Mesoporous Titanium Dioxide and Silica Materials and its High Application in Photocatalytic Performance: A Review

Dinh Cung Tien Nguyen, Chang Sung Lim and Won-Chun Oh[1]

Department of Advanced Materials Science & Engineering, Hanseo University, Seosan, Chungnam, Korea, 356-706

Abstract: Even though heterogeneous photocatalysis appeared in many forms, photodegradation of organic pollutants has recently been the most widely investigated. By far, titanium dioxide has played a much larger role in this scenario compared to other semiconductor photocatalysts due to its cost effectiveness, inert nature and photostability. Silicate mesoporous materials have received widespread interest because of their potential applications as supports for catalysis, separation, selective adsorption, novel functional materials, and use as hosts to confine guest molecules, due to their extremely high surface areas combined with large and uniform pore sizes. Over time a constant demand has developed for larger pores with well-defined pore structures. The structure, composition, and pore size of these materials can be tailored during synthesis by variation of the reactant stoichiometry, the nature of the surfactant molecule, the auxiliary chemicals, the reaction conditions, or by post synthesis functionalization techniques. This review focuses mainly on a concise overview of silicate mesoporous materials together with their applications and an overview of the dramatic trend in the use of the TiO_2 photocatalyst for remediation and decontamination of wastewater, report the recent work done, important achievements and problems.

Keywords: Self-assembly, Graphene based composite, photodegradation, TiO2, SiO_2.

1. Introduction

Organic chemicals which may be present as pollutants in wastewater effluents from industrial or domestic sources must be removed or destroyed before the water can be discharged into the environment. Besides, dyes and pigments play an important role in the development of various industries, such as the paper, food, plastics, leather, textile, and cosmetic industries. However, the excessive use of dyes causes serious harm to the health of human, flora, and fauna as well as the environment, resulting in the presence of undesirable organics in nature.[2,3] Therefore, contamination of water and air with harmful organic compounds, especially resulting from industries, remains a major pollution problem, since they are often responsible for disruption of ecosystems as well as illness in

the human body. Current environmental regulations require treatment and stabilization of these hazardous constituents, and are anticipated to become more stringent in the future. To develop clean and safe chemical processes and materials contributing to this issue in accordance with the principles of green chemistry is our obligation, which should be undertaken with great urgency.[4] The increased public concern over these environmental pollutants has prompted the need to develop effective removal operations, which are known as advanced oxidation processes (AOPs).[5] These processes are based on the production of hydroxyl radicals (OH•) as strong oxidizing agents to mineralize the organic pollutants.[6] Among the various AOPs, semiconductor mediated photocatalysis has been accorded great significance in recent times due to its potential to mineralize a wide range of recalcitrant organic pollutants at ambient temperature and pressures into harmless substances.[7,8,9]

Mesoporous materials have attracted considerable interest for their applications as catalysts, gas separators, sensors, and energy converters.[10] The photocatalytic oxidation of organic pollutants in waterand airas anadvanced oxidationprocess has been proved to be an effective technique for environmental remediation.[11] To develop efficient photocatalytic systems, high-quality semiconductor-based materials have been actively studied in recent years.[12,13] Titanium dioxide is the most important semiconductor with large potential in photocatalysis, solar cells, photochromism, sensing, and other applications in nanothecnology.[14,15,16,17,18,19] For many of these applications, the porosity, surface area, structure, crystal phase, particle size, and presence of dopants are factors that influence dramatically the activity and performance of titanium dioxide.[20,21,22,23] For its practical application, it is very important to improve the efficiency of titanium dioxide -based photocatalysts because titanium dioxide with high photocatalytic activity usually has a relatively lower surface area and low pore volume, which leads to its low adsorption capability of organic pollutants.[24] This limits their practical application because in the dark or under the irradiation of weak light, these titanium dioxide photocatalysts could not efficiently decrease the concentration of pollutants in air or water for later irradiation.[25] Therefore, a photocatalyst with both high photocatalytic activity and adsorption capability is desirable.[26] To overcome this problem, two strategies have been developed: one is the synthesis of mesoporous titanium dioxide with high specific surface area and another is the combination of titanium dioxide materials with absorbent.[27]

Ordered mesoporous silica (SiO_2) have become popular materials with potential applications in numerous fields, including ceramics, catalysts, pharmaceutical products, electronic packaging, photonic and chemical–mechanical polishing due to their ordered mesostructure, large surface area, flexible pore size, and thermal stability.[28,29] Due to such advantages, silica nanoparticles (SiO_2) have been considered to have be photocatalyst with higher efficiency than TiO_2.[30,31,32] With this reason, Kexin Li *et al* reported the photocatalytic activity of TiO_2 was greatly improved by introducing graphene and silica in the presence of the non-ionic surfactant P123 towards atrazine degradation under simulated sunlight irradiation.[33] Tetraethyl orthosilicate (TEOS) is considered to be one of the best silica precursors. The TEOS/EtOH, titanium tetrachloride/titanium

tetraisopropoxide/ethanol ($TiCl_4$/TTIP/EtOH), and graphene/EtOH/H_2O solutions were successively added dropwise into the P123/HCl solution. After stirring the resulting mixture for 24 h at room temperature, a semi-transparent sol was obtained. From that to form the ordered mesoporous graphene–titanium dioxide /silica composites. Its photocatalytic activity was higher than that of pure TiO_2, and the degradation of atrazine reached near to 90% after Xe lamp irradiation for 3 h. Follow to the authors, the excellent photocatalytic activity of the graphene and silica co-doped titanium dioxide composites with ordered mesostructure is primarily attributed to three reasons. First, the incorporation of graphene can result in enhanced quantum efficiency, thus contributing to the electron-accepting and electron-transporting properties of graphene.[34,35,36] On the other hand, the band gap of the graphene-doped composites narrowed compared with that of pure TiO_2 or TiO_2/SiO_2, which had a positive effect by increasing the photocatalytic activity. Last reason is the ordered mesoporous structure and perfect textural properties played important roles in the photocatalytic activity of the photocatalysts.

On the other hand, graphene is a flat monolayer of carbon atoms with perfect sp^2-hybridized two-dimensional carbon structure.[37] Its fascinating high conductivity, superior electron mobility, extremely high specific surface area and easy functionalization make graphene a good substrate to produce graphene-based composites.[38] Especially, graphene–metal oxide composites have attracted extensive attention for their potential applications in environmental and energy-related areas.[39,40,41,42,43] The development of graphene-based composites provides an important milestone to improve the application performance of metal oxide nanomaterials in different fields such as energy harvesting, conversion and storage devices, photovoltaic devices, photocatalysis, etc., because the hybrids have versatile and tailor-made properties with performances superior to those of the individual oxide nanomaterials.[44,45,46,47] Considerable efforts of decorating graphene with metal oxides NPs have recently been reported. To date, various kinds of metal oxides have been synthesized and supported on graphene, which include TiO_2, ZnO, SnO_2, MnO_2, Co_3O_4, Fe_3O_4, Fe_2O_3, NiO, Cu_2O, etc.[48,49,50] To this end, many excellent studies have been published on the anchoring of the photocatalyst particles onto supports that are readily removable. As a response, several workers have coated photocatalysts onto a variety of surfaces, such as glass, silica gel, metal, ceramics, polymer, thin films, fibres, zeolite, alumina clays, activated carbon, cellulose, reactor walls and others.[51,52,53,54,55,56,57]

2. Developments of Porous Materials

Zeolites and porous silicas take their place among the important porous materials for their wide applications in separation and catalysis. Zeolites are members of a large family of crystalline alumino silicates. They were first discovered in 1756 by the Swedish scientist Cronstedt when an unidentified silicate mineral was subjected to heat; these strange minerals were found to bubble and froth, releasing bursts of steam. In the nineteenth century, zeolite minerals began to be well documented although there was a lack of general scientific interest. The term molecular sieve was derived from McBain in 1932 when he found that chabazite, a mineral, had a property of selective adsorption of molecules smaller

than 5 Å in diameter.[58] In other words, molecular sieves retain the particles that fit within the channels and let the larger ones pass through. The term molecular sieves are used to describe a class of materials that exhibit selective sorption properties (i.e., that can separate a class of mixtures based on molecular size and shape). However, Barrer and coworkers studied the sorptive properties of chabazite and other porous minerals and reported that nitrogen and oxygen could be separated using a zeolite that had been treated to provide the necessary shape selectivity for discrimination between the molecular dimensions.[59] Later, synthetic zeolites began to be used in large amounts to produce pure oxygen from air. Between 1949 and 1954, Breck and coworkers were able to synthesize many new zeolites (types A, X, and Y) which were produced in large scale to be used for the separation and purification of small molecules.[60] Since then, the nomenclature of this kind of porous material has become universal. The success of synthesizingcrystalline aluminosilicates, the emergence of the new family of aluminophosphates and silicoaluminophosphates, made the concept of zeolites and molecular sieves more complicated.[61,62]

The small pore entrances (diameters) in zeolites (e.g., 0.4 nm in zeolite A) were attractive for commercial applications because they provided the opportunity for selective adsorption based on small differences in the size of gaseous molecules. In addition, these materials caught the attention of scientists who were interested in catalysis. At the beginning, the oil industry was reluctant to accept the idea, since it was thought that these materials had pores too small to be of interest for cracking activity (break down of long hydrocarbon molecules into gasoline and other useful products).[63] The zeolite marketing prospects were improved when Breck and coworkers showed rare earth-containing zeolites had the ability to handle cracking activity. There has been, however, a continually growing interest in expanding the pore sizes of zeotype materials from the micropore region to mesopore region in response to the increasing demands of both industrial and fundamental studies.[64] Examples are the separation of heavy metal ions, the separation and selective adsorption of large organic molecules from waste water, the formation of a supramolecular assembly of molecular arrays, the encapsulation of metal complexes in the frameworks, and the introduction of nanometer particles into zeolites and molecular sieves for electronic and optical applications.[65] Therefore, to meet these demands, numerous experiments to create zeotype materials with pore diameters larger than those of the traditional zeolites were carried out. Since it was thought that most of the organic templates used to synthesize zeolites affect the gel chemistry by filling the voids in the growing porous solid, many of these attempts used larger templates. It was not until 1982 that success was achieved by changing the synthesis gel compositions when the first so-called ultra large pore molecular sieve, which contains 14-membered rings, was discovered.[66] Indeed, this not only broke the deadlock of the traditional viewpoint that zeolite molecular sieves could not be constructed with more than 12-membered rings, but also stimulated further investigations into other ultra large pore molecular sieves, such as VPI-5 with an 18-tetrahedral ring opening, cloverite, and JDF-20.[67] While these zeolites attracted much attention and were of scientific importance, they have not found any significant applications because of their inherently poor stability, weak acidity, or small pore size (0.8–1.3 nm). Therefore, they seem to be inferior compared to pillared layered clays.[68]

Yanagisawa *et al.* described in the early 1990s the synthesis of mesoporous materials that have characteristics like that of MCM-41.[69] Their preparation method is based on the intercalation of long-chain (typically C-16) alkyltrimethylammonium cations, into the layered silicate kanemite, followed by calcination to remove the organic species, which is later called surfactant, yielding a mesoporous material. The silicate layers condensed to form a three-dimensional structure with nanoscale pores.[70] Si solid-state NMR spectroscopy indicated that many the incompletely condensed silica site $Si(OSi)_3(OH)$ (Q3) species were converted to the completely condensed silica site $Si(OSi)_4$(Q4) species during the intercalation and calcination processes. The X-ray powder diffraction gave only an uninformative peak centered at extremely low angles. Unfortunately, there were no further characterization data available which lead to disregard of the results of Yanagisawa *et al.*

In 1992, researchers at Mobil Corporation discovered the M41S family of silicate/ aluminosilicate mesoporous molecular sieves with exceptionally large uniform pore structures and later they were produced at Mobil Corporation Laboratories.[71] The discovery resulted in a worldwide resurgence in this area. The synthesis of this family of mesoporous materials is based on the combination of two major sciences, sol-gel science and surfactant (templating) science. The template agent used is no longer a single, solvated organic molecule or metal ion, but rather a self-assembled surfactant molecular array as suggested initially. Three different mesophases in this family have been identified, i.e., lamellar (MCM-50), hexagonal (MCM-41), and cubic (MCM-48) phases.[72] The hexagonal mesophase, denoted as MCM-41, possesses highly regular arrays of uniform-sized channels whose diameters are in the range of 15–100 Å depending on the templates used, the addition of auxiliary organic compounds, and the reaction parameters. The pores of this novel material are nearly as regular as zeolites; however, they are considerably larger than those present in crystalline materials such as zeolites, thus offering new opportunities for applications in catalysis, chemical separation, adsorption media, and advanced composite materials. MCM-41 has been investigated extensively because the other members in this family are either thermally unstable or difficult to obtain.[73]

In 1998, prominent research produced another type of hexagonal array of pores namely Santa Barbara Amorphous no 1 (SBA-15).[74] SBA-15 showed larger pore size from 4.6 to 30 nm and discovery of this type of material was a research gambit in the field of mesoporous material development.[75] This SBA-15 mesoporous material has not only shown larger pores, but also thermal, mechanical and chemical resistance properties and that makes it a preferable choice for use as a catalyst.[76] The formation of ordered hexagonal SBA-15 with uniform pores up to 30 nm was synthesized using amphiphilic triblock copolymers in strong acidic media was reported in the literature.[77] A detailed review on types, synthesis, and applications towards Biorefinery Production of this SBA 15 mesoporous material has already been published in the literature.[78]

3. Application of These Materials in Environmental Pollution Control Processes

Contamination of water streams by transition metals, heavy metals, and radioactive compounds (e.g., nickel, copper, lead, mercury, cadmium, uranium, and thorium) remains

a concern in the field of environmental remediation. These materials enter the environment through a variety of avenues that include: mining, nuclear power plants, and industrial processing plants. Furthermore, some natural waters contain naturally high concentration levels of metals.[79] The presence of even low concentrations (ppb) of some heavy metals or radioactive substrates in natural water systems can have a harmful effect on both wildlife and humans. However, at these low concentrations of metal ions the sample often requires pre-concentration before analysis can be undertaken. Adsorption onto solid substrates (e.g., activated carbons, zeolites, aluminas, and silicas) provides one of the most effective means for adsorption, separation and removal of trace pollutants (heavy metal ions, radioactive compounds, etc.) from aqueous streams.[80] A wide variety of novel materials can be prepared by the chemical modification of ordered mesoporous materials, since numerous organic and inorganic functionalities can be used for this purpose. In addition to their use in chromatographic separations, these materials have been increasingly used as heterogeneous catalysts in liquid phase organic reactions. It is their characteristics, such as viability and environmental safety, which makes them alternatives to traditional absorbent materials such as activated charcoal and zeolites. Their use as efficient materials for the selective adsorption and separation, and high capacity uptake of trace metals from aqueous systems is due to their unique characteristics such as high surface area, large pore size, and presence of reactive groups on the surfaces.[81]

Many of the more recent advances have been focused on the use of modified silicas for clean technology. One area of research in which modified silicas are used for clean technology applications, other than catalysis, is in the adsorption, separation, removal, and analysis of trace components in aqueous systems. A wide variety of analytical techniques have been developed to separate and determine trace metal concentrations in natural water. Several methods have been employed in the adsorption and separation of metal ions from aqueous solutions, such as activated charcoal, zeolites, clays, solvent extraction using a chelating agent and the use of polymeric resins. These methods suffer from a number of drawbacks. The use of activated charcoal, zeolites and clays showed low loading capacities and relatively small metal ion binding constants. However, the use of chelating reagents (i.e., iminodiacetate resin) is time consuming, whereas organic resins possess low surface area and low mechanical stabilities, and the time taken for the metal ion to be complexed, can be of the order of hours. Conventional methods such as precipitation are unfavorable especially when dealing with large volumes of matter which contain heavy metal ions in low concentration. Typically, these ions are precipitated as hydrated metal oxides or hydroxides or sulfides using calcium oxide. Precipitation is accompanied by flocculation or coagulation, and one major problem is the formation of large amounts of sediments containing heavy metal ions. In addition, these methods are often unselective towards the metal being analyzed, with interference from alkaline earth metals being particularly problematic. In recent years, the use of modified mesoporous silica in the pre-concentration and separation of trace metal ions has been investigated.[82] Modified silica gels offer the advantages of high surface areas and increased chemical and mechanical stability.[83] Nitrogen-containing organic groups have been shown selectively to bind to first row transition metals from solution. Thus, Marshall and Mottola

prepared an immobilized quinolin-8-ol complex for the pre-concentration and separation of copper (II) ions. By varying the pH of the solution, a variety of transition metal (II) ions could be extracted selectively, even in the presence of alkali and alkaline earth metal ions. This makes the material useful for separation and analysis of trace metals in natural waters where alkaline earth metals are to be expected.[84] There are factors that affect the adsorption and selectivity such as the pH and ionic strength of the water medium, the concentration ratio of the metal ion to the adsorbent, and the agitation time.[85] However, the unitary silica framework of siliceous MCM-41 limits its practical application, especially in catalysis owing to the lack of active sites. Therefore, great efforts have been focused on surface modification to expand the area of applications and many elements have been doped into the wall of MCM-41 including Al, Fe, Zn, Ti, V, Cu, Ni, W and Mn[86] Many researches have been focused on manganese oxides, owing to their ion-changing, molecular adsorption, catalytic, and magnetic properties and use as catalysts for environmental treatment of water.[87] The detailed application of mesoporous materials as host-guest chemistry, environmental technology, adsorption, chemical sensors and electrode catalysis or adsorption is broadly reported in the published paper.[88]

4. Mechanism of photocatalysis

The mechanisms of photocatalytic oxidation of organic compounds at particulate semiconductor substances involve multiple processes. Initially, an electron–hole (e^-/h^+) pair is generated in the semiconductor particles when radiation of energy greater than or equal to the band gap is shone on the surface.[89] Electrons are excited from the valence band (VB) to the conduction band (CB) of the semiconductor, thus creating an electronic vacancy at the valence band edge. The valence band hole is strongly oxidizing, whereas the conduction band electron is strongly reducing. A hole can migrate to the surface and oxidize an electron donor; in turn, while at the surface, the semiconductor can donate electrons to reduce an electron acceptor. Consequently, the semiconductor particle can act as either an electron donor or an electron acceptor for molecules in the surrounding medium, depending on the charge transfer to the adsorbed species.[90,91] Overall, the mechanism of photocatalyisis can be categorized into five steps: (1) transfer of reactants in the fluid phase to the surface; (2) adsorption of the reactants; (3) reaction in the adsorbed phase; (4) desorption of the products; and (5) removal of products from the interface region.[92]

5. Mesoporous titanium dioxide

5.1. TiO$_2$ structures and properties

Titanium dioxide (TiO_2) exists as three different polymorphs; anatase, rutile and brookite.[93] The primary source and the most stable form of TiO_2 is rutile. All three polymorphs can be readily synthesised in the laboratory and typically the metastable anatase and brookite will transform to the thermodynamically stable rutile upon calcination at temperatures exceeding ~ 600 °C.[94] In all three forms, titanium (Ti^{4+}) atoms are co-ordinated to six oxygen (O_2^-) atoms, forming TiO_6 octahedra.[95] Anatase is made up of corner (vertice) sharing
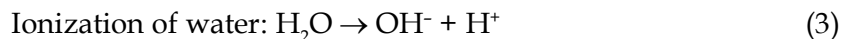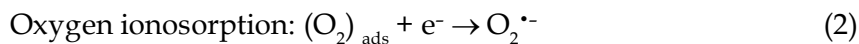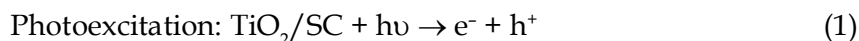
octahedra which form (0 0 1) planes (**Fig. 1a**) resulting in a tetragonal structure. In rutile the octahedra share edges at (0 0 1) planes to give a tetragonal structure (**Fig. 1b**), and in brookite both edges and corners are shared to give an orthorhombic structure (**Fig. 1c**).[96,97,98,99]

Titanium dioxide is typically an n-type semiconductor due to oxygen deficiency.[100] The band gap is 3.2 eV for anatase, 3.0 eV for rutile, and ~ 3.2 eV for brookite.[101,102,103] TiO_2 is the most widely investigated photocatalyst due to high photo-activity, low cost, low toxicity and good chemical and thermal stability.[104,105,106,107] In the past few decades there have been several exciting breakthroughs with respect to titanium dioxide. The first major advance was in 1972 when Fujishima and Honda reported the photoelectrochemical splitting of water using a TiO_2 anode and a Pt counter electrode.[108] Titanium dioxide photocatalysis was first used for the remediation of environmental pollutants in 1977 when Frank and Bard reported the reduction of CN^- in water.[109,110] This led to a dramatic increase in the research in this area because of the potential for water and air purification through utilization of "free" solar energy.[111] Other significant breakthroughs included Wang *et al.* (1997), who reported TiO_2 surfaces with excellent anti-fogging and self-cleaning abilities, attributed to the super hydrophilic properties of the photoexcited TiO_2 surfaces and use of nano titanium dioxide in an efficient dye sensitized solar cell (DSSC), reported by Graetzel and O'Regan in 1991.[112,113]

5.2. Basic principles of photocatalysis

Heterogeneous photocatalysis is a discipline which includes a large variety of reactions: organic synthesis, water splitting, photoreduction, hydrogen transfer, O_2^{18}–O_2^{16} and deuterium–alkane isotopic exchange, metal deposition, disinfection and anti-cancer therapy, water detoxification, gaseous pollutant removal, etc.[114] Among these appearances titanium dioxide -assisted heterogeneous photocatalytic oxidation has received more attention for many years as alternative method for purification of both air and water streams.

The basic photophysical and photochemical principles underlying photocatalysis are already established and have been reported in many literatures.[115,116] Vinodgopal and Kamat reported that the dependence of the rate of 1,3-diphenylisobenzofuran photodegradation on the surface coverage.[117] In other words, only the molecules that are in direct contact with the catalyst surface undergo photocatalytic degradation. Photocatalytic reaction is initiated when a photoexcited electron is promoted from the filled valence band of semiconductor photocatalyst (SC) to the empty conduction band as the absorbed photon energy, hõ, equals or exceeds the band gap of the semiconductor photocatalyst leaving behind a hole in the valence band. Thus, in concert, electron and hole pair (e^- – h^+) is generated. The following chain reactions have been widely postulated

$$\text{Photoexcitation: } TiO_2/SC + h\upsilon \rightarrow e^- + h^+ \tag{1}$$

$$\text{Oxygen ionosorption: } (O_2)_{ads} + e^- \rightarrow O_2^{\bullet-} \tag{2}$$

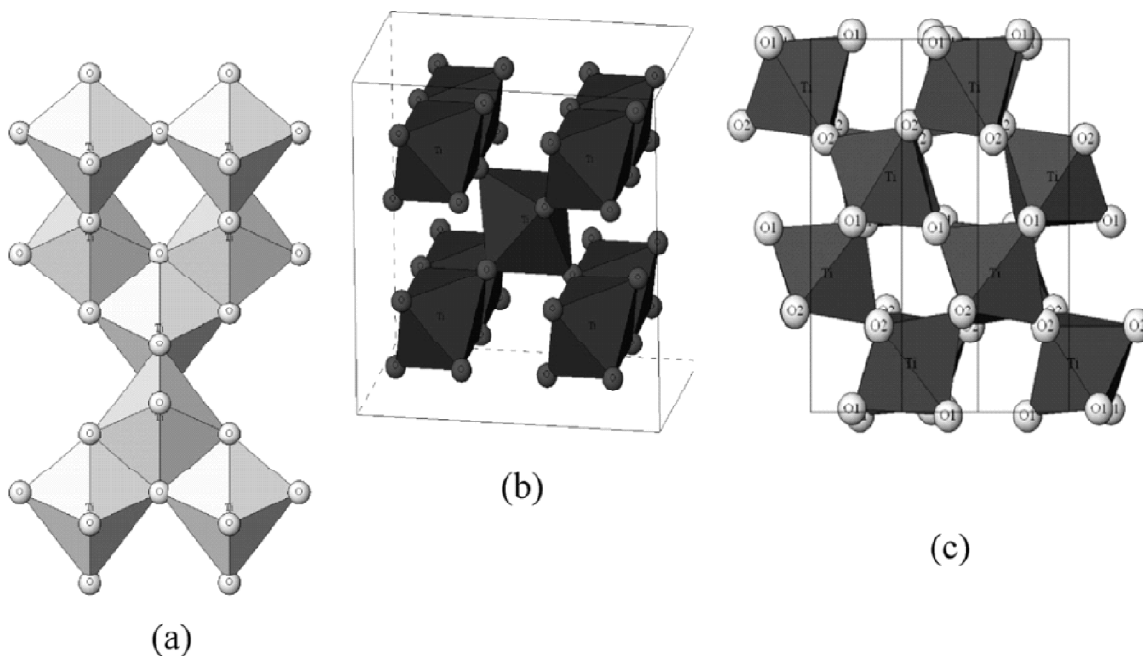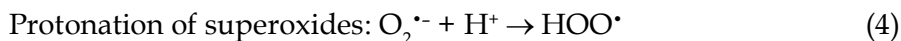$$\text{Ionization of water: } H_2O \rightarrow OH^- + H^+ \tag{3}$$

Figure 1: Crystalline structures of titanium dioxide (a) anatase, (b) rutile, (c) brookite (Reprinted with permission from Katsuhiro Nomura, Ref. 93 (*nomura-k@aist.go.jp; http://staff.aist.go.jp/nomura-k/english/itscgallary-e.htm*) Copyright (2002))

$$\text{Protonation of superoxides: } O_2{}^{\bullet-} + H^+ \rightarrow HOO^{\bullet} \qquad (4)$$

The hydroperoxyl radical formed in (4) also has scavenging property as O_2 thus doubly prolonging the lifetime of photohole:

$$HOO^{\bullet} + e^- \rightarrow HO_2{}^- \qquad (5)$$

$$HOO^- + H^+ \rightarrow H_2O_2 \qquad (6)$$

Both the oxidation and reduction can take place at the surface of the photoexcited semiconductor photocatalyst (**Fig. 2**). Recombination between electron and hole occurs unless oxygen is available to scavenge the electrons to form superoxides ($O_2{}^{\bullet-}$), its protonated form the hydroperoxyl radical ($HO_2{}^{\bullet}$) and subsequently H_2O_2.

5.3. Different methods to synthesis mesoporous titanium dioxide nanoparticles

There are different methods which have been established concerning the preparation of mesoporous titanium dioxide. Building mesosized pore spaces (2-50 nm) and arranging them in assembled array might provide prestigious advantages over numerous kinds of applications. Widely synthesis methods such as hydrothermal, microwave, sonochemical as well as solegel assisted with surfactants have brought a different perspective towards the enhancement of the materials for the intended applications.
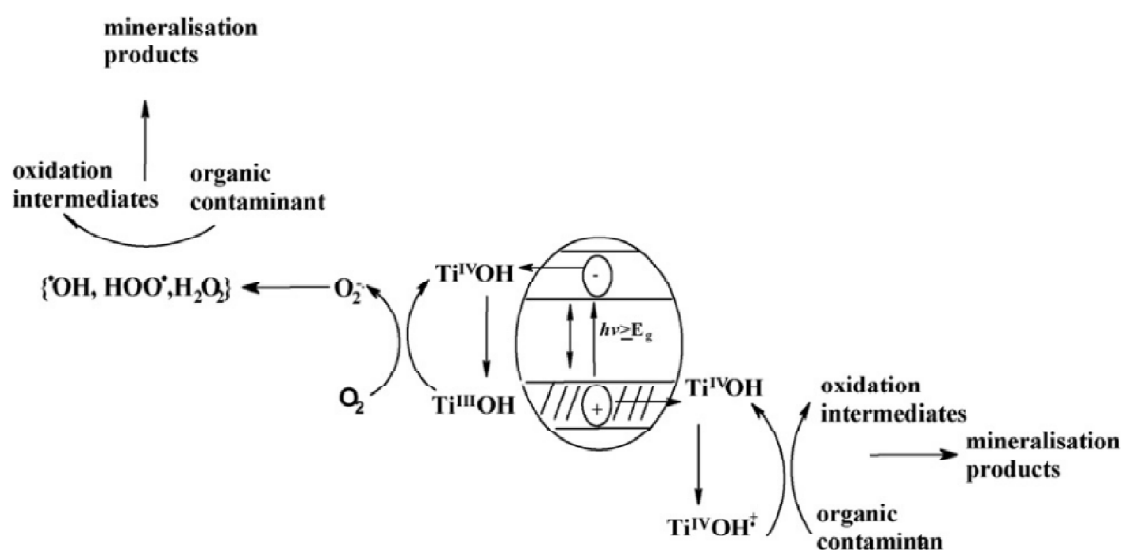
Figure 2: Conceptual diagram for the primary processes involved in photomineralisation of organic compounds. (Reprinted with permission from Umar Ibrahim Gaya, Ref. 116 (*halim@science.upm.edu.my*) Copyright (2008))

5.3.1. Hydrothermal processing

Hydro- or solvothermal processing are interesting approaches to directly prepare micro- and nanometer-sized crystalline titanium dioxide powders with high level of control of the shape. The synthesis is typically conducted on the steel autoclave vessel under relatively high temperatures, reaching vapour pressure saturation resulting in agglomerated of the crystals. In some cases, additives, such as stabilizing agents, have been used to inhibit agglomeration. Generally, hydrothermal technique is focused on the heterogeneous process in the presence of solvents (aqueous or nonaqueous) or mineralizers by employing high temperature or pressure to dissolve and recrystallize (recover) materials which are not soluble with normal conditions.[118,119] Laudise (1970) also declared that hydrothermal is the development of a crystal from the aqueous phase at near-ambient or ambient conditions.[120] Meanwhile, Rabenau (1985) clarified hydrothermal as the heterogeneous process in the aqueous medium with temperature above 100 °C and pressure above 1 bar Byrappa (1992) defined hydrothermal as anything that involves heterogeneous reaction in an aqueous solution conducted above room temperature and pressure larger than 1 atm.[121,122] Later, Lobachev states that the technique is some kind of method whereby crystallization is conducted from heated aqueous phase at high pressure.[123] Roy (1994) defined it as the synthesis involving water as the promoter and sometimes as a component of solid phases in the synthesis at higher temperature (>100 °C) and pressure (larger than a few atmosphere).[124] Another definition concerning hydrothermal is that, the reaction is occurring under the conditions of high-temperature and highpressure (>100 °C, >1 atm) in the aqueous phase in a closed system.[125]

5.3.2. Microwave processing

In the past decades, the microwave oven was a necessary appliance practically in most kitchens. Time's consumption and energy savings over traditional food preparation methods are the key benefits of using this modern appliance. Even though the use of microwaves for preparing meals is extensive, the employment of this technology for material processing is somewhat a brand-new development.[126] In the electromagnetic array, the microwave radiation range is located between infrared radiation and radio waves. Microwaves possess wavelengths of 1 mm to 1 m, equivalent to frequencies between 0.3 and 300 GHz. In this percentage of the electromagnetic array, there are frequencies used for radar, television satellite and cellular phones. Pertaining to microwave heat, two frequencies, set-aside because of the Federal Devices Fee (FCC) intended for commercial, scientific, along with medical (ISM) purposes are normally used by microwave heat. The two most normally used frequencies are 0.915 and 2.45 GHz. Lately, microwave furnaces that allow processing at variable frequencies from 0.9 to 18 GHz have been developed for processing of new material.[127]

Within the microwave dielectric heat, microwave energy is directly applied into the reactor by the energy source to the reaction container. The microwave radiation passes through the walls of the container and particularly heats only the reactants, not the reaction container itself. In addition, microwave energy is directly applied to the solution through molecular interaction with the electromagnetic field. In heat transfer, energy is conveyed due to thermal ramps, but microwave heating is the conveying of electromagnetic energy to thermal energy and the process explain the energy conversion, rather than heat transfer. Since microwaves can infiltrate materials and store energy, heat can be produced throughout the volume of the material. The transfer of energy does not depend on dispersion of heat from the surfaces, and it has the potential to reach uniform and fast heating of thick materials. If the machine is properly designed, the heat increase will be uniform throughout the sample, which often can cause less byproducts and/or decomposition products. Within pressurized systems, it is possible to increase the temperature of the solvent higher than its relative boiling point. Furthermore, the microwave energy provides numerous application in mineral and metal recovery processes such as smelting, grinding, leaching, roasting, carbothermic reduction of oxide minerals, pretreatment of refractory gold ore, spent carbon regeneration and waste management.[128] Nonetheless, microwave-assisted hydrothermal approaches have become increasingly popular in recent years in synthesizing titanium dioxide nanomaterial due to several advantages, such as shorter reaction times, transferring of energy instead of heat, volumetric heating ability, heating of selective material, heating starts from interior of material body and in many cases smaller particle sizes, and that high purity materials can be obtained. In the presence of a surfactant, such as a triblock copolymer, even anatase nanorods with mesopores and rather high specific surface areas of larger than 250 m²/g have been synthesized. However, an amorphous material was obtained from the synthesis, which resulted in anatase nanorods only after calcination at 400 ºC. Combinations of different processes, such as solegel processing combined with microwave treatment of

the resulting powder, allow for the conversion of a nanoparticulate solegel product with particle sizes of around 9 nm and specific surface areas of larger than 550 m^2/g to nanocrystalline anatase titanium dioxide tubes with a diameter of about 5 nm.[129]

5.3.3. Sonochemical processing

Sonochemical or sonochemistry is known for its acoustic cavitation which concerned with the production, growth and collapse of bubbles in a liquid. The implosive collapse of a bubble produces a localized hot spot; a temperature of ~5000 K and pressure ~1800 atm, with the degree of cooling which exceed 109 Ks^{-1}. These exceptional conditions can be used to produce structured nanomaterials. The rate of sonochemical process depends on several parameters such as the precursor should be volatile, since the primary sonochemical reaction site is the vapor inside the cavitation bubbles. Sonochemical approaches require the application of powerful ultrasound radiation (20 kHz-10 MHz) in the synthesis procedure. Nanophase, crystalline titanium dioxide has been synthesized via this approach already some years ago and research in this area is still ongoing. It was stated that a better dispersion of the nanoparticles, a marginally higher surface area, a better thermal stability and phase purity can be obtained by the sonication. Besides that, ultrasound could also affect the crystallization process via its cavitation and acoustic characteristic, but it appears to be mostly efficiently by means of not only generate nucleation (sononucleation) but also in reproducible capability in the process. Further benefits of using sonochemical approaches are; control of mineral growth, influence on minerals size distribution, helping to morphological control, elimination of impurities in the mineral, improvement in solideliquid separation performance, and elimination of the need to add seed minerals.[130,131,132]

5.3.4. Sol-gel processing

Sol-gel is defined as the preparation of ceramic nanomaterials (metal oxides, nitrides, and carbides) by preparation of a sol, formation of gel from the sol, and removal of the solvents by drying or heating. The sol can be produced from organic and inorganic precursors (e.g., nitrates, metal alkoxides or metal chloride) and may also contain dense oxide particles or polymeric substances. A sol is a colloidal suspension of solid particles in a liquid. In solegel process, the precursor (source or starting material) for preparation of a colloid consist of a metal or metalloid element surrounded by various ligands. Methyl alkoxide is a common precursor and members of the family of metalorganic compounds, which have an organic ligand attached to a metal or metalloid atom. The metal alkoxide react readily with water and the reaction called hydrolysis, since hydroxyl ions attached to the metal atom. The process is then followed by polycondensation by removing alcohol and/or water molecules from the gel to form small particles size known as xerogel (xero means dry). Further heating of the xerogel material to a certain temperature will yield a dense ceramic with high surface area and larger pore diameter (**Fig. 3**).[133,134,135]

In sol-gel synthesis, the micelle creation and their organization are driven by solvent evaporation, specifically known as evaporationinduced self-assembly (EISA). Various
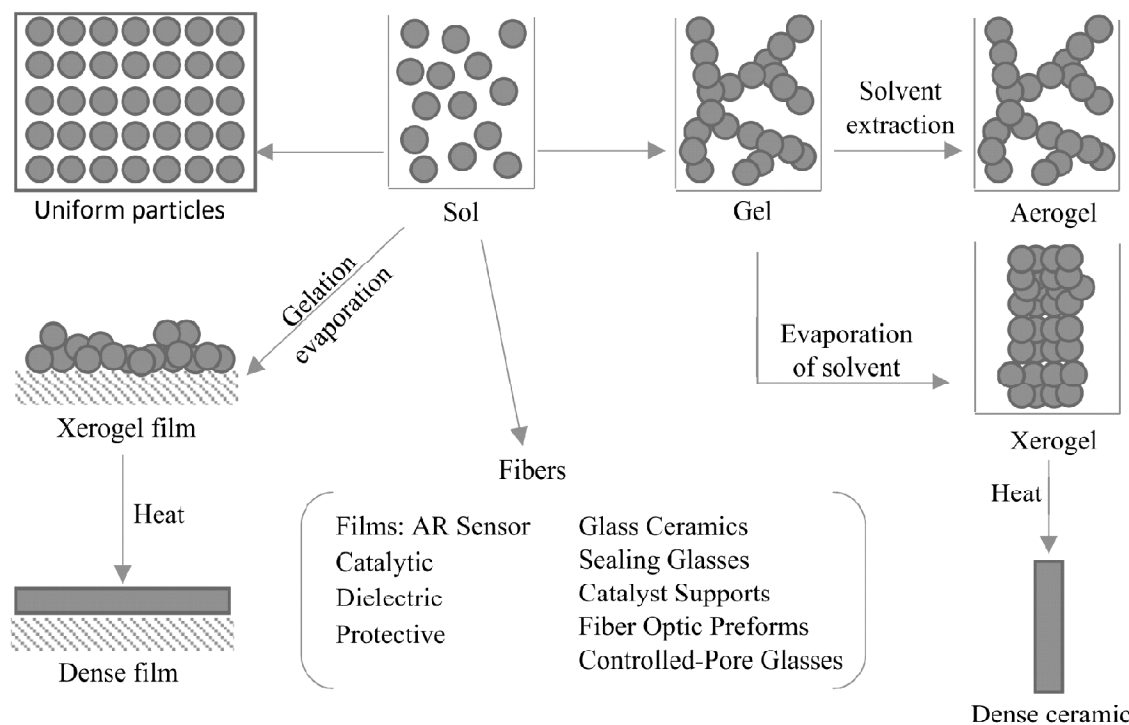
Figure 3: The diagram illustrating the process flow by means of solegel method. (Reprinted with permission from C.J. Brinker, Ref. 132, Copyright (1990))

parameters such as withdrawal rate, relative humidity and temperature in the deposition room, must be carefully controlled so that mesoporous material can be obtained. By this technique, it is possible to fabricate different types of mesoporous ordered thin films; the most common are silica, transition metal oxides, hybrid inorganic-organic oxides, phosphates or carbon mesoporous films.[136,137,138,139,140]

5.4. Applications of mesoporous titanium dioxide in photocatalysis/water treatment analysis via solar energy conversion

There are numerous applications of mesoporous titanium has been reported to date. Owing to its attractive properties along with inexpensive available chemicals for synthesis has made this nanomaterial rising star in various fields of technology. Mesoporous titanium dioxide is a fascinating material for photocatalytic applications due to its continuous particle framework, which might be helpful as compared to separated individual nanoparticles, particularly for catalyst retrieval.[141] In addition, solar energy is known for its great advantages such as clean and free, obviously abundant, and renewable alternative energy. The use of solar energy for photodegradation of organic pollutant in polluted water, and hydrogen production has brought great attention to scientists worldwide. The method known as Advance Oxidation processes (AOPs) or photocatalysis is widely used

by research scientist aiming the mineralization and chemical oxidation of the pollutant in the water recovery process.[142] In photocatalysis, the hydroxyl radical is being produced by the redox reaction occurred at the surface of the titanium dioxide photocatalyst. This reaction is induced by the photons from the solar energy. Moreover, the generation of this powerful oxidizing agent (hydroxyl radical), will have the capability to attack the organic compounds present at the surface of titanium dioxide. Consequently, it will destroy the toxic and biological resistant compounds into harmless species such H_2O and CO_2 (**Fig. 4**).[143,144,145]

Mesoporous titanium dioxide has been studied on its catalytic activity towards degradation of organic contaminant in polluted water. In 2004, Yu *et al.* (2004) synthesized zeolite-like mesoporous titanium dioxide thin films via th modified solegel method. The prepared titanium dioxide was used to degrade acetone as the model contaminant and the catalytic activity of the catalyst has been measured. From the study, the mesoporous titanium dioxide films exhibited better catalytic activity than conventional titanium dioxide films (prepared via the solegel method in the absence of surfactant). The best performance of the catalyst was obtained when the calcination temperature of 500 ºC was used. The catalyst has been characterized and displayed higher surface area of ~100 m^2/g, porosity
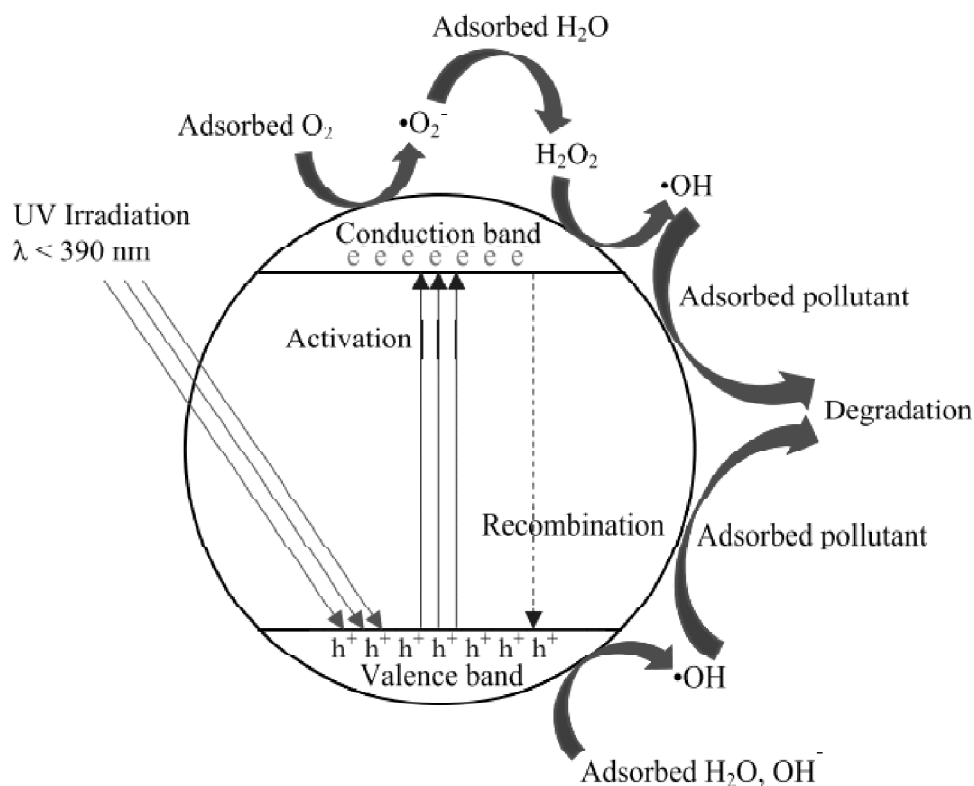

Figure 4: Schematic diagram illustrating the mechanism of titania photocatalyst. (Reprinted with permission from A.R. Khataee, Ref. 142, Copyright (2010))

of 40 % and large band gap energy of 3.3 eV. The film possessed a cubic ordered mesoporous structure and three-dimensional connected pore systems.[146]

The interest of using a surfactant in synthesizing mesoporous titanium dioxide nanoparticles is extremely growing. This can be seen from the investigation made by Peng *et al.* (2005) on photocatalytic degradation of Rhodamine B (RhB) by mesoporous titanium dioxide. The titanium dioxide has been synthesized by adding structure-directing agent such as cetyltrimethylammonium bromide (CTAB) into the titanium precursor solutions. A significant activity can be seen from the results obtained whereby 97% of RB has been successfully degraded in 2 h of reaction times. The superior performance exhibits by mesoporous titanium dioxide was due to the higher surface area of 317.5 m^2/g, mean pore size of 2.5 nm and crystallite size of 3.1 nm.[147] Nevertheless, the catalyst underwent calcination temperature of higher than 600 °C would destroy the mesoporous structure, thus, leading to poor performance in photocatalytic activity. This statement is inconsistent with research done by Wang *et al.* (2005), whereby the catalytic activity of mesoporous titanium dioxide towards degradation of ethylene has reduced significantly. The destruction of mesochannels and loss of mesoporosity at higher temperature of 800 °C made the catalyst completely transformed into rutile phase and nearly inactive.[148]

5.4.1. *The effect of anatase and rutile phases of synthesized titanium dioxide in photocatalysis*

The effect of anatase and rutile phases formed in the bulk matrices of titanium dioxide has brought remarkable attention with regards to its interesting applications such as photocatalysis and wastewater treatment. For instance, the investigation has been conducted by Venkatachalam *et al.* (2007) on photodegradation of aqueous Bisphenol-A (BPA) using titanium dioxide as the photocatalyst. Several parameters have been taken into consideration in preparing the titanium dioxide nanoparticles via solegel route, such as type of hydrolysing agent used, molar ratio of water added, aging time and calcination temperature. Based on the experimental results, the optimum condition of titanium dioxide was obtained by using acetic acid as the hydrolysing agent, molar ratio of precursor: solvent: water (1:10:350), aging temperature of 70 °C for 12 h with calcination temperature of 500 °C. The prepared catalyst exhibited average surface area of nearly 110 m^2/g, band gap energy of 3.28 eV and anatase to rutile ratio (82:18). The photodegradation of BPA was successfully conducted and such significant enhancement in photocatalytic activity was observed in comparison to Degussa-P25. In this study, it shows that the amount of anatase present in the catalyst sample play substantial role in degrading organic compound in polluted water.[149]

Another studied has been conducted by Loryuenyong et al. (2012) in preparing titanium dioxide nanoparticles via solegel method. The best conditions of titanium dioxide prepared was achieved by using isopropanol as the solvent, with calcination temperature of 500 °C. A significant enhancement could be observed when the prepared titanium dioxide exhibited 55% of anatase phase as compared to other titanium dioxide prepared with ethanol as the solvent (20% anatase). Despite of lower surface area, the rate of hydrolysis is reduced when using isopropanol and contributed to the higher percentage of anatase

phase.[150] The efficiency of the best titanium dioxide prepared was investigated in degradation of methylene blue. The percentage of methylene blue removal has reached 20% in a period of 120 min under the irradiation of UV-light.[151] In conclusion, it was clear that specific surface area, crystal structure, and the phases formed are important factors determining the photocatalytic efficiency of titanium dioxide. The use of appropriate solvent, possibly will reduce the anatase-rutile transformation through the control of hydrolysis rate. Therefore, a higher mass fraction of anatase phase retained at higher temperatures, and effective photocatalytic activity was achieved.

5.5. Effect of operational parameters

5.5.1. Light intensity

Photocatalytic reaction rate depends largely on the radiation absorption of the photocatalyst.[152] Refs.[153,154] revealed increase in the degradation rate with increase in light intensity during photocatalytic degradation. The nature or form of the light does not affect the reaction pathway.[155] In other words, the band-gap sensitization mechanism does not matter in photocatalytic degradation. Unfortunately, only 5% of the total irradiated natural sunlight has sufficient energy to cause effective photosensitization.[156] Besides, energy loss due to light reflection, transmission and energy loss as heat is inevitable in the photoprocess.[157] This limitation largely invited more research in the application of TiO_2 to decontamination.

5.5.2. Nature and concentration of the substrate

Organic molecules which can adhere effectively to the surface of the photocatalyst will be more susceptible to direct oxidation.[158] Thus the photocatalytic degradation of aromatics depends on the substituent group. It is reported that nitrophenol is much stronger an adsorbing substrate than phenol and therefore degrades faster.[159] In the degradation of chloroaromatics, Huqul *et al.* pointed out that mono-chlorinated phenol degrades faster than di- or tri-chlorinated member.[160] In general, molecules with electron withdrawing group such as nitrobenzene and benzoic acid were found to adsorb significantly in the dark compared to those with electron donating groups.[161] During photocatalytic oxidation the concentration of organic substrate over time is dependent upon photonic efficiency.[162] At high-substrate concentrations however, the photonic efficiency diminishes and the titanium dioxide surface becomes saturated leading to catalyst deactivation.[163]

5.5.3. Nature of the photocatalyst

There is direct correlation between of organic pollutant and surface coverage of TiO_2 photocatalyst.[164] Kogo et al. reported that the number of photons striking the photocatalyst controls the rate of the reaction.[165] The latter is an indication that the reaction takes place only in the adsorbed phase of the semiconductor particle. A very important parameter influencing the performance of photocatalyst in photocatalytic oxidation is the surface morphology, namely the particle size and agglomerate size.[166] Numerous forms of TiO_2 have been synthesized by different methods to arrive at a photocatalyst exhibiting desirable

physical properties, activity and stability for photocatalytic application.[167] Evidently, there is a clear connection between the surface properties, the rational development of improved synthesis routes and the possible usefulness of the material prepared in application.[168] For instance, smaller nano-particle size is reported to give higher conversion in gaseous phase photomineralisation of organic compounds over nano-sized titanium dioxide.[169]

5.5.4. Photocatalyst concentration

The rate of photocatalytic reaction is strongly influenced by concentration of the photocatalyst. Heterogeneous photocatalytic reactions are known to show proportional increase in photodegradation with catalyst loading.[170] Generally, in any give photocatalytic application, the optimum catalyst concentration must be determined, to avoid excess catalyst and ensure total absorption of efficient photons.[171] This is because an unfavourable light scattering and reduction of light penetration into the solution is observed with excess photocatalyst loading.[172]

5.5.5. pH

An important parameter in the photocatalytic reactions taking place on particulate surfaces is the pH of the solution, since it dictates the surface charge properties of the photocatalyst and size of aggregates it forms. In the current update of the points of zero charge (PZC) by Kosmulski Degussa P-25, 80% anatase and 20% rutile is reported to have PZC 6.9.[173] Under acidic or alkaline condition, the surface of titanium dioxide can be protonated or deprotonated respectively according to the following reactions:

$$TiOH + H^+ \rightarrow TiOH_2^+ \tag{7}$$

$$TiOH + OH^- \rightarrow TiO^- + H_2O \tag{8}$$

Thus, that titanium dioxide surface will remain positively charged in acidic medium (pH < 6.9) and negatively charged in alkaline medium (pH > 6.9).[174] Titanium dioxide is reported to have higher oxidizing activity at lower pH but excess H$^+$ at very low pH can decrease reaction rate.[175] The effect of pH on the photocatalytic reactions of organic compounds and adsorption on TiO$_2$ surface has been extensively studied.[176] Change in pH can result in enhancement of the efficiency of photoremoval of organic pollutants in presence of titanium dioxide without affecting the rate equation.[177] At optimized conditions better degradation has been reported.[178]

5.5.6. Reaction temperature

Experimental studies on the dependence of the reaction rate of degradation of organic compounds on temperature have been carried out since 1970s. Many researchers established experimental evidence for the dependence of photocatalytic activity on temperature.[179,180,181,182,183] Generally, the increase in temperature enhances recombination of charge carriers and desorption process of adsorbed reactant species, resulting in decrease of photocatalytic activity. This is in conformity with Arrhenius equation, for which the apparent first order rate constant K_{app} should increase linearly with exp(–1/T).

5.6. Trends in improving the activity of titanium dioxide

Various strategies have been adopted for improving the photocatalytic efficiency of TiO_2. They can be summarized as either morphological modifications, such as increasing surface area and porosity, or as chemical modifications, by incorporation of additional components in the TiO_2 structure. Although visible light active (VLA) TiO_2 photocatalysts require chemical modifications, which will be reviewed in the next section, their overall efficiencies have been significantly enhanced by controlling the semiconductor morphology.

The most commonly used TiO_2 morphology is that of monodispersed nanoparticles wherein the diameter is controlled to give benefits from the small crystallite size (high surface area, reduced bulk recombination) without the detrimental effects associated with very small particles (surface recombination, low crystallinity).[184] One dimensional (1D) titanium dioxide nanostructures (nanotubes, nanorods, nanowires, nanobelts, nanoneedles) have been also formed by hydrothermal synthesis but high emphasis was given in titanium dioxide self-assembled nanotubular films grown by electrochemical anodization on titanium metal foils. Advantages of such structures is their tailored morphology, controlled porosity, vectorial charge transfer and low recombination at grain boundarie that result in enhanced performance in photoinduced applications, mainly in photocatalysis.[185,186,187] An interesting use of TiO_2 nanotubes in photocatalytic applications is the growth of free standing flow-through membranes.[188]

6. Mesoporous silica

6.1. SiO$_2$ structures and properties

Mesoporous silica nanoparticles (MSNs) have become apparent as a promising and novel drug vehicle due to their unique mesoporous structure that preserving a level of chemical stability, surface functionality and biocompatibility ensure the controlled release, and target drug delivery of a variety of drug molecules.[189] Mesoporous silica materials was discovered in 1992 by the Mobile Oil Corporation have received considerable attention due to their superior textual properties such as high surface area, large pore volume, tunable pore diameter, and narrow pore size distribution.[190] Mesoporous nanoparticles have a solid framework with porous structure and large surface area, which allows the attachment of different functional group for targeted the drug moiety to a particular site.[191] Chemically, MSNs have honeycomb-like structure and active surface.[192] Active surface enables functionalization to modify surface properties and link therapeutic molecules.[193] Various pore geometric structures were shown in **Fig. 5**.[194]

Mesoporous silica nanoparticles due to their low toxicity and high drug loading capacity, so they are used in controlled and target drug delivery system. Basically, silica is widely present in the environment in comparison to other metal oxides like titanium and iron oxides it has comparatively better biocompatibility.[195] The mesoporous form of silica has unique properties, particularly in loading of therapeutic agents at high quantities, and in the subsequent releases.[196] Due to strong Si-O bond, silica-based mesoporous nanoparticles are more stable to external response such as degradation and mechanical
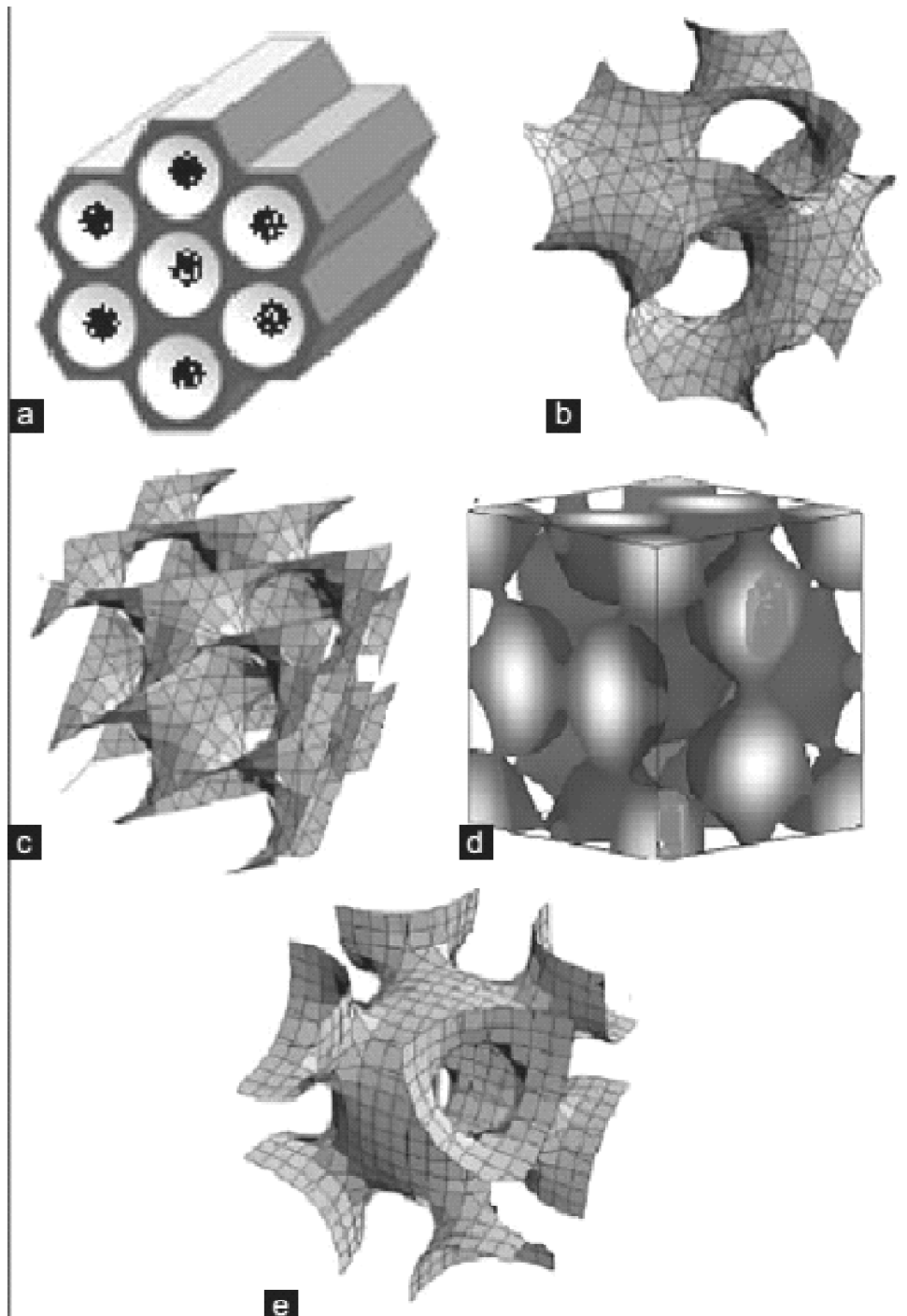
Figure 5: Various pore geometrics of mesoporous structure (a) 2D hexagonal p6 mm, (b) bicontinuous cubic Ia3d, (c) bicontinuous cubic pn3 m, (d) cage type pm3n, (e) cage type Im3 m. (Reprinted with permission from Charu Bharti, Ref. 193. Copyright (2017))

stress as compared to niosomes, liposomes, and dendrimers which inhibit the need of any external stabilization in the synthesis of MSNs.[197]

Synthetic amorphous silica consists of nano-sized primary particles of nano or micrometer-sized aggregates and of agglomerates in the micrometer-size range.[198] It has been used in a wide variety of industrial and consumer applications including food, cosmetics, and pharmaceutical products for many decades.[199] Based on extensive physico-chemical, ecotoxicology, toxicology, safety, and epidemiology data, no environmental or health risks have been associated with these materials.[200] It does not produce any toxicological effects on medicines and approved by generally recognized as safe.[201]

6.2. Synthesis of mesoporous silica nanoparticles

The synthesis of MSNs occurs at a low surfactant concentration to make the structure of the ordered mesophases strongly dependent on the interaction between the growing anionic oligomers of orthosilicic acid and cationic surfactant, which changes limits of the structure of mesophases to small sizes.[202]

6.2.1. Mesoporous silica nanoparticles synthesis based on solution

The most widely used types of MSNs are mobile crystalline material (MCM-41), it consists of ordering hexagonally arrangement of cylindrical mesopores. Synthesis of MCM-41 required liquid crystal is templating of an alkyl ammonium salt that is, cetyl trimethyl ammonium bromide.[203] High concentration of amphipillic surfactant assembles into a spherical micelle in the water and hydrophilic soluble precursor like polysilicic acid or silica acid. By electrostatic and hydrogen bonding interaction, the silica precursor is concentrated at the hydrophilic interface and form an amorphous silica, which is a mold of the mesoporous product. Removal of remaining surfactant can be done by calcination and extraction method.[204]

6.2.2. Evaporation-induced self-assembly

This method was established in 1997. It is starting by forming a homogeneous solution of soluble silica and surfactant in ethanol, water with an initial surfactant concentration of critical micelleconcentration. The Solvent evaporation process will start during dip coating for increase surfactant concentration. Then driving a mixture of silica/surfactant micelles, and their further formation occur into liquid crystalline mesophases as shown in **Fig. 6**. Film process was done by use of aerosol processing to direct the formation of mesoporous nanoparticles. Evaporationinduced self-assembly is a non-volatile component that can be introduced into an aerosol droplet incorporated within the MSNs.[205]

6.3. Sol-gel process

This process requires two-step consideration: hydrolysis and condensation. Hydrolysis produced colloidal particles in aqueous solution, which can be stimulated at alkaline and acidic pH.[206] At neutral pH, condensation reaction takes place in which gel-like 3D network
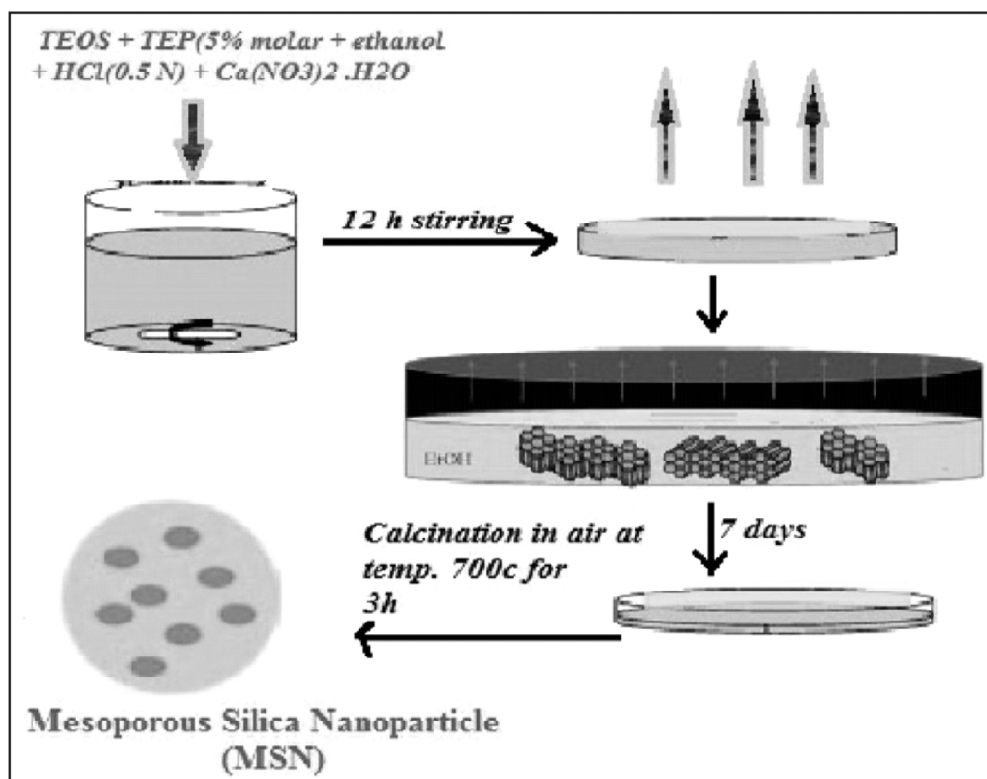
Figure 6: Evaporation self-induced assembly. (Reprinted with permission from Charu Bharti, Ref. 204 Copyright (2017))

structure formed by cross-linking through silioxane bond. After drying at ambient temperature, the different biomolecules embedded in a matrix structure of silica gel as shown in **Fig. 7**. This process involves the formation of the (MCM-41) under the size range of 60-1000 nm. Several advantages of the sol-gel process like, it is a simple and cost-effective process used to provide MSNs with controlled mesoporous structure and surface properties.[207] Sol-gel process is not a multistep process, so its time-saving process and required less excipients.

6.3.1. Synthesis mechanism of mesoporous silica nanoparticles

The synthesis process of MSNs involves the replication of a surfactant liquid crystal structure and polymerization of metal oxide precursor. Removal of organic surfactant through the calcination process which form a porous structure. Silica precursor used in mesoporous silica nanoparticles.

6.3.2. Organically modified precursors

They are prevented hydrolysis because an organic group attached directly to a silicon atom, which does not need oxygen bridge. It is conceded that organo-silica nanoparticles
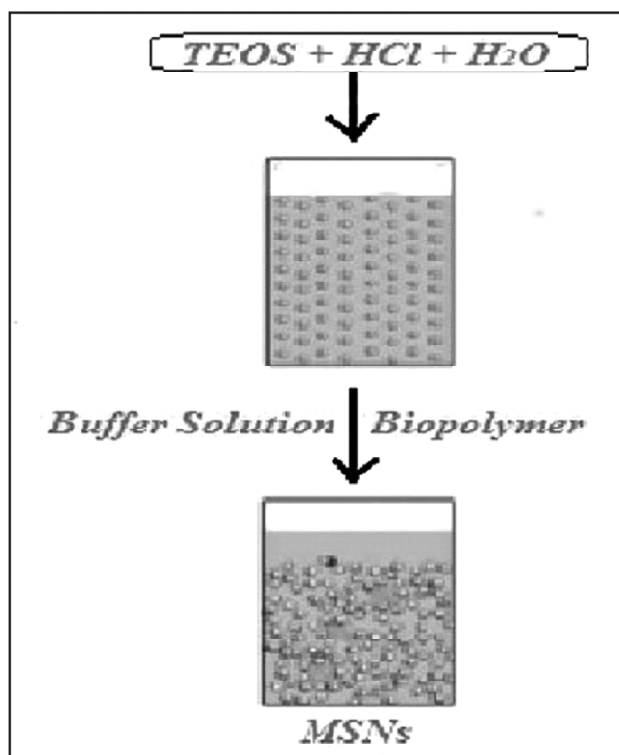
Figure 7: Sol-gel process in the synthesis of mesoporous silica nanoparticles. Reprinted with permission from Charu Bharti, Ref. 205. Copyright (2017))

consist of better properties including large surface area, less condensed silioxane structure, and low density.[208] The limited accessibility and high cost of organic template lead to its restricted use in practical applications. Commonly used silica precursors are glycerol-derived polyol-based silanes, orthosilicic acid, sodium metasilicate, tetraethyl orthosilicate (TEOS) or tetramethoxysilane (TMOS), and tetrakis (2-hydroxyethyl) orthosilicate.[209]

1. Tetraethyl orthosilicate or TMOS was commonly used in MSNs synthesis.[210] However, their poor water solubility requires additional organic solvent and alcohol and needs extreme conditions of pH and high temperature, which restricts their use.[211]

2. Tetrakis (2-hydroxyethyl) orthosilicate had been investigated to address the problems associated with TEOS and TMOS. It is now used in many studies as MSNs precursor because it is more biocompatible with biopolymers, more water soluble than TEOS and TMOS, and can process jellification at ambient temperature with a catalyst.

6.3.3. Glycerol-derived polyol-based silane precursors

They are not pH dependent but very sensitive to the ionic strength of the sol. This can form optically clear monolithic MSNs. The residuals can be either removed or retained,

therefore, the shrinkage during long-term storage can be minimized.[212] Orthosilicic acid was used as a silica precursor in the past but due to the extensive time consumption and requirement of freshly prepared acid, so it is not widely used anymore now a day.[213]

6.3.4. Sodium metasilicate

It is another precursor to sol-gel-derived silica. Formation of sodium chloride was investigated, which can cause a problem if a significant amount is generated. Later researches suggested that removing of this salt formulation by dialysis process, but it is a time and cost consuming procedure.[214] Hence, alkoxides and pure alkoxysilanes are currently widely used.

6.4. Advantages and disadvantages of porous silica material and applications

Porous silica based materials are among the most beneficial compounds which can provide more opportunities for treatment of cancer therapy and provide a pathway toward the treatment of challenging diseases. Silica or silicon has various versatile and broad range advantages such as versatility, non-toxicity, biocompatibility, biodegradability, high surface area, pore volume, homogenous distribution of guest molecules in porous space, the ability for surface charge control, and free dispersion throughout the body. The major disadvantage of porous silica nanoparticles is attributed to the surface density of silanol groups interacting with the surface of the phospholipids of the red blood cell membranes resulting in hemolysis. Another disadvantage is related to metabolic changes induced by porous silica nanoparticles leading to melanoma promotion.

Most of the applications reported in literature are in the fields of catalysis and sorption. Although these catalysts are certainly advanced materials, such applications shall not be covered here in detail, since other journals are more appropriate for this. DCT Nguyen *et al* also synthesized a mesoporous SiO_2/Cu_2O-graphene composite was prepared using a sol-gel method.[215] A facile route was implemented to synthesize the mesoporous SiO_2/Cu_2O-graphene using tetraethyl orthosilicate (TEOS) as the silica precursor at a pH of 9.5-10 (**Fig. 8**). The dispersion medium consisted of a mixture of water and ethanol. In this case, the authors used the cetyltrimethylammonium bromide (CTAB) as the structure creator, and the silica mesoparticles formed after hydrolysis. CTAB is known as a quaternary ammonium compound that is not sensitive to pH, like the amines, and is widely studied in the formation of mesoporous silica that combines with other nanomaterials.[216] The typical morphologies of the mesoporous SiO_2/Cu_2O-graphene nanomaterials were confirmed in **Fig. 9**. It was clear that the spherical silica nanoparticles with a pore diameter smaller than 2 ìm were successfully hanged on the graphene surface. Besides, the existence of the Cu_2O quantum dot size was confirmed through the nanoparticles, which were covered on the spherical shapes of the mesoporous SiO_2. The photocatalytic degradation of rhodamine B (RhB), methylene blue trihydrate (MB), and reactive black B (RBB) in an aqueous solution under visible light irradiation was observed via UV spectrophotometry after measuring the decrease in their concentrations. The results of the photodegradation suggest that the mesoporous SiO_2/Cu_2O-graphene composite is

much more effective photocatalyst than both Cu_2O-graphene and Cu_2O-graphene-TiO_2 composites when under the same experimental conditions. The photocatalytic activity of the mesoporous SiO_2/Cu_2O-graphene composite reflects two factors that influence the degradation rate: the adsorption capacity due to the mesoporous structure and the decomposition effect through catalysis. Besides, the mesoporous structure of the silica nanoparticles plays a major role in increasing the photodegradation effect as well as the surface of the graphene sheets.[217,218]

Instead, we will focus on the applications in optics and electronics. A recent review covers such applications in more detail,[219] the most important ones will be highlighted here. The development with the highest application promise by far is the use of ordered mesoporous silica films as low-*k* materials. Ever decreasing feature sizes in integrated circuits make it mandatory to use materials with dielectric constants lower than preferably. Making silica (bulk dielectric constant 3.8) porous is one way to obtain low-*k* materials. In addition to having a low dielectric constant, a novel material needs to be fully compatible with the processing implemented at present in the microelectronics industry, since it will be prohibitively expensive to change the whole production process. It seems possible to meet this requirement with ordered mesoporous silica.

The first report on the dielectric properties of ordered mesoporous silica films was published in 1998, but no details except the values for h between 1.4S and 2.1 were given, together with the information that larger porosities generally gave lower h values for the
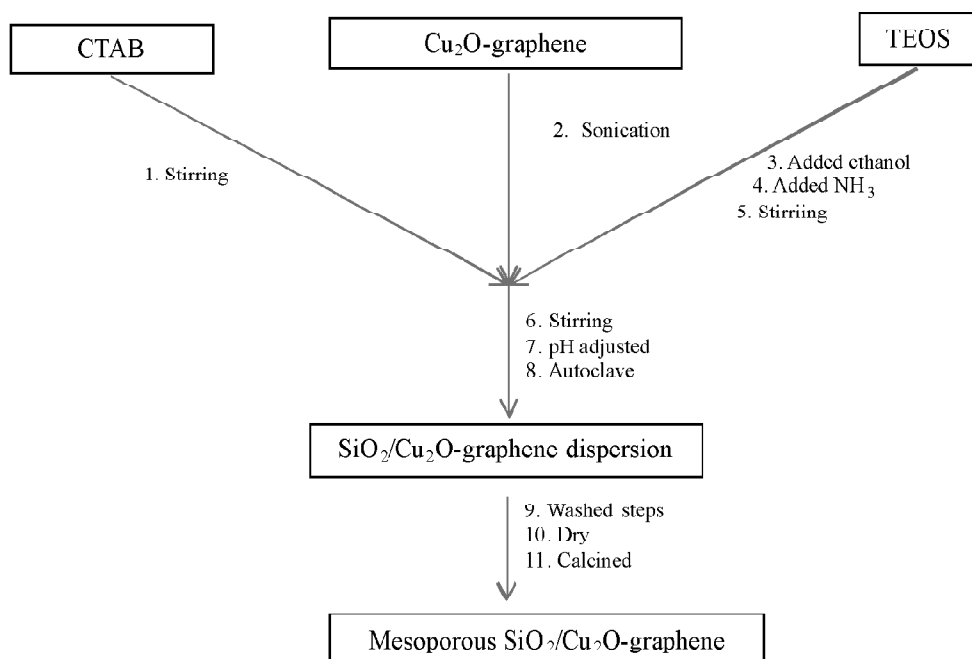

Figure 8: Schematic of the synthesis of mesoporous SiO2/Cu2O-graphene by a simple self-assembly method. Reprinted with permission from Ref. 214. Copyright © 2017 The Royal Society of Chemistry

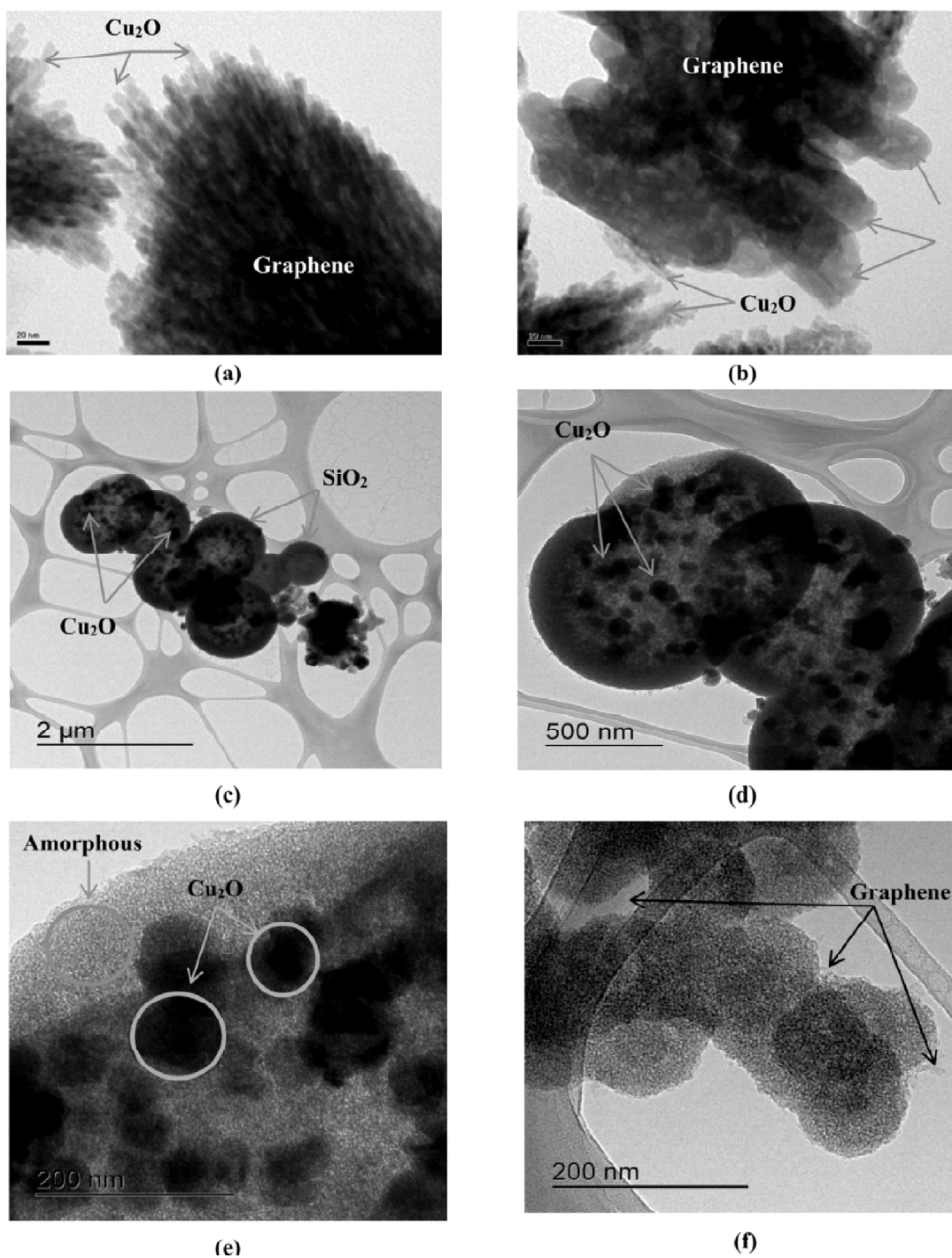**Figure 9:** TEM image of the Cu2O–graphene (a), Cu2O–graphene–TiO2 (b) and mesoporous SiO2/Cu2O–graphene (c and d) composites and HRTEM image of mesoporous SiO2/Cu2O–graphene (e and f). Reprinted with permission from Ref. 214. Copyright © 2017 The Royal Society of Chemistry

same structure.[220] The film had been made by dip-coating with Pluronic type triblock copolymers as surfactant. Subsequent publications confirmed values in this range. Values between 1.8 and 2.S have been reported for spin-coated films structured with a polyoxoethylene ether surfactant,[221] and between 1.4 and 2.S for spin-coated films with the triblock copolymer P123 surfactant. With the help of polypropylene glycol as swelling agent in the synthesis (using P123 as surfactant) to increase porosity, a material with h = 1.3 could be produced.[222]

Low-*k* films can be prepared from ordered mesoporous silica. However, as-prepared or aged films nor- mally have relatively high dielectric constants exceeding even those of silica. This is attributed to the polarizability induced by the surface silanol groups and adsorbed water. It is thus mandatory to hydrophobize the materials. Various possible treatments have been suggested, including the reaction of surface silanols with trimethylchlorosilane, hexamethyldisilazane, or heat treatment in different gas atmospheres. As an example, **Fig. 10** shows how the dielectric constant develops with different treatment steps to reduce the number of free silanols from an already low concentration to begin with due to in-situ derivatization of the precursor solution with trimethylchlorosilane. In the film with the lowest h from this series, h increased only by 0.1 over three weeks storage under ambient conditions, demonstrating the high hydrophobicity and promising long-term stability.
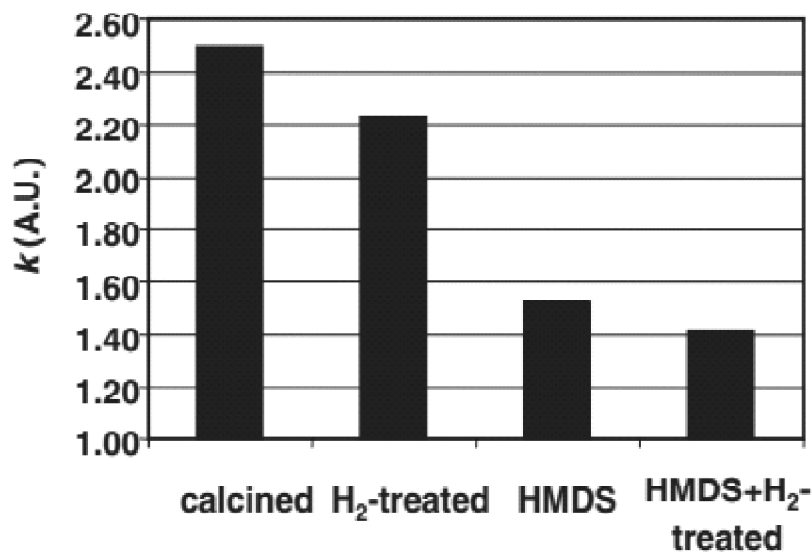

Figure 10: Dielectric constant of a film of mesoporous silica at an electric field of 2 MV cm–1. The original film had been synthesized with the triblock copolymer P123, and the precursor sol had been reacted with trimethylchlorosilane before spin coating to remove a major part of the silanol groups and hydrophobize the material. Indicated on the graph are the different subsequent treatments the samples have received. Calcination was performed at 400 °C, hydrogen treatment with S% H2 in N2 was performed at 400 °C, hexamethyldisilazane treat- ment (HMDS) was performed in HMDS vapor at 1S0 °C. Reprinted with permission from Charu Bharti, Ref. 221. Copyright (2017))

In addition to the good electrical properties, all data on the mechanical properties of the films indicate that they would be compatible with the processing steps necessary in microelec- tronics industry. The elastic modulus was reported to be 14–17 GPa for a film with a porosity of about SS%, corresponding reasonably well to a value of 13 GPa for a film with 43% porosity.[223] Very promising with respect to further improving materials properties is the use of silsesquioxane precursors to introduce organic functionality in the walls and not only on the surface of the films. It was found that increasing amounts of ethylene bridges between silicon atoms not only led to a decrease in the dielectric constant, but simultaneously to an increase of the elastic modulus and the hardness. It will be interesting to see how much the performance of the films can be improved by using fluorinated hydrocarbons as organic bridging species in the silsesquiox- anes. However, even with existing methods and technology, the use of ordered mesoporous materials as low-*k* dielectrics seems to be commercially viable. In fact, IBM has announced that such materials will be a component in one of the next generations of chips.[224]

Applications in other fields, especially in optics, are further away from industrial implementation. There are a number of reports on the use of laser-dye doped materials to generate amplified spontaneous emission (also sometimes called mirrorless lasing, since the feedback is missing).[225] Some of these reports did not only demonstrate amplified spontaneous emis- sion, but also showed that it is possible to integrate lasing systems in more complicated structures, e.g., integration by patterning into a structure for a distributed feedback laser.[226] Such structures indeed showed lasing behavior with three or more modes. The application of the patterned structures including lasers and waveguides was possible again by using the low-h materials, which also corresponded to a low refractive index of films made of ordered mesoporous materials. Only by using such a film with a very low refractive index as a support it was possible to confine the light to the waveguide structures and thus to build an optical "chip". There are other optical elements as well that are realized based on ordered mesoporous materials, such as photochromic structures based on optical switching of spiropyrans or spirooxazines.[227] Components are thus available to produce logical circuits based on host–guest systems composed of porous solids with guests bearing the optical function.

Exploiting electronic or magnetic properties of modified mesoporous materials seems to be less promising. There are reports on semiconducting mesoporous frameworks, for instance reduced niobia,[228] or on the incorporation of magnetic particles or clusters in the pore system of ordered meso- porous silica. However, at present, the use of anodic alumina seems to be preferable to spatially order wires or particles, since the pore structure can be adjusted over wider ranges, and one obtains directly a material with a known relationship between macrostructure and pore orientation. Thus, such structures are more frequently employed for the generation of spatially organized nanoparticles, the magnetic and electronic properties of which are being studied in detail.[229]

7. Conclusions

The literature review also explains detailed systematic studies on these materials as well as some technical improvements in preparing and utilizing them. An overview of sol-gel

science involved in the synthesis of mesoporous silica has been described. Functionalization of the surface of these mesoporous materials with organic or inorganic functional groups leads to new physical and chemical properties.

Mesoporous titanium dioxide has magnetized great attention to bring about a harmonize developments in industrial technology because of its fascinating properties such as low cost, environmental friendly, plentiful polymorphs, good chemical and thermal stability, and excellent electronic and optical properties. Different techniques used to synthesize the mesoporous titanium dioxide nanoparticles such as hydrothermal, sonochemical, microwaves and solegel process. Each method has its own benefits and unique characteristic depending on the intended applications. Nevertheless, this review is mainly focused on the use of hydrothermal and solegel process because of their available material, easy-handling and better physical and chemical properties such as high surface area, high pore size and pore diameter, and produce crystalline size. In these two methods, it is critical to control the hydrolysis and condensation rate of titanium precursors and cooperative assembly of the surfactants in order to obtain mesoporous structure of titanium dioxide. Agglomeration and pore collapse has greatly affected the properties and catalytic activity of this catalyst and thus, it is vital to prepare the mesoporous titanium dioxide with certain precaution such as that the addition of hydrolysis agent, structure-directing agent (surfactant), pH alteration, calcination temperature and other relevant factors. Furthermore, the type of the phases available in the bulk matrices of the catalyst also plays an important role in the catalytic activity of titanium dioxide such as anatase, rutile or brookite. The mesoporous support such as titanium dioxide contributed to the well dispersed and stable metal particles on the surface upon calcination as well as an improved catalytic performance. Nevertheless, these initial inferences and expectations required further study and investigation.

Mesoporous silica materials show promise as adsorbents that could be tailored for the efficient separation of functional food ingredients, particularly biological macromolecules. They can be synthesised with high surface areas and pore volumes as well as a variety of porous architectures with uniform pore sizes in the mesoporous range, allowing access for large molecules. Introduction of organic groups in the mesoporous materials permits the tuning of surface properties, alteration of the surface reactivity, protection of the surface from chemical attack, hydrophobization of the surface by silylation to preclude water attack, and modification of the bulk properties of the materials while at the same time stabilizing the materials towards hydrolysis. Separation of transition metals, heavy metal ions or radioactive materials from aqueous streams is currently one of the most significant and fascinating problems to be challenged, severely hampered by the presence of a large excess of competing ionic species. Therefore, materials to be used for the adsorption and separation of these toxic substances are required to be specific enough to differentiate between transition metals, heavy metal ions and radioactive compounds on the one hand and on the other benign metal cations. A key issue for the applicability of these mesoporous materials is associated with the thermal, and more importantly the hydrothermal and mechanical stabilities.

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