required, natural process, cheaper</td>
<td>Lower conversion efficiency, long operation cycle</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ultrafiltration</td>
<td>Membrane removes micro-particles from the water under the applied pressure</td>
<td>Higher recovery of fresh water, compact modules</td>
<td>Concentrated waste from membrane backwash during membrane cleaning, concentrate from the filtration operation</td>
<td>Removal of trace oil and grease, microbial, soluble organics, divalent salts, acids, and trace solids. These can be targeted by the selection of the membrane.</td>
<td></td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>Pure water is squeezed from contaminated water under pressure differential</td>
<td>Higher recovery of fresh water, compact modules</td>
<td>High energy, membrane fouling, low MW organics, salts, etc</td>
<td>Removal of sodium chloride, other monovalent salts, and other organics. Some organic species may require pretreatment. While energy costs increase with higher TDS, RO is able to efficiently remove salts in excess of 10,000 mg/L.</td>
<td></td>
</tr>
<tr>
<td>Activated sludge</td>
<td>Using oil degrading microorganisms to degrade contaminants within water</td>
<td>Cheaper, simple and clean technology</td>
<td>Oxygen requirement, large dimensions of the filter</td>
<td>Sludge waste at the end of the treatment</td>
<td>Removal of suspended and trace solids, ammonia, boron, metals, etc. Post-treatment is normally required to separate biomass, precipitated solids, dissolved gases, etc.</td>
</tr>
</tbody>
</table>
Table 1.1: Particle size removal capabilities of different technologies [25]

<table>
<thead>
<tr>
<th>Technology</th>
<th>Removal Capacity by Particle Size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>API gravity separator</td>
<td>150</td>
</tr>
<tr>
<td>Corrugated plate separator</td>
<td>40</td>
</tr>
<tr>
<td>Induced gas flotation without chemical addition</td>
<td>25</td>
</tr>
<tr>
<td>Induced gas flotation with chemical addition</td>
<td>3-5</td>
</tr>
<tr>
<td>Hydrocyclone</td>
<td>10-15</td>
</tr>
<tr>
<td>Mesh coalescer</td>
<td>5</td>
</tr>
<tr>
<td>Media filter</td>
<td>5</td>
</tr>
<tr>
<td>Centrifuge</td>
<td>2</td>
</tr>
<tr>
<td>Membrane filter</td>
<td>0.01</td>
</tr>
</tbody>
</table>

upstream. Thus, membrane filtration is ideal for separating oil-water nanoemulsions but one of the major problems faced during membrane separation is flux decline due to fouling. The following section describes the need to design and study fouling resistant membranes and fouling recovery processes.

1.3 Need for Fouling Remediation

Fouling is the adsorption or accumulation of unwanted components from the feed onto the membrane surface or in the membrane pores, eventually decreasing flux at constant pressure drop or increasing pressure drop at constant flux. Chemical or mechanical means can be used to decrease fouling. Dynamic shear enhanced membrane filtration creates mechanical shear on the membranes by using a rotating disk or by rotating or vibrating the membrane module [40]. Although this is effective for reducing fouling, it can be highly energy consuming. Thus, using surface active membranes which have preferential wettability towards either the oil or water phase is a more preferred method.

Membranes can be of two types- water passing and oil-passing. By argument of surface energies of surfaces, it is intuitive and easy to obtain organophilic materials for oil-water separation in which case the oil will pass through the membrane and the
water will be rejected. Examples of these materials include kapok, carbon based materials, hydrophobic aerogels, PTFE coating/embedding, PDMS coating/embedding, polydivinylbezen materials and cross-linked polymer gels [117]. However, oleophilic membranes can get easily fouled due to the accumulation of viscous oil in the pores and so it is desirable to use hydrophilic materials instead. Some of the main chemistries used for water-passing and oil-passing membranes have been summarized in Table 1.2. Some of these are currently employed commercially while others are still in development. However, both of them are susceptible to organic fouling in a real application [74, 5, 41].

Currently, backwashing is used in all membrane filtration applications to remove foulants while non-backwashable foulants are removed by chemical cleaning [3]. In most of the cases, the membrane has to also be removed periodically for extensive cleaning. Although these methods are effective for recovering most of the flux, they typically cost high energy, clean water and time. Therefore, it is preferable to have some method of self-cleaning to remove foulants in-situ i.e. under oil-water environment without having to stop or reverse the flow feed.

In order to remove the organic foulants in-situ, it is necessary to use methods
Table 1.2: Compilation of different techniques used to achieve oil-water separation using membranes

<table>
<thead>
<tr>
<th>Principle</th>
<th>Materials</th>
<th>Oil/water passing</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Electric field</td>
<td>FluorodecylPOSS&lt;sup&gt;a&lt;/sup&gt;+x-PDMS&lt;sup&gt;b&lt;/sup&gt;[47]</td>
<td>water-passing</td>
</tr>
<tr>
<td>2 Hygro-responsive chemistry</td>
<td>FluorodecylPOSS+x-PEDGA&lt;sup&gt;c&lt;/sup&gt;[44]</td>
<td>water-passing</td>
</tr>
<tr>
<td>3 Oleophilic chemistry</td>
<td>PTFE&lt;sup&gt;[24]&lt;/sup&gt;, PDMS&lt;sup&gt;[51]&lt;/sup&gt;, PS&lt;sup&gt;d&lt;/sup&gt;/PET&lt;sup&gt;e&lt;/sup&gt;[108], n-perfluoroeicosane&lt;sup&gt;[42]&lt;/sup&gt;, SWCNT&lt;sup&gt;f&lt;/sup&gt;network&lt;sup&gt;[90]&lt;/sup&gt;, Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;/C&lt;sup&gt;[12]&lt;/sup&gt;, Fluoropolymer&lt;sup&gt;[118]&lt;/sup&gt;, Lauric acid&lt;sup&gt;[115]&lt;/sup&gt;, F-PBZ&lt;sup&gt;[89]&lt;/sup&gt;, OTS&lt;sup&gt;h&lt;/sup&gt;&lt;sup&gt;[91]&lt;/sup&gt;</td>
<td>oil-passing</td>
</tr>
<tr>
<td>4 pH responsive</td>
<td>P2VP&lt;sup&gt;i&lt;/sup&gt;-PDMS&lt;sup&gt;[123]&lt;/sup&gt;, PAA&lt;sup&gt;j&lt;/sup&gt;&lt;sup&gt;[14]&lt;/sup&gt;</td>
<td>water/oil passing</td>
</tr>
<tr>
<td>5 Hydrophilic chemistry</td>
<td>Hydrogel PAM&lt;sup&gt;k&lt;/sup&gt;&lt;sup&gt;[117]&lt;/sup&gt;, PMAPS&lt;sup&gt;[125]&lt;/sup&gt;, Hydrogel PEDOT-PSS&lt;sup&gt;l&lt;/sup&gt;&lt;sup&gt;[101]&lt;/sup&gt;, PDA-NDM&lt;sup&gt;m&lt;/sup&gt;&lt;sup&gt;[8]&lt;/sup&gt;</td>
<td>water-passing</td>
</tr>
<tr>
<td>6 Hydrophilic chemistry</td>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;[29]&lt;/sup&gt;[121][71], ZnO&lt;sup&gt;[103]&lt;/sup&gt;, Zeolite&lt;sup&gt;[111]&lt;/sup&gt;, Cu(OH)&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;[56]&lt;/sup&gt;[121]</td>
<td>water-passing</td>
</tr>
<tr>
<td>7 Temperature responsive</td>
<td>PNIPAAm&lt;sup&gt;n&lt;/sup&gt;&lt;sup&gt;[116]&lt;/sup&gt; [92]</td>
<td>oil/water passing</td>
</tr>
<tr>
<td>8 Photo-responsive</td>
<td>Azobenzene,Spiropyran&lt;sup&gt;[107]&lt;/sup&gt;</td>
<td>?</td>
</tr>
<tr>
<td>9 Amphiphilic</td>
<td>Cellulose/Fluorinated Silica particles&lt;sup&gt;[30]&lt;/sup&gt;, PVDF&lt;sup&gt;p&lt;/sup&gt;&lt;sup&gt;[100]&lt;/sup&gt;</td>
<td>oil/water passing</td>
</tr>
</tbody>
</table>

<sup>a</sup>polyhedral oligomeric silsesquioxane  
<sup>b</sup>cross-lined polydimethylsiloxane  
<sup>c</sup>cross-linked poly(ethylene glycol) diacrylate  
<sup>d</sup>Poly(styrene)  
<sup>e</sup>poly(2-vinylpyridine)  
<sup>f</sup>poly(acrylic acid)  
<sup>g</sup>polyacrylamide  
<sup>h</sup>poly(3-(N-2- methacryloxyethyl-N,N-dimethyl) ammonatopropanesultone  
<sup>i</sup>poly(3,4-ethylenedioxythiophene)-poly(styrenesulfinate  
<sup>j</sup>polydopamine n-dodecyl mercaptan  
<sup>k</sup>poly(N -isopropylacrylamide)  
<sup>l</sup>poly(vinylidene fluoride)
other than mechanical means to break or weaken the adhesion of organic foulants on the membrane surface. Photocatalytic materials are good choice in this regard as they can break down organic pollutants in the presence of light of appropriate wavelengths and thus rid themselves from foulants. Titanium dioxide is one such material which is cheaply available that can be employed for this purpose. This work studies the recovery of Titanium dioxide nanoporous surfaces from fouling under oil-water environment in the presence of UV light. This can be applied to fouling recovery in ceramic membranes that are made of or coated with titania and used for oil-water separation.
Chapter 2

Use of Titanium dioxide

The element Titanium is the ninth most abundant element in the earth’s crust (0.63% by mass) [6] and the largest use of this element is in the form of its oxide, Titanium dioxide (TiO$_2$). The commercially important ores of TiO$_2$ are rutile (TiO$_2$) and ilmenite (FeTiO$_3$). Although the first laboratory synthesis of pure Titanium dioxide from its ore was done during the early 1800s, it took almost a century to scale up the process for mass production. During the early years of industrial scale production, Titanium dioxide was majorly used as a pigment in paints, plastics, tiles and paper[110] for its brightness and opacity. Over the recent years, it has begun to be used extensively in the nanoparticle form in the food, cosmetics and drugs industry as well to impart color and texture. The US Food and Drug Administration (FDA) allows upto 1% concentration of TiO$_2$ in food products if used as an inactive ingredient[43] but it is still unknown if exposure to TiO$_2$ nanoparticles can have adverse long term effects on human health and environment[119].

The use of TiO$_2$ was restricted to pigments until the 1970s when the discovery of its water-splitting property in the presence of UV light by Fujishima and Honda [26] gave rise to new fields of research exploring the various photo-responsive applications[13] of TiO$_2$ including photo-watersplitting for hydrogen production, photocatalysis for water purification, photoinduced-superhydrophilicity for self cleaning surfaces, photo-electrochromic devices, photo-voltaics for dye sensitized solar cells etc. Due to its high chemical stability, cheap availability and non-toxicity, TiO$_2$ has a lot of potential for
Figure 2-1: A schematic of various applications of TiO$_2$ by Nakata et al. [67]

commercial applications [68] in both energy production and environment protection as shown in Figure 2-1.

The major application of titania has been in photocatalytic air/water treatment to remove organic fouling agents and microbial content [59, 73, 15]. Recently, TiO$_2$ has been gaining attention in the fields of anti-fogging and oil-water separation using surface modified membranes due a combination of its intrinsic and photo-induced hydrophilic properties. As mentioned in the previous chapter, one of the major problems with current methods of membrane separation is membrane fouling. Owing to the photocatalytic and hydrophilic nature of titania, it is possible to create self-cleaning membranes for oil-water separation. This work is aimed at proving and characterizing in-situ recovery of fouled titania surfaces under UV light in an oil-water environment.

Instead of using chemical methods to study recovery of surfaces from fouling, water wettability was used as a probe to study contamination and self-cleaning. In order to study wetting behavior of titania, it is important to understand some basic terms, concepts and equations related general wetting phenomena and photocatalysis.
Sections 2.1 and 2.2 introduce the basic terms and equations related to wetting physics. Sections 2.3 and 2.4 describe the mechanisms proposed in literature for photocatalysis and hydrophilicity on TiO₂ respectively.

2.1 Basics of Wetting

Designing membranes for oil-water separation requires the understanding of basic principles involved in wetting and interfacial phenomena. An interface is the boundary between two or more entities which could be solid, liquid or gas. When there is just one uniform phase which extends to infinity there are no interfaces. The introduction of another phase/medium introduces interfaces immediately which are 2-D in nature. When a third component is introduced and all three phases are in contact with each other, it happens along a thin line called the contact line. Introducing any more phases can cause the components to meet at the contact line or contact points. Even though this boundary may look clear and sharp at the macroscale, the two phases gradually pass into one another at the molecular level. Gibbs defined a theoretical boundary called "dividing surface" for convenience and simplicity while mathematically modeling these systems [37].

Surface tension is a force arising from the effective summation of short-range attractive forces exerted on a molecule by the neighboring molecules. When a molecule is brought from the bulk to the surface these forces are not balanced on all sides giving rise to an excess energy which is called surface energy.

A simple mathematical model for a three phase contact line was proposed by Thomas Young in 1890 and since then this has been the basis for all studies in this field. By balancing the interfacial surface tension forces at the contact line as shown in Figure 2-2, we can obtain the Young-Dupré equation [120].

\[
\cos \theta_v = \frac{\gamma_{s,v} - \gamma_{s,l}}{\gamma_{l,v}} \tag{2.1}
\]

where \(\gamma_{s,v}\), \(\gamma_{s,l}\) and \(\gamma_{l,v}\) represent the interfacial tensions of the solid-vapor, solid-
Figure 2-2: Balance of interfacial forces at a three phase contact line and definition of contact angle $\theta_y$

liquid and liquid-vapor interfaces respectively. $\theta_y$ refers to the angle formed by the liquid-vapor and liquid-solid surface tension lines and it is called Young’s contact angle. Since the surface tension force (Force/Length) can also be interpreted as surface energy per unit area (Force x Length/Area), we can obtain the above equation from energy arguments too. However, this equation is defined for ideal surfaces which are physically and chemically homogeneous. In reality, there are microscopic asperities even on surfaces which look smooth on the macroscale and there are small domain of chemical discontinuities depending the surface preparation. In order to account for this, Wenzel [112] and, Cassie and Baxter [10] came up with new models which accounted for topographical heterogeneity of surfaces and calculated the corresponding apparent contact angles depending on the wetting regime.

Wenzel predicted that the contact angle is dependent on the roughness of a given surface if the water drop impregnates the surface features. Roughness (r) is defined as the total surface area per unit project area of surface. Hence r is always greater than or equal to one.

$$\cos \theta_r = r \cos \theta_y$$  \hspace{1cm} (2.2)

Cassie however discovered that another state is possible where the drop could sit suspended on the asperities without impregnating them. The energy balance for this state gives the following relation.

$$\cos \theta_{cb} = f_{s,l} \cos \theta_y - f_{l,a}$$  \hspace{1cm} (2.3)
where $f_{s,l}$ and $f_{l,a}$ are the areas of the solid-liquid and liquid-air interfaces on an unit projected area of solid.

### 2.2 Hydrophilicity and Underwater Oleophobicity

With definitions of contact angles in place, the different wettability regimes on a solid surface can be studied using contact angle as a parameter. In general, a substrate is said to be hydrophilic if the contact angle of water on the substrate is $0 < \theta < 90^\circ$. It is said to be superhydrophilic if the water drop spreads on the surface forming a negligible contact angle (less than $10^\circ$). Similarly, a substrate is said to be oleophobic when the contact angle of oil is greater than $90^\circ$. Another parameter used to study wetting is the spreading coefficient $S$.

\[
S_{w,a} = \gamma_{s,a} - (\gamma_{s,w} + \gamma_{w,a})
\]

\[
S_{o,a} = \gamma_{s,a} - (\gamma_{s,o} + \gamma_{o,a})
\]

where $S_{w,a}$ is the spreading coefficient of water on solid in air medium and $S_{o,a}$ is the spreading coefficient of oil on solid in air medium. When $S > 0$, the liquid wets the surface completely and when $S < 0$, there is partial wetting or complete non-wetting of the liquid on the solid surface.

Figure 2-3 shows how the wettability of a solid surface can be tuned by modifying its surface energy relative to those of oil and water. A high surface energy solid ($\gamma_{s,a} \gg (\gamma_{s,w} + \gamma_{w,a})$) would tend to be wet by both water and oil i.e, the surface would be hydrophilic-oleophilic. This is generally observed for everyday materials like metals and glass. When the surface energy of a solid is extremely low ($\gamma_{s,a} \ll (\gamma_{s,w} + \gamma_{w,a})$), the surface would be hydrophobic-oleophobic in air. This is generally difficult to achieve unless the surface is functionalized with Fluorine or Chlorine groups like those in fluorodecyl POSS [61]. Similarly, an intermediate solid surface energy can give rise to hydrophobic-oleophilic surfaces like Teflon and other plastics. From the above description, it can be seen that there is no case where the
surface is hydrophilic-oleophobic in air. This case is difficult to achieve in general unless the surface is functionalized in some way to enhance polar interactions. Introducing surface groups which reorient themselves to attract water molecules like PEG groups [44] or cellulose [75] can create these kind of surfaces.

However, it is quite possible to achieve hydrophilic-oleophobic surfaces in an oil-water environment and this is termed as "Underwater oleophobicity". This phenomena was first reported by Jiang’s and Bhushan’s groups [42, 55] while studying oil repellency of fish scales underwater. The following sequence of equations describe how the underwater contact angle of oil can be derived in terms of the respective contact angles in air and interfacial tensions.

\[
\begin{align*}
\cos \theta_{w,a} &= \frac{\gamma_{s,a} - \gamma_{w,w}}{\gamma_{w,a}} \\
\cos \theta_{o,a} &= \frac{\gamma_{s,a} - \gamma_{s,o}}{\gamma_{o,a}} \\
\cos \theta_{o,w} &= \frac{\gamma_{s,w} - \gamma_{s,o}}{\gamma_{o,w}} \\
\cos \theta_{o,w} &= \frac{\gamma_{o,a} \cos \theta_{o,a} - \gamma_{w,a} \cos \theta_{w,a}}{\gamma_{o,w}}
\end{align*}
\] (2.4)

Figure 2-4 shows the various possible scenarios for the solid-water-oil interface and Figure 2-5 shows the graphical representation of Equation 2.4 assuming interfacial tensions of water-air, oil-air and water-oil to be 72 mN/m, 27 mN/m and 51 mN/m respectively. The yellow boxed region represents the currently accessible wettability.

Figure 2-3: The different water and oil wettabilities achievable by modifying surface energy of solid
regimes as the surface energy of solids practically possible today cannot produce contact angles beyond the box region for flat surfaces. The bottom-right quarter of the box represents the region of underwater superoleophobicity.

Thus, even if a material is amphiphilic in air it can be oleophobic underwater. A membrane coated with this kind of material can be used for oil-water separation as demonstrated by a number of studies in the recent years - TiO$_2$ [29, 124, 71, 31, 52], ZnO [103], Zeolite [111], Cu(OH)$_2$ [56, 121]. Figure 2-6 shows some of the oil-water separation demonstration using titania coatings. In order to understand the
mechanism behind the hydrophilic nature of titania, is it essential to understand the origin of its photocatalytic behavior as well.

Figure 2-6: Oil-water separation using titania-coated meshes exploiting underwater oleophobicity; (a) TiO₂ nanotube arrays in Ti mesh [70], (b) SWCNT/TiO₂ composite film [29], (c) LBL (silicate/TiO₂)₂₀ coated SS mesh [124], (d) uncoated mesh (left) and TiO₂ nanoparticles spray coated on SS mesh (right) [31]

**2.3 Photocatalytic Property of Titania**

The photocatalytic properties of TiO₂ arise from its semiconductor nature. The band gap of TiO₂ is about 3.2 eV and its excitation requires a light spectrum with frequencies in the ultraviolet (UV) region. When UV irradiation is incident upon TiO₂, the electrons in the valence band get excited to the conduction band and electron (e⁻) - hole (h⁺) pairs are created.
Photoexcitation: \( \text{TiO}_2 + h\nu \rightarrow e^- + h^+ \)

These electron-hole pairs help with oxidation and reduction reactions on the surface of TiO\(_2\) leading to photocatalysis [15][45].

There are a number pathways that can be taken after the electron-hole pairs are formed. Figure 2-7 is a schematic showing the reactions that take place on the surface and bulk of TiO\(_2\) in the presence of the appropriate exciting wavelength. The \( e^- \) and \( h^+ \) diffuse through the material and get trapped at surface trapping sites.

**Charge-carrier trapping of \( e^- \):** \( e^-_{CB} \rightarrow e^-_{TR} \)

**Charge-carrier trapping of \( h^+ \):** \( h^+_V \rightarrow h^+_R \)

where CB,TR and VB represent conduction band, trapped and valence band electrons/holes respectively. Here, the \( e^- \) can either react with acceptor molecules (path d) or recombine with holes to get to the ground state (path a).

**Electron-hole recombination:** \( e^-_{TR} + h^+_R \rightarrow e^-_{CB} + \text{heat} \)

**Photoexcited \( e^- \) scavenging:** \((O_2)_{ads} + e^- \rightarrow O_2^- \)

Similarly, the \( h^+ \) can react with donor molecules (path c) or can recombine with free trapped electrons (path a). Sometimes, electron-hole recombination can take place in the bulk too releasing heat in the process (path b).

**Oxidation of hydroxyls:** \( \text{OH}^- + h^+ \rightarrow \text{OH}^- \)

The hydroxyl radicals attack long chain organic molecules and break them into smaller molecules using a series of free radical initiation, propagation and termination reactions. A number of intermediate species like oxy- and peroxy- radicals are formed during the reaction which result in chain scission [80] of long chain organic molecules.

**Photodegradation by \( \text{OH}^- \):** \( \text{R-H} + \text{OH}^- \rightarrow \text{R}^- + \text{H}_2\text{O} \)
TiO$_2$ is called a catalyst because it provides a low energy pathway for reactions to proceed efficiently but does not get consumed in the reaction. Further, it is a photocatalyst since it acts as a catalyst only when photons of energy greater than or equal to the band gap strike the material. One of the major problems with using TiO$_2$ extensively in applications is that its large band gap requires light of wavelengths 400 nm or lower for excitation which means that natural sunlight will not be self-sufficient to have optimal efficiency (since UV constitutes only 7.6 % of the Solar Constant[35]). This issue can be overcome by extending the excitation wavelength to visible light range by various techniques like metal oxide doping and non-metal oxide doping [102].

Another factor that determines the efficiency of the catalyst is the electron-hole recombination rate (path a and b in Figure 2-7). Minimizing recombination of e$^-$-h$^+$ pairs can ensure better use of absorbed energy and the crystalline structure of TiO$_2$ plays an important role in this process. The most studied crystalline phases of titania are rutile and anatase of which the former is more thermodynamically stable. Figure 2-8 shows the structure of two major crystalline phases of TiO$_2$. The band gaps of anatase and rutile phases are 3.2 eV and 3.0 eV respectively [87] and it has been reported that anatase form is more photocatalytically active compared to the rutile form. A number of researchers have proposed reasons for the higher activity of

Figure 2-7: Possible pathways for the e$^-$-h$^+$ pairs on the TiO$_2$ surface and bulk after light excitation [28]
Figure 2-8: TiO₂ Crystal Structures [53]

anatase. Ahmed et al. [4] compared the activity of the single crystal anatase (101) surface to rutile (001),(100) and (110) surfaces and concluded that anatase (101) surface is the most photocatalytically active of them all. Since (101) is the most thermodynamically stable facet of the anatase phase, he concluded that the higher activity of anatase is due to the availability of high number of (101) faces. Other studies [57, 23] on the synthesis of anatase phase with exposed high energy (001) facets show that this facet can influence the photocatalytic properties more than the (101) facet. Recently, Luttrell et al. [60] attributed the higher photocatalytic activity of anatase TiO₂ films to charge carriers being excited at greater depths in the bulk. Zhang et al. [122] found that anatase’s indirect band gap (rutile has direct band gap) enhances the lifetime of the photogenerated e⁻-h⁺ pairs and the lighter effective mass of electrons and holes facilitates faster migration of charge carriers to the surface trap sites.

Apart from the crystalline phase, different structural designs of TiO₂ such as spherical nanoparticles, cylindrical nanotubes and planar nanosheets can contribute
uniquely towards different applications in terms of surface area to volume ratio, fabrication ease, adhesion to substrate and structural strength [67]. As discussed in the beginning of the chapter, titania also possesses superhydrophilic property under UV irradiation which is of interest for oil-water separation. The following section describes important qualitative and quantitative studies on superhydrophilicity of TiO₂ and the proposed mechanisms.

2.4 Titania and Hydrophilicity

Titanium dioxide converts from a hydrophilic to a superhydrophilic surface under UV irradiation. This was reported first by Wang et al. [105] and since then, this phenomena has been studied extensively by various groups with interest in anti-fogging and self-cleaning applications[54]. Figure 2-9a shows the induction of superhydrophilicity upon UV irradiation and the recovery under dark storage. Other inorganic oxides such as Zinc oxide, Vanadium oxide, Tungsten oxide etc have also been found to show switchable wettability towards water under UV irradiation [65]. The reason behind this phenomena has been under debate for many years and most of the proposed theories are divided between surface hydroxyl group formation upon UV irradiation and photocatalytic degradation of surface contaminating species. The various mechanisms are elaborated below-

**Removal of Organic Species**

A hydrophilic surface can be rendered hydrophobic by a thin layer of carbonaceous species on the surface. If this organic species is removed from the surface by some cleansing method, then the surface can be restored to its natural hydrophilic state. Therefore many studies on photo-induced wetting attributed the change in wettability to the inherent photocatalytic nature of the material. The claim was that any organic species on the surface of the substrate would be degraded in the presence of UV light and would render the surface clean and hydrophilic [82, 62, 126]. Upon storage in the dark or heat treatment [93], the surface regains its hydrophobicity due to the adsorption of organic species.
Figure 2-9: Photoinduced hydrophilicity on titania under UV irradiation and recovery under dark conditions; (a) Water spreads as a thin film on the TiO$_2$ surface under UV, maintaining transparency [105], (b) Water contact angle evolution with time on TiO$_2$ surface upon exposure to UV (top) and storage in the dark (bottom) in air (dashed line) and in oxygen atmosphere (solid line) [106].
The counter argument for this was that certain inorganic oxides like SrTiO$_3$ which exhibited photocatalytic activity did not show photoinduced hydrophilicity and vice versa [65]. Also, careful decontamination of TiO$_2$ and ZnO surfaces with NaOH solution did not induce superhydrophilicity [95]. These arguments led to the idea that the mechanisms must be different for photocatalysis and photo-induced hydrophilicity.

**Dissociative adsorption of water molecules**

Highfield and Grätzel [38] observed that presence of water vapor delayed the process of electron-hole recombination. Lo et al. [58] showed that the photogeneration of Ti$^{3+}$ species on TiO$_2$ was important for the chemisorption of O$_2$, H$_2$ and H$_2$O molecules on the (100) surface. Wang et al. [104] tested the effects of UV irradiation and heat treatment under vacuum and Argon environment to confirm that water vapor played an important role in the hydrophilicity conversion. All of these studies lead to the hypothesis of dissociative adsorption of water molecules (vapor or in solution) on photogenerated oxygen vacancies on the surface of the TiO$_2$ upon UV irradiation [95, 106, 96, 84]. It was also observed that upon storage in the dark or heat treatment, the surface is restored to its not so hydrophilic state by adsorbing oxygen molecules from atmosphere [114, 107, 9]. Wang et al. also proved that recovery in the dark in enhanced by the presence of oxygen as shown in Figure 2-9b. Figure 2-10a illustrates the mechanism of dissociative adsorption of water molecules on TiO$_2$ surface with and without oxygen defects. The following equations describe steps leading to the creation of oxygen vacancies.

**Photoexcitation:** $\text{TiO}_2 + h\nu \rightarrow e^- + h^+$

**Trapping of e^-:** $e^- + \text{Ti}^{4+} \rightarrow \text{Ti}^{3+}$

**Creation of O$_2$ vacancies:** $2h^+ + O_2^2- \rightarrow \frac{1}{2}O_2$

**Molecular adsorption of water molecules**

Some studies have reported the growth of multilayers of water molecules on TiO$_2$ surface with UV irradiation by molecular adsorption of water molecules without dissociation[72, 66] as shown in Figure 2-10b. Their argument is that if water is
Figure 2-10: Mechanism of (a) dissociative water adsorption on TiO$_2$ [110] surface without defects (top) and with oxygen vacancies (bottom) [46], (b) molecular water adsorption on TiO$_2$ surface (plausible structure based on NMR study) [72]

dissociatively adsorbed, the resulting hydroxyl groups must not be easily removed by oxygen exposure as seen in experiments. Henderson [36] and Kurtz [46] observed both dissociative and molecular adsorption at different conditions. Recently, Lee et al. [50] studied temporal growth dynamics of the water layer on TiO$_2$ under visible, near-infrared and UV light conditions and proved that the superwetting of titania is due to water-layer growth via delocalised surface electrons and "water wets water mechanism".

**Other mechanisms**

Some studies say that it is combination of both photocatalysis and water adsorption which leads to photo-induced wetting [33, 49]. Takeuchi [98] claims that the surface tension of H$_2$O clusters reduces due to desorption of water molecules from the TiO$_2$ surface by heating from the light source and causes further wetting. Rico et al. [81] say that different mechanisms come into play for photocatalysis (which is dependent on crystalline phase) and wetting (which is independent of crystalline...
phase) and that they cannot be directly correlated.

Although TiO$_2$ is amphiphilic (wettable by both oil and water) in air, it is underwater superoleophobic which has been exploited by many groups for achieving oil-water separation. Although, there are a number of quantitative studies on wetting of titania in air which can be used for anti-fogging applications, there have been no quantitative studies on wetting under oil environment which is the case in oil-water separation applications. Thus, there is a need for studying in-situ wetting of titania in liquid-liquid environments to understand self-cleaning capabilities of titania.

2.5 Study of In-situ wetting on titania

Early studies on TiO$_2$ were focused on proving that the water wettability on titania changed with UV illumination [95, 65, 106]. Some specifically studied the wetting properties of different faces of single crystalline titania such as (110), (100) etc under UV irradiation [109]. Sahoo et al. studied wetting kinetics on visible light active N$_2$ doped TiO$_2$ [82]. All of these studies were performed in air medium and Figure 2-11 shows the data obtained under UV irradiation in some of these studies.

There are a few studies which measure contact angles after exposure to water or organic contaminants. Sakai et al. [83] observed that the fluid friction on a surface coated with TiO$_2$ reduced under UV illumination (See Figure 2-11c). Nishimoto et al. studied the contact angle change on a oleic acid contaminated surface of TiO$_2$ in the presence of UV irradiation [70] and flowing water [71]. Sakai et al. [86] and Nishimoto [69] reported that the hydrophilicity induced by UV irradiation could be reversed by ultrasonication in pure water. Some of these are shown in Figure 2-12. Although these studies measure the change in wetting of water on TiO$_2$ flat surfaces, it is unclear in most of the studies if the surface was irradiated in-situ with the water drop already present or if the drop was placed on the surface after irradiation for the contact angle measurement. The kinetics could be greatly different between the two cases. Also, none of these studies were performed using an oil environment. In order to have self-cleaning membranes for oil-water separation, it is important to achieve
Figure 2-11: Evolution of water contact angle in air with time upon UV irradiation and storage in the dark; (a) UV light 0.1-50 mW/cm² (left) and dark storage (right) [95], (b) UV light 40 mW/cm² on [110] face (solid line) and [001] face (dashed line) [109], (c) UV light 2 mW/cm² (left) and dark storage (right) [83], (d) UV light 2.0 mW/cm² [65], (e) cos θ under sunlight 10 mW/cm² (left) and dark storage (right) [82]

photocatalytic cleaning in an oil-water environment. An in-situ study would mimic an actual application where both oil and water are present in the environment and UV light is irradiated under liquid medium for self-cleaning through photocatalysis.

Fujishima et al. reported detachment of oil from titania surface under water in the presence of UV as depicted in Figure 2-13a [27] and Gondal et al. [32] reported the wetting of water on TiO₂ under oil. Li et al. used hierarchical TiO₂ nanotubes for integration of oil-water separation, flow-through photocatalysis and self-cleaning [52] (See Figure 2-13b. However, all of these studies did not rigorously quantify the wetting behavior.

Besides quantification, very few studies have tried to model the wetting kinetics of TiO₂ films under UV irradiation. Sakai et al. obtained data for wetting of water on dipcoated anatase TiO₂ thin films in air and modeled the kinetics using inverse of contact angle as their main parameter as shown in Figure 2-14a but this did not have any physical significance [85]. Later, Seki et al. remodeled the same data using cosine of the contact angle as the main parameter as shown in Figure 2-14b [88]. This
Figure 2-12: (a) Reversing UV induced superhydrophilicity by ultrasonication [69] (b) UV induced superhydrophilicity on Titania surface under flowing water conditions [71] (c) Repeatability of contamination-UV recovery cycles on TiO₂ demonstrated using θ₀,we and θ₀,w [70]
Figure 2-13: Self cleaning of TiO$_2$; (a) Oil drop displaced by water under UV irradiation [27], (b) Integration of oil-water separation with UV flow-through photocatalysis on TiO$_2$ meshes [52].

Figure 2-14: Wetting kinetics on TiO$_2$; (a) Modeling using inverse of contact angle as a function of time [85], (b) Modeling using cosine of contact angle as a function of time (left) and rate constants as a function of UV intensity [88].

had some physical significance as the interfacial energies can be directly related to the cosine of contact angles using Young’s relation. They also gave a model for the dependence of the extracted rate constants as a function of UV intensity which was based on electron-hole pair generation and recombination kinetics (See Figure 2-14b). Later Sahoo et al. used the same model to in their work to explain water wetting on visible light active N$_2$ doped titania films [82].

Thus there is a lack of literature which both characterize the in-situ photo-active wetting on titania surfaces under oil-water environments and provide a model for the same. Most oil-water membrane separation happens in submerged environments and hence there is a need for studying wetting of titania in liquid-liquid environments to understand in-situ self-cleaning capabilities of titania for fouling recovery. This
work studies the recovery kinetics of TiO$_2$ nanoporous surfaces from oil fouling under oil-water environment in the presence of UV light but unlike other photocatalysis studies, it uses contact angle as a probe to study this phenomena. A relation between wetting and photocatalysis was developed by modeling the processes under dark and various UV intensities. While this work focuses on analyzing the kinetics of the wetting, further studies need to be conducted using spectroscopic methods to clarify the intrinsic mechanism of water wetting on titania surfaces.
Chapter 3

Experiment Section

In order to study the self-cleaning of titania, nanoporous films of titania were prepared using Layer by layer (LBL) assembly of TiO$_2$ nanoparticles and photo-induced wetting properties of these films were studied using continuous contact angle measurements on a goniometer in the presence of UV light. The following sections describe the procedures for sample preparation, characterization, contamination, UV light illumination and contact angle measurement.

3.1 Fabrication of Titania Surfaces

A number methods can be used to create both flat and nanostructured films of TiO$_2$ [13] including Sol-gel method, Sol method, Hydrothermal method, Chemical Vapor Deposition, Atomic Layer deposition, Electrodeposition, Direct oxidation method, Magnetron sputtering [99], layer by layer assembly etc. Some of these methods can be tuned to produce specific crystalline phase of TiO$_2$ by modifying the process conditions while some of them produce amorphous phase of TiO$_2$ which then needs to be annealed in appropriate conditions to get anatase or rutile phase. In order to analyze the effect of texture on the wetting of titania, flat and nanoporous films were fabricated. The flat surfaces were fabricated using Atomic Layer Deposition (ALD) technique and the nanoporous surfaces were fabricated using Layer-by-layer (LBL) self assembly of TiO$_2$ nanoparticles.
3.1.1 Preparation of nanoporous titania films

Layer by layer (LBL) deposition method was used to assemble TiO$_2$ nanoparticles onto flat substrates to generate nanoporous surfaces. LBL is a self-assembly technique which has been gaining attention over the last 1.5 decades [48, 11]. It is the process of sequential adsorption of oppositely charged species onto a substrate by electrostatic attraction in order to create uniformly deposited bilayers or multilayers of these species. The adsorbed species could be polyelectrolytes or inorganic nanoparticles/nanosheets/nanotubes etc and the method of substrate solution-contact can be dip coating or spray coating. Figure 3-1 shows the LBL process used for the deposition of titania nanoparticles. The detailed procedure followed for LBL assembly is described below-

**Substrate Preparation**

The films were deposited on glass (VWR Vistavision Microscope Slides) or silicon
substrates (2" Test Wafer, University WAFER ¹). After achieving uniform deposition on these substrates, the same deposition protocol was extended to metal or polymer substrates depending on the application. The glass/silicon substrates were first washed with DI water (Millipore De-ionized water 18 MΩ) and then sonicated in a soap solution (Alconox Powder Detergent) for 1 hour to remove organics and other contaminants on the surface. Then they were rinsed with DI water and sonicated in a 10% by weight Sodium hydroxide solution for 1 hour to strip off the remaining organic contaminants to expose the pristine surface. Finally, they were washed and stored in DI water to prevent any contamination from air. The substrates were removed from the water just prior to LBL deposition and treated in oxygen plasma to induce a mild negative charge on the surface. This negative charge is created because the Si-O-H bonds on the surface are broken by the bombardment of ions during the plasma treatment. Simultaneously, residual organic contaminants are also oxidized and removed. Thus, clean charged substrates were prepared for attracting the first layer of charged species in the LBL process.

**Dispersion Preparation**

The protocol followed for the fabrication of titania nanoparticle thin films was similar to the one used by Cohen et al. in their work on LBL TiO₂ for anti-fingerprint surfaces [17]. In this work, TiO₂ nanoparticles served as the negative species while a positive polyelectrolyte, Poly(allyamine Hydrochloride) (PAH) was used as the positive species.

1. **Positive species**: PAH was obtained in powder form (Sigma Aldrich, M.W. = 58,000) and dissolved in DI water (Millipore De-ionized water 18 MΩ) by using a magnetic stirrer. The pH of the solution was adjusted to 7.5 ± 0.1 using 0.1 M Sodium hydroxide solution (Sigma Aldrich²). It is essential to adjust the pH of both the nanoparticle and polymer solutions so that there is sufficient electrostatic attraction between the layers and optimal growth of the film.

¹Product No.:155125, P Type, B doped, <100> Orientation, 1-100 Ω-cm, Thickness 320-350 μm, SSP Polish
²Product No.:319481 FLUKA, Sodium hydroxide solution, volumetric, 0.1 M NaOH 0.1 N)
2. **Negative species**: Anatase Titanium dioxide nanoparticles were preferred for this work due to their higher photocatalytic activity. Commercially prepared concentrated Anatase TiO$_2$ nanoparticle dispersion was obtained (Svaya Nanotechnologies$^3$) and diluted down to 0.03% by wt. in DI water (Millipore De-ionized water 18 MΩ) by using a magnetic stirrer. The average particle size was quoted to be 20 ± 5 nm. The pH of this dispersion was adjusted to 9.0 ± 0.1 using 0.1 M Hydrochloric acid (Sigma Aldrich$^4$). The pH adjustment was important for the nanoparticle dispersion because the zeta potential of the dispersion must be away from the iso-electric point to prevent agglomeration of particles. The iso-electric point of TiO$_2$ nanoparticles is approximately between 5 and 7 [79][97] and this depends on the ionic strength of the solution and also the particle size. Similarly, rinse water solutions were prepared for both the cationic and anionic LBL solutions using DI water and their respective pH values were adjusted to 7.5 ± 0.2 and 9.0 ± 0.2 respectively.

3. **pH adjustment**: pH of newly prepared solutions take time for reaching equilibrium and incorrect readings may be obtained if not measured in the right way. Polyelectrolyte and nanoparticles were first well-dissolved/dispersed in aqueous medium before starting the pH adjustment. In order to adjust the pH, acid/base was added while stirring the solution and it was allowed to mix well. The pH reading was taken while stirring the solution at 200 rpm (substrate rotation speed used during the LBL dipping step) and it was taken multiple times to ensure that the reading was stabilized and that there was no drift over time. This process was repeated a couple of times (by adding acid or base) in order to get the pH close to the required value. It was preferred that pH be adjusted slowly to approach the required value rather than overshoot it because the addition of neutralizing acid/base causes formation of salts which could affect the growth rate of the films.

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$^3$Titanium dioxide nanoparticles (20 ± 5 nm diameter), 10% by wt. aqueous solution  
$^4$Product No.:94015 FLUKA, Hydrochloric acid solution, volumetric, 0.1 M HCl (0.1 N)
Dip coating

The substrates were dip-coated in the prepared LBL dispersions by using an automated dipcoating machine (Nanostrata Inc.). 8 beakers were used in total comprising of 1 cationic solution, 1 anionic solution and 3 rinse solutions for each. The dipping time in the cationic and anionic solutions were 10 min each with 30 s of drying between each layer. The dipping times in the rinse solutions were 2 min, 1 min and 1 min for each of the layers. The substrate was spun in all solutions and during drying steps as well. The drying steps helped in removing residual water from the substrate before beginning the deposition of every layer, thus avoiding cross-contamination.

Calcination

Since the LBL process used a polyelectrolyte for the intermediate layers between TiO₂ layers, it was necessary to remove this organic content because the polyelectrolyte layers made the coating hydrophobic while the final application needed hydrophilic coatings. In order to remove the polymer layer, samples were calcined (heat treated) in air at 400°C for 2 hours. Temperatures above 550°C cause the anatase phase to convert into rutile phase and this was not preferred.

3.1.2 Preparation of flat titania films

In order to have a comparison of the wetting behavior of the nanoporous films to a flat titania surface, Atomic Layer Deposition (ALD) was used to obtain smooth thin films of controlled thickness. The films were fabricated by CambridgeNanoTech (Waltham, MA 02453) according to the following specifications. The films were deposited on clean glass (Microscope slides) at 250 °C with target thickness of 100 nm.

3.2 Characterization of Fabricated Surfaces

The fabricated films were characterized for their thickness, morphology and titania phase using profilometry, Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD).
3.2.1 Nanoporous TiO$_2$ Surface

LBL process can be tuned to achieve a specific thickness of coating based on the number of bilayers deposited. This film growth characteristics is shown in Figure 3-2 and it was observed that the growth of film is approximately linear with respect to increase in the number of bilayers. It was independently verified that the removal of polymer from the film by calcination affects the film thickness by less than 10 nm for the range of thicknesses studied. The crystalline phase of the TiO$_2$ nanoparticles was anatase and remained so even after calcination at 400 °C as verified by XRD analysis shown in Figure B-1. Figure 3-3a shows both the top and cross-sectional views of the film which illustrate the nano-porosity of these films. Figure 3-4a shows the surface morphology of the nanoporous samples obtained through AFM and the surface roughness was found to be 15.1 µm. Samples with 30 bilayers of TiO$_2$/PAH were prepared and calcined for experiments with UV light. The average thickness of these calcined films was approximately 120 nm.

3.2.2 Flat TiO$_2$ Surface

The thickness of the flat ALD film was interpreted from the SEM. It was found to be approximately 100 nm. The micrographs of the sample in Figure 3-3b show that the deposition is uniform but has some non-uniform domains formed during the atomic
depositon process. Figure 3-4b shows the surface morphology of the uncalcined flat ALD samples obtained through AFM and the surface roughness is 7.6 μm. Although the roughness of the flat films were lower than that of nanoporous films, there were tiny domains on the flat surface which could act as pinning sites. Hence the wetting behavior of these films showed multiple pinning-depinning transitions (compared to smooth wetting on nanoporous films) which were unrepeatable. The films were also found to be amorphous in nature and conversion to anatase phase by annealing was not repeatable. Therefore, these films were finally not used for quantitative studies.

![Micrographs of (a)LBL (25 BL) and (b)ALD (100 nm) TiO₂ films](image)

**Figure 3-3**: Micrographs of (a)LBL (25 BL) and (b)ALD (100 nm) TiO₂ films

![Height profile obtained through AFM; (a) LBL TiO₂ (30 BL), (b) ALD TiO₂ (100nm)](image)

**Figure 3-4**: Height profile obtained through AFM; (a) LBL TiO₂ (30 BL), (b) ALD TiO₂ (100nm)
3.3 Contamination of TiO$_2$ coating

In order to observe the underwater/underoil self-cleaning effect of titania, it was necessary to contaminate the surface before the UV experiment. Some of the essential properties of the contaminant to conduct this study were immicibility with water and oil, stability under UV irradiation in the absence of titania, reproducibility of coating across samples, hydrophobic nature and ability of be degraded by titania in the presence of UV. Silanes were initially thought be ideal for this study. However, it was seen that although they satisfied most of the conditions they were difficult/inconsistent to break down under UV light in the presence of titania. This maybe due to the fact that silanes repelled water strongly and prevented it from reaching the nanoparticle surface [32]. Since photocatalysis requires the creation of hydroxyl species in-situ, the blocking of access to water prevented/slowed down the reaction process. Hence these were found to be ineffective for the study of wetting dynamics. On the other hand, pure alkane contamination allowed for partial wetting of the water on the surface and hence allowed for immediate reaction on the surface. Dodecane (anhydrous >99%, Sigma Aldrich) was chosen as the contaminant oil for these experiments.

The calcined samples were first washed in acetone, IPA/ethanol and dried in air. The samples were immersed in the model contaminant oil for 18-24 hours before water contact and UV exposure. Some of these substrates were sampled out at different times and water droplets of constant volume 3 $\mu$l were inserted on these surfaces under oil (dodecane) to observed the advancing contact angle. The advancing angles were observed to increase with the time of contamination and it is explained in detail in the next chapter.

The time of immersion was chosen to be 18-24 hours instead of greater than 24 hours because water drop starts rolling on a completely repelling surface and it was difficult to have control for contact angle studies. Also, a completely repelled water droplet did not wet the surface immediately after UV irradiation as the photocatalytic process is inhibited by the covering oil layer just as in silane contamination. Thus, in order to ensure that the drop can be pinned to the surface, the time of immersion
Figure 3-5: Water contact angle measured under oil (hexadecane) for ALD TiO$_2$ substrates immersed for different amounts of time was kept under 24 hours. A similar experiment was done for the flat amorphous ALD surfaces using hexadecane as the contaminant oil and it was observed that the advancing and receding contact angles saturated at 118° and 40° respectively (See Figure 3-5). The existence of a finite hysteresis even after long exposure explains why the receding contact angles were zero for the nanoporous surface.

3.4 Contact Angle and In-situ UV Exposure

In-situ measurements of liquid-liquid contact angle were performed using a quartz cell (1"x2"x2") on a goniometer stage (ramé-hart model 590-F1). High power density UV irradiation was provided through a fiber optic cable from a Mercury Vapor Short Arc UV lamp source (Omnicure S2000). Figure 3-6 shows a schematic of the setup where the sample is placed in the quartz cell and UV light is irradiated from the top.

It was chosen to irradiate the surface from the top in order to eliminate intensity losses in the light path from the source to the target surface. A small tubular cap was fabricated to prevent the liquid from touching the fiber optic cable wires. Since the light spectrum of the lamp source had some visible light component in the 400-450 nm
Figure 3-6: Experimental setup schematic: Water in oil contact angle imaging is performed on a goniometer using a quartz cell. Sample is placed inside the quartz cell and irradiated with UV light using a 5 mm diameter probe.

range (See Figure B-2), it interfered with the silhouette imaging on the goniometer which depended on strong back-lighting for clear resolution of droplet boundaries. In order to circumvent this problem, a UV Pass filter (Edmund Optics 46-081 - Filter Band U-360 12 MM Dia) was used at the outlet of the fiber optic cable to eliminate all wavelengths of light above 400 nm (See Figure B-3) which allowed for clear imaging. Figure 3-7 shows a picture of the setup where the UV light is being irradiated on a sample.

The distance between the UV filter and drop was 3 mm for all experiments. In order to know the intensity of UV at the surface of TiO$_2$, the source was calibrated in air environment (with the filter). Figure 3-8 shows the variation of absolute intensity of UV light in air. The intensities were found in the liquid environments by using attenuation coefficients of oil and water. The attenuation coefficients ($\lambda$) were found using a simple characterization experiment for air, water and oil. Figure 3-9 shows the decay of intensities under air, water and oil environments from which the attenuation coefficients were extracted. The attenuation coefficients of UV in water and dodecane
Figure 3-7: Experimental setup: The UV probe is inserted into the quartz cell to irradiate the sample with UV light. This configuration is imaged using a goniometer to obtain contact angle changes.

were found to be $1.24 \times 10^2 \text{ m}^{-1}$ and $1.06 \times 10^2 \text{ m}^{-1}$ respectively. This implies that 28% of UV is transmitted through 3 mm of water or oil to reach the substrate. This is much higher than the literature value ($\lambda_w = 2 \times 10^{-2} \text{ m}^{-1}$[18]) probably because the light beam is not exactly parallel (See Figure B-7). Here, the divergence of the beam is taken into account in the attenuation coefficient. Also, it seems like the attenuation coefficient of air is much larger. This maybe due to Fresnel losses from the visible light filter. Thus the intensity at the substrate for the water drop in oil experiments were calculated by the following formula.

$$I_{surface} = I_{peak}e^{-\lambda_ol}$$

(3.1)

where $l = 3 \text{ mm}$, $\lambda_o = 1.06 \times 10^2 \text{ m}^{-1}$ and $I_{peak}$ is calculated from Figure 3-8.

In UV irradiation experiments, contact angle was recorded for a few seconds before UV irradiation was started in order to ensure that the drop was stable prior to UV
Figure 3-8: UV source calibration: absolute intensities at various shutter openings. A linear fit was used to find intermediate intensities.

Figure 3-9: UV attenuation coefficients of air, water and dodecane calculated by fitting intensity data measured using a radiometer (inside a quartz cell) at various distances from the source.
exposure. The measurement was stopped after the contact angle drop was less than 0.05° s\(^{-1}\). 6 different intensities were used for the experiments. All the fits were performed using MATLAB. The outcome of these experiments is described in the next section and a simple model has been proposed to explain the observations.
Chapter 4

Results and Discussion

Titania is intrinsically hydrophilic and once the surface is wet by water, it is difficult to displace the water with oil which is why titania is oleophobic underwater. However, when the surface is exposed to some contamination by hydrocarbons, oil tends to stick to the surface of titania even in the presence of water and this leads to the hydrophilic surface becoming hydrophobic with time. This is where photocatalytic cleaning becomes important to recover the surface from contamination. Since the material is intrinsically hydrophilic, the contact angle of water is an indication of how clean the surface is. If the surface is pristine, the water would completely spread on the surface in the presence of oil but if there are contaminants the water would tend to bead up. The degree of beading up indicates the level of contamination. This study examines the evolution of contact angles of water on contaminated TiO$_2$ surfaces in oil environment under UV irradiation.

As a base experiment, contact angles were measured for both flat and nanoporous surfaces in air environment. As seen in Table 4.1, the contact angle of water and oil on the LBL surfaces is much lower than the same on flat TiO$_2$ surfaces due to the porous nature of the film.
Table 4.1: In-air contact angle measurements on the flat ALD and LBL titania films

<table>
<thead>
<tr>
<th>TiO₂ Surfaces</th>
<th>$\theta_{w,a}^{adv}$</th>
<th>$\theta_{o,a}^{adv}$</th>
<th>$\theta_{w,a}^{rec}$</th>
<th>$\theta_{o,a}^{rec}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LBL TiO₂ (Calcined)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Flat ALD Amorphous (Vacuum stored)</td>
<td>57</td>
<td>3</td>
<td>4</td>
<td>5</td>
</tr>
</tbody>
</table>

There were three reasons for performing ‘water drop in oil’ experiments instead of ‘water drop in air’ experiments.

- **Contaminant:** The oil itself acts as like a contaminant and its removal from the surface can be studied.

- **In-situ cleaning:** For application to oil-water separation, it would be ideal to have in-situ self-cleaning in an water-oil environment. Hence it is more useful to study kinetics of wetting on these surfaces under water-oil environment.

- **Uncertainties in air environment:** Water in air experiments are subject to the uncertainties which arise due to evaporation of water drop into the environment. Unless the humidity of the chamber is well-controlled these experiments are difficult to perform especially with a heat generating UV source. Also if an oil (like hexadecane/dodecane) is used as the contaminant, it tends to cloak the water drop in air.

Therefore, in order to study the self-cleaning properties of nanoporous titania films, LBL TiO₂ samples were contaminated with dodecane and irradiated with UV light in the presence of a water drop under oil environment to observe the fouling recovery of the surface. In order to measure the kinetics of wetting under contamination and photocatalysis, the contact angle of water drop under oil ($\theta_{w,o}$) was monitored both under dark condition (UV absent) and in the presence of UV light on various prepared samples. Under dark condition, the surface was observed to become increasingly non-wetting towards water as the time of contamination increased while under UV irradiation, the surface tended towards superhydrophilicity and oleophobicity.
4.1 Wettability change under oil contamination

The advancing contact angle of water $\theta_{w,o}$ on a clean TiO$_2$ surface was observed to be almost zero even after immersion under oil due to the intrinsic hydrophilicity of titania. But this angle was found to increase with increasing time of contamination as seen in 4-1. The corresponding receding contact angles were found to be 0° for all the times. It is interesting to note that the surface does not become repelling to water immediately after immersion under oil but instead takes finite time for it to change its wetting behavior. This means that there is some kinetics involved in the contamination process. When the surface is completely covered by adsorbed oil molecules, the contact angle reaches 180° i.e. water is completely repelled from the surface. When an oil molecule is adsorbed onto the surface, it is difficult for water to displace it even though titania is intrinsically hydrophilic.

Although it takes finite time for adsorption of oil onto the TiO$_2$ surface, this is not the case for water adsorption on a clean TiO$_2$ surface. If a clean surface is first immersed in water and an oil drop is inserted immediately over it, the surface is non-wetting towards oil because water adsorbs strongly onto the TiO$_2$ surface. This is why titania meshes impregnated with water are suitable for oil rejection in oil-water separation. In these studies, the TiO$_2$ mesh is generally impregnated with water before introducing the oil-water mixture. However, any kind of oil contact would destroy the hydrophilic property of the mesh.

4.2 Wetting under UV Irradiation

Water was found to preferentially wet a TiO$_2$ surface under UV light even in the presence of an oil background as seen in Figure 4-2. Figure 4-3 shows the evolution of the water contact angle and drop width with time of UV irradiation for a single intensity. The increasing width shows that the contact angle decrease is due to water drop spreading and not evaporation. When the intensity of UV light was increased, the rate of contact angle change also increased as seen in Figure 4-4. An interesting
observation here is that the timescale for contamination is much higher than the time scale for fouling recovery. While it take many hours to completely contaminate a surface, it takes only minutes to recover the hydrophilicity. This is useful in a real application where we want to minimize the ratio of recovery time with respect to fouling time.

The flat amorphous titania samples also showed similar behavior where the water wet the surface preferentially over oil but it had a lot of pinning-depinning transitions

Figure 4-2: Contact angle evolution with time for water drop immersed in dodecane environment on titania LBL sample (I = 160 mW/cm²)
Figure 4-3: Contact angle evolution with time for water drop immersed in dodecane environment on calcined titania LBL sample ($I = 160 \text{ mW/cm}^2$)

Figure 4-4: Contact angle of water in oil environment against time of UV irradiation at various intensities
4.3 Modeling Kinetics of Wetting of Water under Oil

In order to model the kinetics, we need to understand the various physicochemical processes taking place under UV light and dark (contamination) conditions. When the titania sample is immersed under oil, although the oil spreads on the surface instantly, it does not adsorb on the surface immediately [113]. There is an adsorption-desorption equilibrium between the bulk oil phase and the surface which causes the delay in adsorption. If a water drop is inserted before complete surface coverage, the water can partially wet the surface occupying the uncovered sites. The degree of partial wetting is dependent on the surface coverage of oil which is a function of time as seen in Figure 4-1. The reported $\theta_{w,o}$ angles are a measure of advancing contact angle on the LBL TiO$_2$ surface while the receding angles are always zero due
to penetration of water drop into the texture. When the surface is contaminated long enough \( t_{\text{contamination}} > 24 \text{ hrs} \), the water drop is completely repelled from the surface with an advancing contact angle of 180° and zero. Therefore the change in wettability under dark conditions can be explained by change in surface chemistry through adsorption of oil on the surface. In the presence of UV irradiation, it is observed that water preferentially wets over oil. While the mechanism of water wetting over oil could be photodegradation of adsorbed oil molecules or simply displacement of oil molecules by water molecules in the nanoporous layer, the ultimate effect of these two processes can be seen as creation of hydrophilic sites on a contaminated hydrophobic surface. Photodegradation of dodecane on TiO₂ in aqueous medium has been studied previously [76, 77]. The conditions under which the 'water drop in oil' experiments were performed were favorable for photocatalysis as well. Hence, the rates of wetting under UV were characterized by kinetics of titania photocatalysis.

The Langmuir-Hinshelwood (LH) mechanism [16] has been used to model heterogeneous photocatalytic degradation of organic contaminants on TiO₂ in many studies [63, 21, 64]. In a typical case, the reactant adsorbs onto the solid catalyst, the reaction takes place on the surface of the catalyst (in the presence of light of appropriate wavelength for photocatalysis) and the products detach from the catalyst surface allowing for new reactant to adsorb at the same site. The rates of degradation is therefore determined by the intrinsic reactivity of the photoactivated surface, the concentration of reacting species and the Langmuir adsorption-desorption equilibrium of the reactant on the catalyst. Since photocatalysis is expected to be the mechanism behind the water wetting, the LH mechanism was used to model the processes taking place in our experiments. Here, the important species in the reaction were recognized to be the contaminant \( (C) \), substrate \( (S) \) and the degradation products \( (P) \). Equation 4.1 represents a general equation in heterogeneous photocatalysis.

\[
S + C \xrightarrow{\text{c_\text{a}}} \xrightarrow{k_c} \xrightarrow{k_{-c}} \xrightarrow{k_{\text{sc}}}(S + P)
\]  

where \( k_c, k_{-c} \) and \( k_{\text{p}} \) are the adsorption, desorption and photocatalytic rate constants.
in the reaction. \( k_p \) is a function of light intensity while \( k_c \) and \( k_{-c} \) were assumed to be independent of the same. \( c_s \) and \( c_{sc} \) are the concentration of free sites and contaminant occupied sites on the substrate respectively.

The concentrations were calculated by assuming a Langmuir model for surface coverage of oil molecules on the substrate. In this model, the surface is assumed to be a two dimensional and comprising of a fixed number of sites, each of which can hold at most one molecule of adsorbent (monolayer coverage). It also assume that all sites are equivalent and that there are no interactions between the adsorbed molecules. In our case, the symbols 'S' and 'C' represent the substrate TiO\(_2\) and the contaminant dodecane respectively. Therefore there are two types of sites on the surface - clean site (S) and contaminated site (SC). Let the surface fraction of clean sites and contaminated sites be \( f_s \) and \( f_{sc} \) respectively. Then,

\[
f_s + f_{sc} = 1 \quad (4.2)
\]

It has been reported in literature that n-alkane adsorption on gold surface follows first order kinetics based on Langmuir adsorption model [113]. It has also been reported that dodecane degradation by TiO\(_2\) in UV in aqueous medium follows first order reaction kinetics [94, 78] and that it is irreversible. Therefore, first order kinetics was used to obtain the rate of change of concentration of surface species, ‘S’ and ‘SC’ during adsorption and photocatalysis in the titania-oil-water system. Zeroth order dependency was assumed with respect to the concentration of reactant bulk phase ‘C’ because the oil, dodecane was used in its pure form. Also, ‘C’ was held constant in all experiments. Thus, the surface fraction of hydrophobic sites was obtained as a function time of UV irradiation.

\[
\frac{d}{dt} c_{sc}(t) = k_c c_S - k_{-c} c_{sc} - k_p c_{sc} \quad (4.3)
\]

\[
\Rightarrow \frac{d}{dt} f_{sc}(t) = k_c f_s - k_{-c} f_{sc} - k_p f_{sc} \quad (4.4)
\]
Substituting Eqn. 4.2 and solving the first order differential equation,

\[ f_{sc}(t) = \frac{k_c}{k_c + k_{-c} + k_p} - \left( \frac{k_c}{k_c + k_{-c} + k_p} - f_{sc}(0) \right) e^{-(k_c + k_{-c} + k_p)t} \]  (4.5)

Since the surface species were not directly monitored in our experiments, we needed to relate the wetting data to the surface composition. Although contact angle was the measured parameter during the water drop-in-oil UV wetting experiments, it did not directly relate to any physical phenomena. Its cosine however could be related to the interfacial energies of the surface, liquid and the medium assuming topographical and chemical homogeneity during equilibrium and it is given by Equation 4.6. This was also done in Seki’s analysis[88] while characterizing UV induced wetting of water on titania in air.

\[ \cos \theta_{w,o} = \frac{\gamma_{s,o} - \gamma_{s,w}}{\gamma_{w,o}} \]  (4.6)

For a composite surface, the effective contact angle was derived by Cassie using surface energies of each component [10]. Thus knowing the surface density of the individual species on TiO₂, we can find the effective contact angle on such a chemically heterogeneous surface by using the Cassie-Baxter equation.

\[ \cos \theta_{w,o}^{eff} = \sum_{i=1}^{n} f_i \cos \theta_{w,o}^i \]  (4.7)

where \( \theta_{w,o}^{eff}, f_i \) and \( \theta^i \) are the effective contact angle on composite surface, surface fractions of component ‘i’ and contact angle on component ‘i’ respectively. It is important to note that \( \theta_{w,o}^i \) is the effective contact angle of water under oil at each component ‘i’. In the TiO₂-water-oil system, the hydrophilic sites are bare TiO₂ sites (S) and the hydrophobic sites are TiO₂ covered by a monolayer of oil contaminant (SC). The contact angles of water under oil on each of sites are assumed to be 0° and 180° respectively since the bare titania is superhydrophilic and oil covered titania is completely water repelling.
\[
\cos \theta_{w,o}^{eff} = f_s \cos \theta_{w,o}^{a} + f_{sc} \cos \theta_{w,o}^{sc}
\]  \hspace{1cm} (4.8)

\[
\Rightarrow \cos \theta_{w,o}^{eff} = f_s \cos(0^\circ) + f_{sc} \cos(180^\circ)
\]  \hspace{1cm} (4.9)

\[
\cos \theta_{w,o}^{eff} = 1 - 2f_{sc}
\]  \hspace{1cm} (4.10)

Thus we now have a relation between the measured parameter, \( \theta_{w,o}^{eff} \) and surface species concentrations. Assuming quasistatic processes under contamination and UV conditions, the cosine of the contact angle was obtained as function of time of contamination and UV irradiation by substituting equation 4.5 into 4.10. We call this the Langmuir Hinshelwood Cassie Baxter Young (LHCBY) relation. It can be seen that the variation of cosine of the contact angle with time follows an exponential behavior.

\[
\cos \theta_{w,o}^{eff} = 1 - 2 \left[ \frac{k_c}{k_c + k_{-c} + k_p} \left( \frac{k_c}{k_c + k_{-c} + k_p} - f_{SC}(0) \right) e^{-(k_c + k_{-c} + k_p)t} \right]
\]  \hspace{1cm} (4.11)

Figure 4-6 and Figure 4-7 show the cosines of the contact angles of water in oil plotted against the time of contamination and UV irradiation respectively. A range of UV intensities were tested to observe the effects of UV intensity on the kinetics of wetting. The LHCBY model was fit to this data to obtain the rate constants \( k_c \) and \( k_{-c} \) under dark conditions and \( k_p \) for each UV intensity. The adsorption and desorption rate constants were found to be \( 3.54 \times 10^{-5} \) s\(^{-1}\) and \( 3.58 \times 10^{-7} \) s\(^{-1}\) respectively. Thus the adsorption rate constant was about 100 times greater than the desorption rate constant implying that the system tended towards complete surface coverage of contaminant at equilibrium. Although it has been observed that the Langmuir adsorption constants are dependent on the UV illumination conditions, it has been assumed to be equal to the obtained values from dark conditions. The initial surface fraction of hydrophobic sites was calculated from the initial contact angle (before UV illumination) before each UV experiment. An assumption in these experiments is that the water adsorption on bare titania is quick and irreversible.
Contamination in dodecane

$\cos(\theta_{w,o})$

$t_{\text{contamination}}$ (min)

Figure 4-6: Evolution of water-in-oil contact angle with time of immersion in dodecane along with the fit

This means that a water molecule which comes in contact with bare titania which was UV irradiated, would immediately bond to the surface due to photoinduced superhydrophilicity.

The photocatalysis rate constants $k_p$ were found to increase with UV light intensity. Effect of UV light intensity on rate of photocatalytic degradation has been studied in literature and it has been observed that the rate of photocatalytic reaction is a conditional function of UV intensity ($I$) [64, 21].

$$r \propto \begin{cases} 
I, & \text{at low intensities} \\
I^{0.5}, & \text{at high intensities} \\
I^0, & \text{at very high intensities}
\end{cases} \quad (4.12)$$

At low intensities, the rate is proportional to $I$ as is limited by the photon incidence rate but at high intensities the rate is proportional to $I^{1/2}$ as $e^- – h^+$ pair recombination starts to decrease the efficiency of the reaction. The transition between these two regimes is approximately around 1-10 mW/cm$^2$ [21]. Since the intensities used were much higher that this limit, the rates $k_p$ were found to follow the $I^{1/2}$ power law as
Figure 4-7: Cosine of contact angle of water in oil environment against time of UV irradiation at various intensities shown in Figure 4-8. This is interesting as we can see that photoinduced wetting also follows kinetics similar to that of photocatalysis. This is a useful as findings in one field can be interchangeably applied to the other in future.

4.4 Applications

In the situations where oil-water separation needs to be done with water rich emulsions, it more useful to have kinetics of oil drop wetting on titania underwater. Figure 4-9 shows an oil drop detaching from a contaminated titania surface under UV irradiation in water environment. The oil drop beads up from the surface and saturates at a high contact angle as shown in Figure 4-10. We observe kinetics similar to water-in-oil experiments in the plot of contact angle $\theta_{o,w}^{eff}$ verses time. Although the drop does not detach from the surface on its own, a slight mechanical vibration causes the drop to detach from the mesh surface due to the weakened adhesion at contact line. In order to simulate a practical situation, we fouled an LBL coated ti-
Figure 4-8: First order wetting rate constants \( (k_p) \) vs. UV intensity. \( I^{1/2} \) power law fit was applied to the data in accordance with photocatalysis studies at high intensities.

Figure 4-9: Contact angle evolution with time for oil drop immersed in water environment on calcined titania LBL sample \( (I = 240 \text{ mW/cm}^2) \)

titania stainless steel mesh (pore size 70 \( \mu \text{m} \)) with dodecane and observed its recovery under UV irradiation under water. In Figure 4-11, we can see that the oil dewets from the pores and beads up on the surface. Again, the oil drop leaves the surface upon obtaining sufficient buoyancy or upon small mechanical vibration. This can be applied for in-situ photocatalytic cleaning of membranes coated with titania under water. Other applications that can take advantage of this competitive oil-water wetting include precise control oil-water drop shape on a surface, water drop coalescence on a surface, directional transport of oil-water across membrane etc.
Figure 4-10: Evolution of oil-in-water contact angle with time of UV irradiation ($I = 240 \text{ mW/cm}^2$)

Figure 4-11: Oil beading up from a contaminated mesh under UV irradiation ($I = 300 \text{ mW/cm}^2$) in water environment
This work has quantified and modeled the fouling and recovery kinetics of titanium dioxide nanoporous surfaces under UV irradiation. The main findings of this study are as follows. Although titania is hydrophilic and underwater oleophobic by nature, this property is masked after fouling by oil. The intrinsic hydrophilicity can be recovered by UV irradiation as water preferentially wets titania over oil under UV light. The photoinduced wetting changes are much faster than the fouling-induced wetting changes and hence UV light can be an effective method for fouling recovery. The kinetics of wetting were modeled by using a combination of the first order Langmuir-Hinshelwood equation and Cassie-Baxter equation. The analysis showed that the rates of photoinduced wetting increased with UV intensity in a non-linear fashion similar to those in photocatalysis studies. It was also demonstrated that this fouling recovery from oil can be extended to mesh like structures coated with nanoporous titanium dioxide which have application in membrane oil-water separation.

This work has helped us understand the photocatalytic wetting behavior of titania in an water-oil environment but at the same time has also raised a number of questions that need to be answered by future studies. For example, these experiments were performed on Layer-by-layer assembled TiO$_2$ nanoparticle surfaces and hence the assumptions of Cassie-Baxter equation were justified. However, further studies need to be done on flat titanium dioxide surfaces to obtain information on the evolution of Young’s contact angle of water drop in oil environment under UV
irradiation. Although photocatalysis has been proposed as the main mechanism for wetting, further experiments need to be conducted to find the exact mechanism of water wetting in the presence of oil. UV attenuation losses through the liquid medium need to be minimized by designing innovative light delivery systems. UV light can be eliminated by using visible light active nanoparticles/surfaces instead.

By connecting the two surface phenomena - photocatalysis and wetting, this work will enable us to understand the less understood interfacial wetting behavior of surfaces with the help of well-known photocatalysis mechanisms. While this work focuses specifically on the material titanium dioxide, concepts demonstrated here can be extended to many other catalyst and liquid interface systems and hence has great potential for further research and applications.
Appendix A

Tables
Appendix B

Figures

Figure B-1: X-ray diffraction of the calcined LBL TiO$_2$ film on a glass slide. Anatase phase was confirmed.
Figure B-2: Spectra of the Omnicure S2000 Lamp. Courtesy: Omnicure S2000 Brochure

Figure B-3: UV Pass Filter
Figure B-4: UV source calibration: Variation of absolute intensity at the immediate output of the probe with respect to the percentage shutter opening.

Figure B-5: UV source calibration: Variation of the absolute intensity at a point on the central axis with respect to percentage shutter opening (S.O).
Figure B-6: UV source calibration: Variation of the absolute intensity on the center axis at various shutter openings

Figure B-7: UV source calibration: Radial variation of the absolute intensity at a constant center distance of 4 mm from the optical filter
Bibliography


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