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**ORIGINAL ARTICLE**

# Applications of nano-catalyst in new era

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**Abstract** In the era of nanoscience where all the devices and technologies are going to smaller and smaller in size with improved properties; catalysis is an important field of application. In this review article we are trying to summarize data reported in literature for application of nano sized catalyst in our daily life which are useful for human beings. Improvement in catalytic properties due size of catalyst reduced to nano scale is discussed here. Introductory points regarding nanoscience; their functional approaches; current research are also here.

Main applications of nanocatalysts in water purification; fuel cell; energy storage; in composite solid rocket propellants; bio diesel production; in medicine; in dye; application of carbon nano tubes and several other point of application are discussed here in detail.

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**1. Introduction**

Nanoscience is the study of phenomena on a nanometer scale. Atoms are a few tenths of a nanometer in diameter and molecules are typically a few nanometers in size. The smallest structures humans have made have dimensions of a few nanometers

and the smallest structures we will ever make will have the dimensions of a few nanometers. This is because as soon as a few atoms are placed next to each other, the resulting structure is a few nanometers in size. The smallest transistors, memory elements, light sources, motors, sensors, lasers, and pumps are all just a few nanometers in size like carbon nanotubes, grapheme etc.

Carbon nanotubes (CNTs) have exceptional mechanical properties, particularly high tensile strength and light weight. An obvious area of application would be in nanotube reinforced composites, with performance beyond current carbon-fiber composites. One current limit to the introduction of CNTs in composite is the problem of structuring the tangle of nanotubes in a well-ordered manner so that use can be made of their strength. Another challenge is generating strong bonding between CNTs and the matrix, to give good overall composite performance and retention during wear or erosion of composites. The surfaces of CNTs are smooth and relatively unreactive and so tend to slip through the matrix when it is

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stressed. One approach that is being explored to prevent this slippage is the attachment of chemical side-groups to CNTs, effectively to form ‘anchors’. Another limiting factor is the cost of production of CNTs. However, the potential benefits of such light, high strength material in numerous applications for transportation are such that significant further research is likely (Bakunin et al., 2004; Edelman and Cammarata, 1998).

Graphene is an allotrope of carbon, whose structure is one-atom-thick planar sheets of  $sp^2$ -bonded carbon atoms that are densely packed in a honeycomb crystal lattice. Graphene is most easily visualized as an atomic-scale chicken wire made of carbon atoms and their bonds. The crystalline or “flake” form of graphite consists of many graphene sheets stacked together.

The carbon–carbon bond length in graphene is about 0.142 nanometers. Graphene sheets stack to form graphite with an interplanar spacing of 0.335 nm, which means that a stack of 3 million sheets would be only one millimeter thick. Graphene is the basic structural element of some carbon allotropes including graphite, charcoal, carbon nanotubes and fullerenes. It can also be considered as an indefinitely large aromatic molecule, the limiting case of the family of flat polycyclic aromatic hydrocarbons. The Nobel Prize in Physics for 2010 was awarded to Andre Geim and Konstantin Novoselov “for groundbreaking experiments regarding the two-dimensional material graphene”.

Besides the technological relevance of nanoscience (or perhaps because of the technological relevance) there is an enormous hype associated with it. Fantastic claims have been made about faster computers, cheap production of goods, and medical breakthroughs. Nanotechnology is expected to appear in products such as tennis rackets, self-cleaning cars, paint, food, and cosmetics.

*It's a small, small, small, small world:* Manufactured products are made from atoms. The properties of those products depend on how those atoms are arranged. If we rearrange the atoms in coal, we get diamonds. If we rearrange the atoms in sand (and add a pinch of impurities) we get computer chips. If we rearrange the atoms in dirt, water and air we get grass.

*Nanoscience in physics, chemistry, biology, and medicine:* Physics is the mother of the natural sciences. In principle, physics can be used to explain everything that goes on at the nanoscale. There is active physics research going on in nanomechanics, quantum computation, quantum teleportation, and artificial atoms. While physics can explain everything, sometimes it is more convenient to think of nanostructures in terms of chemistry where the molecular interactions are described in terms of bonds and electron affinities.

Chemistry is the study of molecules and their reactions with each other. Since molecules typically have dimensions of a few nanometers, almost all of nanoscience can be reduced to chemistry. Chemistry research in nanotechnology concerns  $C_{60}$  molecules, carbon nanotubes, self-assembly, structures built using DNA, and supermolecular chemistry. Sometimes the chemical description of a nanostructure is insufficient to describe its function. For instance, a virus can be described best in terms of biology.

Biology is sometimes described as nanotechnology that works. Biological systems contain small and efficient motors. There are more than 50 kinds of motors found in cells. Biological systems produce impressive control systems. The brain of a bee is tiny and consumes little power yet regulates complex flying behavioral patterns. A cell one micron in size can store

1 GB of information in DNA. They self reproduce. They construct tough and strong material. Biology is an important source for inspiration in nanotechnology. Copying engineering principles from biology and applying it to create new materials and technologies is called biomimetics.

Nanomedicine is the medical application of nanotechnology. Nanomedicine ranges from the medical applications of nanomaterials, to nanoelectronic biosensors, and even possible future applications of molecular nanotechnology. Current problems for nanomedicine involve understanding the issues related to toxicity and environmental impact of nanoscale materials.

### 1.1. Nanomaterials

Nanomaterials are those which have structured components with at least one dimension less than 100 nm. Materials that have one dimension in the nanoscale (and are extended in the other two dimensions) are layers, such as thin films or surface coatings. Some of the features of computer chips come in this category. Materials that are nanoscale in two dimensions (and extended in one dimension) include nanowires and nanotubes. Materials that are nanoscale in three dimensions are particles, for example precipitates, colloids and quantum dots (tiny particles of semiconductor materials). Nanocrystalline materials, made up of nanometer-sized grains, also fall into this category. Some of these materials have been available for some time; others are genuinely new (Taniguchi, 1974; Lubick and Betts, 2008; Edelman and Cammarata, 1998).

Two principal factors cause the properties of nanomaterials to differ significantly from other materials: increased relative surface area, and quantum effects. These factors can change or enhance properties such as reactivity, strength and electrical characteristics. As a particle decreases in size, a greater proportion of atoms are found at the surface compared to those inside. For example, a particle of size 30 nm has 5% of its atoms on its surface, at 10 nm 20% of its atoms, and at 3 nm 50% of its atoms. Thus nanoparticles have a much greater surface area per unit mass compared with larger particles. As growth and catalytic chemical reactions occur at surfaces, this means that a given mass of material in nanoparticulate form will be much more reactive than the same mass of material made up of larger particles (Taniguchi, 1974; Lubick and Betts, 2008; Edelman and Cammarata, 1998).

### 1.2. Fundamental concepts

One nanometer (nm) is one billionth, or  $10^{-9}$  of a meter. By comparison, typical carbon–carbon bond lengths, or the spacing between these atoms in a molecule, are in the range 0.12–0.15 nm, and a DNA double-helix has a diameter around 2 nm. On the other hand, the smallest cellular life-forms, the bacteria of the genus *Mycoplasma*, are around 200 nm in length. To put that scale in another context, the comparative size of a nanometer to a meter is the same as that of a marble to the size of the earth.

Two main approaches are used in nanotechnology. In the “bottom-up” approach, materials and devices are built from molecular components which assemble themselves chemically by principles of molecular recognition. In the “top-down” approach, nano-objects are constructed from larger entities without atomic-level control.

*Larger to smaller: a materials perspective:* A number of physical phenomena become pronounced as the size of the system decreases. These include statistical, mechanical effects, as well as quantum mechanical effects, for example the “quantum size effect” where the electronic properties of solids are altered with great reductions in particle size. This effect does not come into play by going from macro to micro dimensions. However, it becomes dominant when the nanometer size range is reached. Additionally, a number of physical (mechanical, electrical, optical, etc.) properties change when compared to macroscopic systems. One example is the increase in surface area to volume ratio altering mechanical, thermal and catalytic properties of materials. Diffusion and reactions at nanoscale, nanostructures materials and nanodevices with fast ion transport are generally referred to nanoionics. Novel mechanical properties of nanosystems are of interest in the nanomechanics research. The catalytic activity of nanomaterials also opens potential risks in their interaction with biomaterials (Lubick and Betts, 2008).

Materials reduced to the nanoscale can show different properties compared to what they exhibit on a macroscale, enabling unique applications. For instance, opaque substances become transparent (copper); stable materials turn combustible (aluminum); solids turn into liquids at room temperature (gold); insulators become conductors (silicon). A material such as gold, which is chemically inert at normal scales, can serve as a potent chemical catalyst at nanoscales. Much of the fascination with nanotechnology stems from these quantum and surface phenomena that matter exhibits at the nanoscale (Lubick and Betts, 2008).

*Simple to complex: a molecular perspective:* Modern synthetic chemistry has reached the point where it is possible to prepare small molecules to almost any structure. These methods are used today to produce a wide variety of useful chemicals such as pharmaceuticals or commercial polymers. These approaches utilize the concepts of molecular self-assembly and/or supramolecular chemistry to automatically arrange themselves into some useful conformation through a bottom-up approach. The concept of molecular recognition is especially important: molecules can be designed so that a specific conformation or arrangement is favored due to non-covalent intermolecular forces. The Watson–Crick base pairing rules are a direct result of this, as is the specificity of an enzyme being targeted to a single substrate, or the specific folding of the protein itself. Thus, two or more components can be designed to be complementary and mutually attractive so that they make a more complex and useful whole (Taniguchi, 1974; Edelstein and Cammarata, 1998).

Such bottom-up approaches should be able to produce devices in parallel and much cheaper than top-down methods, but could potentially be overwhelmed as the size and complexity of the desired assembly increases. Most useful structures require complex and thermodynamically unlikely arrangements of atoms. Nevertheless, there are many examples of self-assembly based on molecular recognition in biology, most notably Watson–Crick base pairing and enzyme–substrate interactions. The challenge for nanotechnology is whether these principles can be used to engineer novel constructs in addition to natural ones (Levins and Schafmeister, 2005).

*Molecular nanotechnology: a long-term view:* Molecular nanotechnology, sometimes called molecular manufacturing,

is a term given to the concept of engineered nanosystems (nanoscale machines) operating on the molecular scale. It is especially associated with the concept of a molecular assembler, a machine that can produce a desired structure or device atom-by-atom using the principles of mechano-synthesis. Manufacturing in the context of productive nanosystems is not related to, and should be clearly distinguished from, the conventional technologies used to manufacture nanomaterials such as carbon nanotubes, nanoparticles (Lubick and Betts, 2008), molecular wire or nanowires (Mihailovic, 2009) and Switches (Emberly and Kriczenow, 2003). Molecular wires (or sometimes called molecular nanowires) are molecular-scale objects which conduct electrical current. They are the fundamental building blocks for molecular electronic devices. Their typical diameters are less than three nanometers, while their bulk lengths may be macroscopic, extending to centimeters or more.

When the term “nanotechnology” was independently coined and popularized by Eric Drexler (who at the time was unaware of an earlier usage by Norio Taniguchi) it referred to a future manufacturing technology based on molecular machine systems. The premise was that molecular scale biological analogies of traditional machine components demonstrated molecular machines were possible: by the countless examples found in biology, it is known that sophisticated, stochastically optimized biological machines can be produced (Edelstein and Cammarata, 1998). It is hoped that developments in nanotechnology will make possible their construction by some other means, perhaps using biomimetic principles. However, Drexler and other researchers have proposed that advanced nanotechnology, although perhaps initially implemented by biomimetic means, ultimately could be based on mechanical engineering principles, namely, a manufacturing technology based on the mechanical functionality of these components (such as gears, bearings, motors, and structural members) that would enable programmable, positional assembly to atomic specification. In general it is very difficult to assemble devices on the atomic scale, as all one has to position atoms are other atoms of comparable size and stickiness (Edelstein and Cammarata, 1998).

*Current research:* This includes subfields which develop or study materials having unique properties arising from their nanoscale dimensions (Das et al., 2007):

- Interface and colloid science has given rise to many materials which may be useful in nanotechnology, such as carbon nanotubes and other fullerenes, and various nanoparticles and nanorods.
- Nanoscale materials can also be used for bulk applications; most present commercial applications of nanotechnology are of this flavor.
- Progress has been made in using these materials for medical applications.
- Nanoscale materials are sometimes used in solar cells which combats the cost of traditional silicon solar cells.

*Bottom-up approaches:* These seek to arrange smaller components into more complex assemblies:

- DNA nanotechnology utilizes the specificity of Watson–Crick base pairing to construct well-defined structures out of DNA and other nucleic acids.

- Approaches from the field of “classical” chemical synthesis also aim at designing molecules with well-defined shape (e.g., bis-peptides) (Lu and Schüth, 2006).
- More generally, molecular self-assembly seeks to use concepts of supramolecular chemistry, and molecular recognition in particular, to cause single-molecule components to automatically arrange themselves into some useful conformation.
- The assembly of nanoparticles of two different materials into a binary nanoparticle superlattice is a promising way of synthesizing a large variety of materials (metamaterials) with precisely controlled chemical composition and tight placement of the components. In theory only a few stable binary superlattice structures can assemble from hard spheres, potentially limiting this approach. But all is not lost because at the nanometer scale there are additional forces (electrostatic, van der Waals and dipolar) that can stabilize binary nanoparticulate structures. There are several methods of synthesis of a dozen novel structures from various combinations of metal, semiconductor, magnetic and dielectric nanoparticles. This demonstrates the potential of self-assembly in designing families of novel materials and metamaterials with programmable physical and chemical properties.

*Top-down approaches:* These seek to create smaller devices by using larger ones to direct their assembly:

- Many technologies descended from conventional solid-state silicon methods for fabricating microprocessors are now capable of creating features smaller than 100 nm, falling under the definition of nanotechnology. Giant magnetoresistance-based hard drives already on the market fit this description, as do atomic layer deposition (ALD) techniques. Peter Grünberg and Albert Fert received the Nobel Prize in Physics for their discovery of Giant magnetoresistance and contributions to the field of spintronics in 2007.
- Solid-state techniques can also be used to create devices known as nano electromechanical systems, which are related to micro electromechanical systems.
- Atomic force microscope tips can be used as a nanoscale “write head” to deposit a chemical upon a surface in a desired pattern in a process called dip pen nanolithography. This fits into the larger subfield of nanolithography.

Focused ion beams can directly remove material, or even deposit material when suitable pre-cursor gasses are applied at the same time. For example, this technique is used routinely to create sub-100 nm sections of material for analysis in transmission electron microscopy.

*Functional approaches:* These seek to develop components of a desired functionality without regard to how they might be assembled:

- Molecular electronics seeks to develop molecules with useful electronic properties. These could then be used as single-molecule components in a nanoelectronic device (Jang, 2006).
- Synthetic chemical methods can also be used to create what forensics call synthetic molecular motors, such as in a so-called nano car.

Recent progress in synthesis of nanomaterials has made it possible to fabricate nanometer-sized materials with controlled structures and functionalities (Lee et al., 2009; Ko and Jang, 2006; Yoon et al., 2007; Choi et al., 2007). In particular, versatile porous materials with nanometer feature sizes have emerged as promising candidates for applications in the fields of catalysis (Ko and Jang, 2006; Yoon et al., 2007; Choi et al., 2007), energy conversion and storage (Moon et al., 2005; Choi and Jang, 2008), separation (Giri et al., 2005), and biomedical science (Yang et al., 2007; Guo et al., 2009; Oh et al., 2010).

### 1.3. Properties of nanomaterials

In tandem with surface-area effects, quantum effects can begin to dominate the properties of matter as size is reduced to the nanoscale. These can affect the optical, electrical and magnetic behavior of materials, particularly as the structure or particle size approaches the smaller end of the nanoscale. Materials that exploit these effects include quantum dots and quantum well lasers for optoelectronics.

For other materials such as crystalline solids, as the size of their structural components decreases, there is much greater interface area within the material; this can greatly affect both mechanical and electrical properties. For example, most metals are made up of small crystalline grains; the boundaries between the grain slow down or arrest the propagation of defects when the material is stressed, thus giving it strength. If these grains can be made very small, or even nanoscale in size, the interface area within the material greatly increases, which enhances its strength. For example, nanocrystalline nickel is as strong as hardened steel (Edelstein and Cammarata, 1998).

## 2. Nanocatalyst: effect of size reduction

Catalytic technologies are critical to present and future energy, chemical process, and environmental industries. Conversion of crude oil, coal and natural gas to fuels and chemical feedstock, production of a variety of petrochemical and chemical products, and emission control of CO, hydrocarbons, and NO, all rely on catalytic technologies. Catalysts are also essential components of electrodes for fuel cells that use either solid oxide ionic or polymeric proton electrolyte. Drivers for development of advanced catalysts include (i) production of high value products with inexpensive raw materials, (ii) energy-efficient and environmentally-benign chemical conversion processes, (iii) increasingly stringent environmental regulations, and (iv) low-cost catalysts such as with reduction or replacement of precious metals (Liu, 2005).

In catalysis, chemical reactions in solid, gases or liquids are accelerated by introducing a solid phase that ideally contains large enough amounts of the right kind of site for chemical reactants to adsorb, react, and desorb. Because optimization of the catalyst requires increasing the numbers of sites to expand surface area, the catalytic particle size must be decreased. In contemporary laboratories, active catalysts tend to consist of carefully prepared nanometer-sized particles on supports with nanometer-sized pores or structural features. Modern catalysts typically consist of multiple-component active phases that may include a support tailored to disperse, isolate, or otherwise enhance the structure or properties of individual catalytic particles. One goal of catalysis research is to understand

how decreasing the size of catalytic particles alters the intrinsic catalytic performance beyond simply expanding surface area. A corollary goal is learning how to design and prepare catalysts with the most effective size and structure.

The exciting prospect of nanoscience is its potential use in almost any conceivable domain. Every field from medicine and electronics to manufacturing and fashion stand to benefit from advances in nanotechnology. And while nano-scale technology is multifaceted in its application, the use of nanocrystals as catalysts is perhaps the most intriguing. The key concept to understanding nanocrystal catalysis involves the ratio of surface area and volume. As an object gets larger, its surface area increases less in relation to its volume. Therefore, smaller objects have more surface area with respect to their volume. This has important implications for chemical reactions. High surface area-to volume ratios are favorable for chemical reactions. Going back to the campfire example, kindling is used to start the fire. The small pieces of wood have a greater surface area with respect to their volume than larger logs. Lighting the kindling therefore results in a quicker combustion. Additionally, if one throws a handful of sawdust onto a burning fire, a giant flare results. This reaction is chemically identical to ordinary wood burning, but it occurs at a much faster rate. The general purpose of catalysts is to increase the speed of a given reaction. This is achieved through kinetic means and does not directly affect the thermodynamic properties of a chemical system. Introducing a catalyst increases the speed of a reaction in one of three ways; it can lower the activation energy for the reaction, act as a facilitator and bring the reactive species together more effectively, or create a higher yield of one species when two or more products are formed. Depending on the application, nano-catalysts can be used in all the ways listed above. Nano-materials are more effective than conventional catalysts for two reasons. First, their extremely small size (typically 10–80 nm) yields a tremendous surface area-to-volume ratio. Also, when materials are fabricated on the nanoscale, they achieve properties not found within their macroscopic counterparts. Both of these reasons account for the versatility and effectiveness of nanocatalysts.

### 3. Applications of nanocatalysts

In era of nanotechnology where size of every object is going to smaller and smaller with their enhanced properties; catalysts of nano size are also used in several chemical processes and beneficial for human being. In this section we are trying to collect all literature data on application of nanocatalyst reported within the last few years.

#### 3.1. Carbon nanotubes

Nano-sized carbon materials (NCMs), especially carbon nanotubes (CNTs) have attracted a lot of attention because of their unique physical and mechanical properties (Saito et al., 1993; Ruoff and Lorents, 1995). CNTs have been used in many fields as field emission sources (Trans et al., 1998), electric nano-conductors (Mintmire et al., 1992), Li ion secondary batteries (Maurin et al., 1999), electric double-layer capacitors (Frackowiak et al., 2000), fuel cells (Bessel et al., 2001), and molecular sieves (Wang et al., 1999). In addition, CNTs have been recently used to adsorb hydrogen (Dillon et al., 1997) since

they are highly porous, light, stable, and non-expensive. Their unique tubular structure is favorable for hydrogen uptake (Darkrim et al., 2002). Hydrogen, owing to its high energy content and non-polluting nature, is considered as an ideal energy carrier which may be widely utilized in the near future (Züttel, 2004; Shi and Hwang, 2007). According to the literature (Fazle Kibria et al., 2001), the material characteristics of CNTs, governed by preparation procedures, significantly affect their hydrogen storage capability. Chang et al. (2008) studied, a novel NCMs preparation method utilizing the Metal Dusting (MD) process which is developed. Moreover, the possibility of using the produced CNTs as a hydrogen storage material, which has not been explored in the literature. The effects of acid post-treatment on the microstructure and hydrogen storage performance of the CNTs are also evaluated. The as-prepared multi-wall CNTs produced at 600 °C show a hydrogen discharge capacity of 57 mAh/g; which was measured; using an electrochemical method under room temperature and pressure. It was found that the post acid treatment in boiling nitric acid solution for 4 h can effectively remove metal particles and deposited amorphous carbon from the as-prepared CNTs. As a result, the hydrogen discharge capacity can be significantly increased to 104 mAh/g. However, further prolonging the etching time not only decreases the crystallinity but also damages the tubular structure of the CNTs, degrading the hydrogen storage performance. The experimental results indicate that MD-produced NCMs are potential candidates for use as hydrogen storage materials.

#### 3.2. Water purification

Hydrogen is the latest in the succession of energy providers, with many social, economic, and environmental benefits to its credit including its utilization in chemical industries which accounts for 40% of its consumption. This implicates the preciousness of H<sub>2</sub> and its high demand to the world today and tomorrow. Considerable amounts of hydrogen is being consumed in the various reduction processes, namely reduction of metal catalysts that are employed for various hydrogenation and other reactions apart from its usage in the hydrogenation reactions itself. Thus, preparation methods that can produce catalysts directly in metallic form without employing any hydrogen for bringing the oxidic or other forms of catalysts to their metallic forms can be highly advantageous in reducing hydrogen consumption. Shashikala et al. (2007) reported that the process of maintaining hydrogen economy by synthesizing nano-metallic particles of silver employing novel electro-chemical deposition method over carbon covered alumina support. This method gives a silver catalyst, which is highly efficient in controlling microbes in water. It is also concluded evidently that the Ag supported catalysts are reusable. The combined characteristics of Al<sub>2</sub>O<sub>3</sub> and carbon like low acidity, high mechanical strength and presence of meso pores in carbon coverage in alumina (CCA) are also helpful for designing highly active AgCCA catalyst.

Liu et al. (2004) studied the use of visible light sensitive N-doped TiO<sub>2</sub> and ZrO<sub>2</sub> nanoparticles to achieve significant improvements in biofilm and *Escherichia coli* bacteria photodegradation efficiency. Result shows that the different nitrogen sources yield TiO<sub>2</sub>-xNx with different photocatalytic performance, which could be explained by the different binding sites of N dopants in a given metal oxide matrix. The abatement of

*E. coli* and biofilm bacteria without extracellular polymeric substance (EPS) showed distinctive kinetic patterns indicating the complexity of bactericidal degradation. Removing the soluble EPS from heterotrophic biofilm bacteria significantly increased the bactericidal efficiency for most of the photocatalysts. EPS is found to play an important role in controlling the bactericidal reaction kinetics through competition for ROS with biofilm bacteria. The degradation of cellular substances takes a much longer time to achieve compared with cell inactivation, although the oxidation of carbohydrate and protein followed similar trend as the bacterial killing. The results of observations suggest that not all types of organism can represent the mixture of bacteria in a natural environment, e.g., biofilm. These findings suggest that nitrogen-doped TiO<sub>2</sub> has potential applications in the development of alternative disinfectants for environmental and medical usage.

### 3.3. Bio diesel production

With the increase of environment protection consciousness and decrease of petroleum reserves, biodiesel, defined as the monoalkyl esters of fatty acids, has been the focus of a considerable amount of recent research as an alternative renewable fuel. More and more biodiesel is being used in many countries such as Germany, France, Italy, USA, Japan and so on (Bozbas, 2008; Sharma and Singh, 2002). The general method for the preparation of biodiesel is trans esterification reaction of oil and alcohol with homogeneous catalyst (Dias et al., 2008; Helwani et al., 2009). However, the homogeneous catalyst has many shortcomings, such as the difficulty in product isolation, requirement of large quantity of water and environmental pollution by the liquid wastes (Martinez et al., 2004; Sharma et al., 2008; Meher et al., 2006). A new trend in the preparation of biodiesel is to use "green" method based on heterogeneous catalyst (Martyanov and Sayari, 2008; Granados et al., 2007). Despite the solid phase catalytic methods being intensively studied, the industrial applications are limited. This fact suggests that further research is necessary to solve current problems (Gryglewicz, 1999; Liu et al., 2008). Heterogeneous catalytic methods are usually mass transfer resistant, time consuming and inefficient (Kouzu et al., 2008). Nanocatalysts have high specific surface and high catalysis activities, may solve the above problems. They have become the focus of recent research (Shu et al., 2007; Bournay et al., 2005). Wen et al. (2010) studied that the solid base nanocatalyst KF/CaO can be used for biodiesel production with yield of more than 96%. The catalyst is well used to convert the oil with higher acid value into biodiesel. It is porous with particle sizes of 30–100 nm. XRD analysis showed the catalyst has new crystal K<sub>2</sub>CaF<sub>6</sub>, which increases catalytic activity and stability. The high specific surface area and large pore size are favorable for contact between catalyst and substrates, which effectively improved efficiency of transesterification. Production of biodiesel from Chinese tallow seed oil has positive impact on the utilization of agricultural and forestry products.

### 3.4. Fuel cell application

There is tremendous interest in the preparation of carbon supported electro-catalysts for fuel cell applications (Ahmadi et al., 1996; Tang et al., 2005; Kim and Popov, 2004; Hirano et al., 1997). It is well known that the performance of catalysts

can be improved by achieving nanosized particles, uniform distribution and high loading of catalysts over large surface area carbons (Wilsn and Gottesfeld, 1992; Liu et al., 2005a,b; Yan et al., 2001). Oh et al. (2007) investigation showed that parameters of Pt colloid prepared by using the polyol process although the adjustment of pH behaves as a key factor in controlling the nanodimension of the Pt particles, a severe reduction in the metal loading is observed with increasing solution pH. According to the zeta potential study, this is attributed to the electrostatic stabilization between Pt particles and carbon supports. The zeta potential of the carbon support decreased to negative values with increasing solution pH while that of the Pt particles remained constant at a negative charge after pH 6. Therefore, poor adsorption or repulsive forces between the metal colloids and the supports occurs, resulting in reduced Pt particle loading. Pt loading and particle size are also affected by the gas environment during Pt/C synthesis in the polyol process. It is observed that carrying out the entire process of Pt/C formation in N<sub>2</sub> showed very good control over Pt particle size whereas the Pt loading is significantly low. When the process of Pt/C formation is carried out in the presence of O<sub>2</sub>, the Pt loading is increased up to 36 wt.%. However, the particle size of Pt increases due to agglomeration at low solution pH. As a modification to the polyol process, the reduction of Pt metal ions at elevated temperature with N<sub>2</sub> purging followed by the further reduction at room temperature with air showed the best results with almost 40 wt.% loading and a small particle size of 2.8 nm.

### 3.5. In drug delivery

Carbon nanomaterials are of great interest in applications for biological fields (Kelly et al., 2008; Yushin et al., 2006). Typically, carbon nanotubes (CNTs) have a feature of endohedral filling of 2–10 nm in diameter leading to encapsulation of small molecules. CNTs can be heterogeneously surface-functionalized and stained cytochemically with nonquenching and non-photobleaching. Accordingly, CNTs may be suitable for bio-applications in biorecognition and drug delivery systems (Hayashi et al., 2007; Jang and Yoon, 2003; Peckys et al., 2002). However the biocompatibility of CNTs is still controversial and the tedious functionalization process of CNT surface remains a major obstacle to practical applications (Magrez et al., 2006; Cheng et al., 2009). Oh et al. (2010) reported the fabrication of carbonized polypyrrole nanoparticles (CPyNs) with controlled diameters and their textural properties and investigated the potential capability of CPyNs as imaging probes and drug carriers based on their porosity, magnetic property and biocompatibility. The guest molecule loading of CPyNs was conducted with pyrene as a typical hydrophobic dye and the guest molecule-releasing test was performed with ibuprofen as a typical hydrophobic drug. Poly Pyrrole nanoparticles with controlled diameters were prepared by micelle templating in oil/water emulsions, and CPyNs with three different sizes (55, 76, and 99 nm) were successfully obtained by carbonization of the polymer pre-cursors. CPyNs showed highly microporous compared to zeolite, resulting in loading guest molecules into CPyNs using phase separation. In addition, the magnetic property of CPyNs provided the selective separation and targeting. CPyNs sustained *in vitro* drug release properties. Importantly, smaller size and amine surface modification of CPyNs provide an improved sustained

property. Due to their superiorities such as microporous structure, monodispersity, magnetism, and biocompatibility, it is believed that the CPyNs open the way to use in fields such as biomaterials science, including bioimaging and magnetic induced drug carriers.

### 3.6. Photocatalytic activity

#### 3.6.1. Photocatalytic decoloration of malachite green dye

High amount of unconsumed dyes produced by textile and printing industries are discharged into the waters every day. The presence of dyes and pigments in water causes considerable damage to the aquatic environment (Robinson et al., 2001; Pearce et al., 2003; Talarposhti et al., 2001). These contaminants result in high chemical oxygen demand (COD), high biochemical oxygen demand (BOD), toxicity, bad smell, and mainly, are responsible for the coloration of wastewaters (Santos et al., 2007; Prado et al., 2004; Chiou and Li, 2002). Even at very low concentrations, the color of this kind of contaminants can be recognized, because the presence of dyes in water is highly visible. This effect is undesirable because the color blocks the sunlight access to aquatic flora and fauna, and it reduces the photosynthetic action within the ecosystem (Srivastava et al., 2004; Cheng et al., 2008). Among many dyes that are applied in manufacture products, malachite green must be highlighted. This dye has been used as a food coloring additive, as a dye for silk, jute, leather, wool, cotton and paper (Culp and Beland, 1996; Chen et al., 2007). Moreover, this compound has also been used as a medical disinfectant, antihelminthic, as well as, in aquaculture as a fungicide and antiseptic (Rahman et al., 2005; Bekc et al., 2008). The application of malachite green in aquaculture dates back 1933, due to its high effect against protozoal and fungal infections (Perez-Estrada et al., 2008; Lee et al., 2001). However, the use of malachite green has been contested due to the effects on the reproductive and immune systems and its potential genotoxic and carcinogenic effects. Many processes have been extensively applied in the treatment of dye-containing waste water such as: incineration, biological treatment, ozonation, and adsorption on solid phases (Garcia-Montano et al., 2008; Chu and Ma; 2000; Prado et al., 2003, 2005). However, these procedures have some limitations. The incineration can produce toxic volatiles; biological treatment demands long periods of treatment and bad smell; ozonation presents a short half-life, ozone stability is affected by the presence of salts, pH, and temperature and the adsorption results in phase transference of contaminant, not degrading the contaminant and producing sludge (Garcia-Montano et al., 2008; Chu and Ma; 2000; Prado et al., 2003, 2005). In this way, the heterogeneous photocatalysis becomes an elegant alternative for dye degradation. This technique presents many advantages over conventional technologies such as the dye degradation into innocuous final products (Torres et al., 2006; Prado et al., 2008). Many photocatalysts have been used to degrade organic pollutants such as ZnO, Nb<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub>. Among these catalysts, TiO<sub>2</sub> is highlighted because of its high catalytic efficiency, high chemical stability, low cost and toxicity. On the other hand, TiO<sub>2</sub> suspension in water presents a hydrocolloid with a high stability, which makes difficult the separation of this catalyst from water. Consequently, the recuperation and re-application of this catalyst in other photodegradation reactions becomes hard and with a low efficiency (Prado et al., 2005, 2008; Torres et al.,

2006; Prado and Leonardo, 2009). In order to avoid this difficult recuperation, Ivanov et al. (2003) synthesized the TiO<sub>2</sub> nanotubes characterized and applied them to the photodegradation of malachite green dye. Recycling studies were followed and compared to traditional TiO<sub>2</sub> anatase photocatalyst in order to demonstrate the advantages of nanostructured TiO<sub>2</sub> in photocatalysis. TiO<sub>2</sub> nanotubes presented a photocatalytic activity lower than TiO<sub>2</sub> anatase to degrade malachite green dye. The catalysts presented their best activity at pH 4. The great advantage of TiO<sub>2</sub> nanotubes is its easy recovery in comparison with traditional TiO<sub>2</sub> catalyst. Consequently, the nanotubes can be recycled and reapplied in many photodegradation cycles, maintaining 80% of their activity after 10 cycles of reaction. The pre-cursor TiO<sub>2</sub> catalyst lost its activity on the second catalytic cycle.

#### 3.6.2. Photodegradation of methylene blue

Soni et al. studied the photocatalytic activity in the visible part of the solar spectrum (442 nm) for demonstrated highly organized mesoporous nanocrystalline titania thin films doped with thiourea. This property, which is of interest for the further development of photovoltaic devices operating in sunlight, is revealed by monitoring the photodegradation of methylene blue upon contact with an N-doped TiO<sub>2</sub> film as a function of irradiation time and film thickness (Soni et al., 2008).

Yuo and Wang, prepared TiO<sub>2</sub> sol for the degradation of methylene blue (MB) solution under ultraviolet (UV) irradiation. The absorption spectra of MB indicated that the maximum wavelength, 663 nm, was almost kept the same. The performance of 92.3% for color removal was reached after 160 min. The particle size of TiO<sub>2</sub> sol was about 22.5 nm. X-ray diffraction showed that TiO<sub>2</sub> consisted of a single anatase phase. The small size and anatase phase probably resulted in high photocatalytic activity of TiO<sub>2</sub> sol. The degradation ratio decreased as the initial concentration of MB increased. The photodegradation efficiency decreased in the order of pH 2 > pH 9 > pH 7. Regarding catalyst load, the degradation increased with the mass of catalyst up to an amount of 1.5 g L<sup>-1</sup> then decreased as the mass continued to increase. The addition of H<sub>2</sub>O<sub>2</sub> to TiO<sub>2</sub> sol resulted in an increase in the degradation ratio (Yao and Wang, 2010).

Choi et al. (2006) describes the application of novel chemistry methods for the fabrication of robust nanostructured titanium oxide (TiO<sub>2</sub>) photocatalysts. Such materials can be applied in the development of efficient photocatalytic systems for the treatment of water. Mesoporous photocatalytic TiO<sub>2</sub> films and membranes were synthesized via a simple synthesis method that involves dip-coating of appropriate substrates into an organic/inorganic sol composed of isopropanol, acetic acid, titanium tetraisopropoxide, and polyoxyethylenesorbitan monooleate surfactant (Tween 80) followed by calcination of the coating at 500 °C. Controlled hydrolysis and condensation reactions were achieved through in-taking of water molecules released from the esterification reaction of acetic acid with isopropanol. The subsequent stable incorporation of Ti–O–Ti network onto self-assembled surfactants resulted in TiO<sub>2</sub> photocatalysts with enhanced structural and catalytic properties. The properties included high surface area (147 m<sup>2</sup>/g) and porosity (46%), narrow pore size distribution ranging from 2 to 8 nm, homogeneity without cracks and pinholes, active anatase crystal phase, and small crystallite size (9 nm). These TiO<sub>2</sub> photocatalysts were highly efficient for the destruction of

methylene blue and creatinine in water. High water permeability and sharp polyethylene glycol retention of the prepared photocatalytic  $\text{TiO}_2/\text{Al}_2\text{O}_3$  composite membranes evidenced the good structural properties of  $\text{TiO}_2$  films. In addition, the multi-coating procedure made it possible to effectively control the physical properties of  $\text{TiO}_2$  layer such as the coating thickness, amount of  $\text{TiO}_2$ , photocatalytic activity, water permeability and organic retention.

### 3.6.3. Photo catalytic degradation of Azo dyes

Liu et al. (2005a,b) examined the photocatalytic degradation of three azo dyes, acid orange 7 (AO7), procion red MX-5B (MX-5B) and reactive black 5 (RB5) using a new type of nitrogen-doped  $\text{TiO}_2$  nanocrystals. These newly developed doped titania nanocatalysts demonstrated high reactivity under visible light ( $\lambda > 390 \text{ nm}$ ), allowing more efficient usage of solar light. Experiments were conducted to compare the photocatalytic activities of nitrogen-doped  $\text{TiO}_2$  nanocatalysts and commercially available Degussa P25 powder using both UV illumination and solar light; result shown that nitrogen-doped  $\text{TiO}_2$

after calcination had the highest photocatalytic activity among all three catalysts tested, with 95% of AO7 decolorized in 1 h under UV illumination. The doped  $\text{TiO}_2$  also exhibited substantial photocatalytic activity under direct sunlight irradiation; with 70% of the dye color removed in 1 h and complete decolorization within 3 h. Degussa P25 did not cause detectable dye decolorization under identical experimental conditions using solar light. The decrease of total organic carbon (TOC) and evolution of inorganic sulfate  $\text{SO}_4^{2-}$  ions in dye solutions were measured to monitor the dye mineralization process.

### 3.6.4. Photo catalysis

$\text{TiO}_2$  is regarded as the most efficient and environmentally benign photocatalyst and has been most widely used for photo-degradation of various pollutants (Fujishima and Honda, 1972; Fujishima et al., 2000; Grätzel, 2001; Hay and Raval; 1998).  $\text{TiO}_2$  photocatalysts can also be used to kill bacteria, as has been carried out with *E. coli* suspensions (Kikuchi et al., 1997). The strong oxidizing power of illuminated  $\text{TiO}_2$  can be used to kill tumor cells in cancer treatment (Sakai

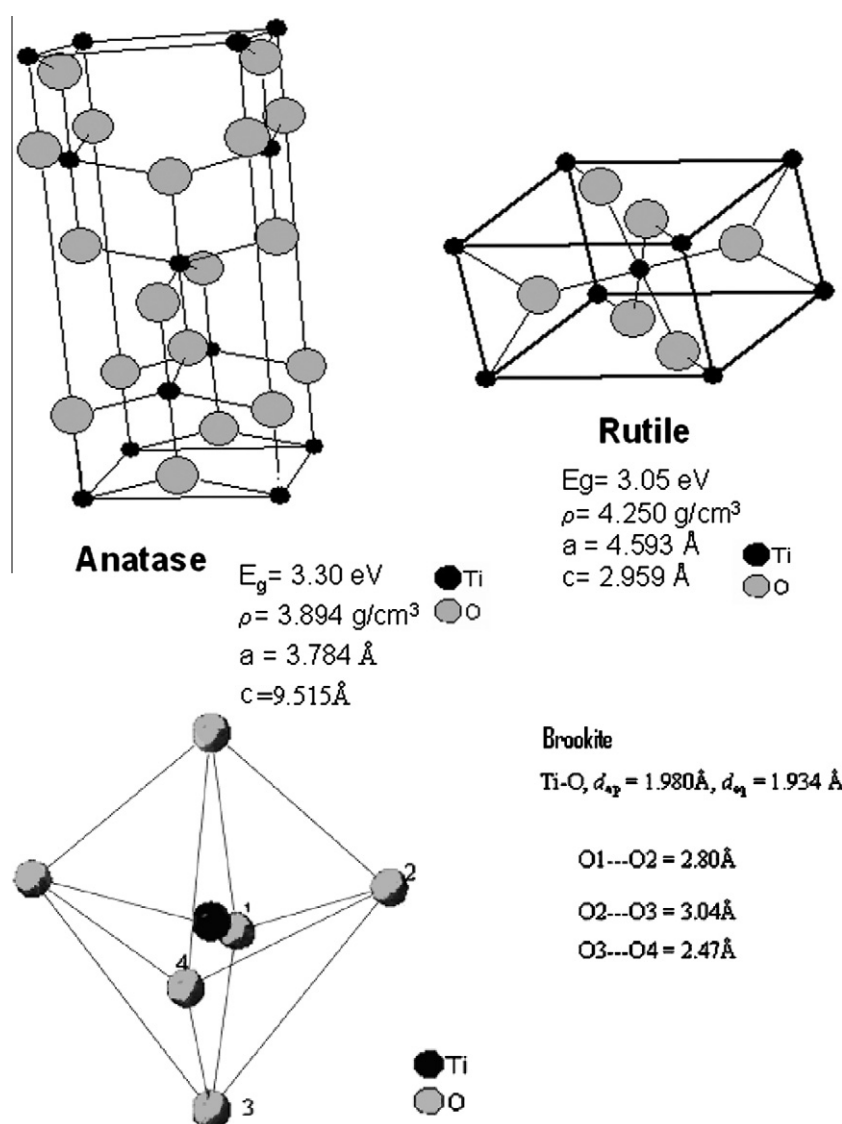
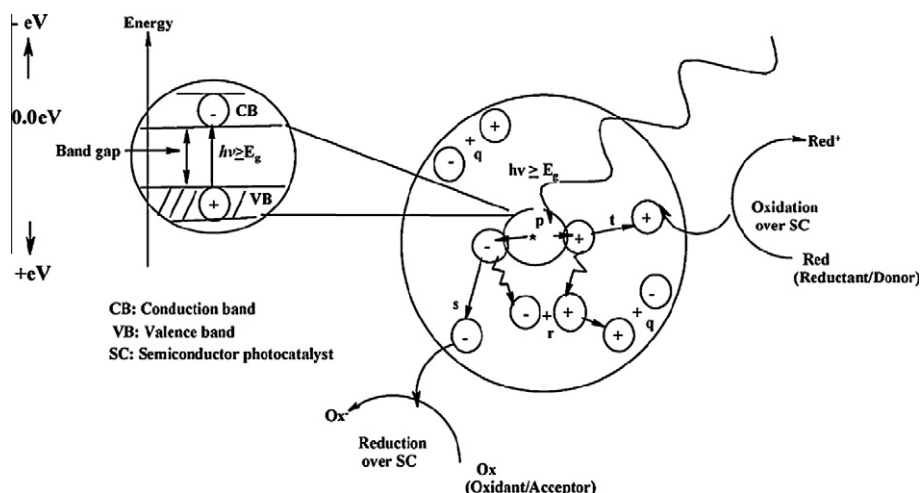


Figure 1 Different forms of  $\text{TiO}_2$ .





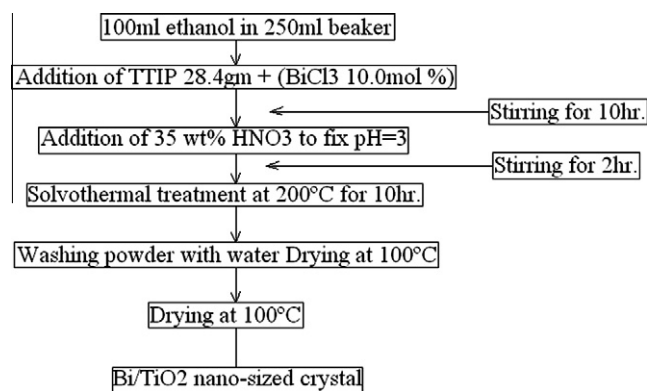
**Figure 2** Schematic diagram of photocatalytic process initiated by photon acting on the semiconductor.

et al., 1995). The photocatalytic reaction mechanisms are widely studied (Fujishima and Honda, 1972; Fujishima et al., 2000; Grätzel, 2001; Hay and Raval, 1998; Beydoun et al., 1999). The principle of semiconductor photocatalytic reaction is straightforward. Upon absorption of photons with energy larger than the band gap of  $TiO_2$ , electrons are excited from the valence band to the conduction band, creating electron-hole pairs. These charge carriers migrate to the surface and react with the chemicals adsorbed on the surface to decompose these chemicals. This photodecomposition process usually involves one or more radicals or intermediate species such as  $\cdot OH$ ,  $O^{2-}$ ,  $H_2O_2$ , and  $O_2$ , which play important roles in the photocatalytic reaction mechanisms. The photocatalytic activity of a semiconductor is largely controlled by: (i) the light absorption properties, e.g., light absorption spectrum and coefficient, (ii) reduction and oxidation rates on the surface by the electron and hole, and (iii) the electron-hole recombination rate. Large surface area with constant surface density of adsorbents leads to faster surface photocatalytic reaction rates. In this sense, the larger the specific surface area, the higher the photocatalytic activity is. On the other hand, the surface is a defective site, therefore the larger the surface area, the faster the recombination. Soni et al studied the photocatalytic activity in the visible part of the solar spectrum (442 nm) for demonstration of highly organized mesoporous nanocrystalline titania thin films doped with thiourea. High temperature treatment usually improves the crystallinity of  $TiO_2$  nanomaterials, which in return can induce the aggregation of small nanoparticles and decrease of the surface area. Judging from the above general conclusions, the relation between the physical properties and the photocatalytic activities is complicated. Optimal conditions are sought by taking these considerations into account and may vary from case to case (Beydoun et al., 1999).

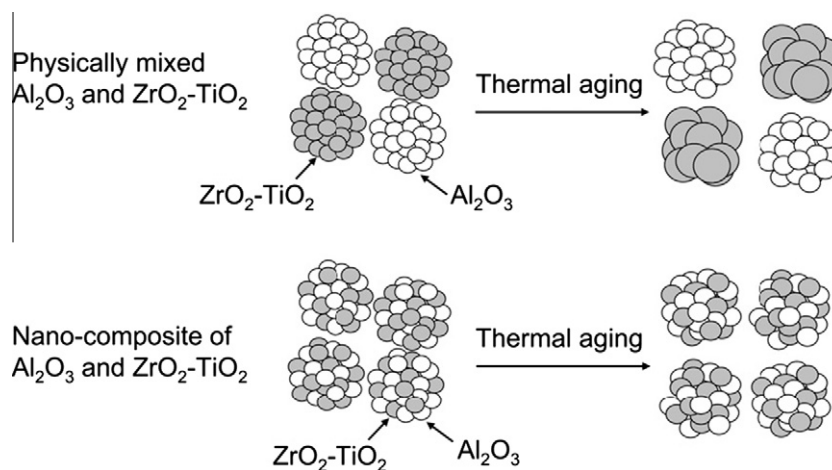
### 3.6.5. Photovoltaic

Photovoltaics based on  $TiO_2$  nanocrystalline electrodes have been widely studied on the so-called dye-sensitized nanocrystalline solar cell (DSSC) (Irie et al., 2003; Chen et al., 2005a,b). The structure and properties of the  $TiO_2$  electrodes play an important role in the performance of the DSSC. The mesoporosity and nanocrystallinity of the semiconductor are important not only because of the large amount of dye that

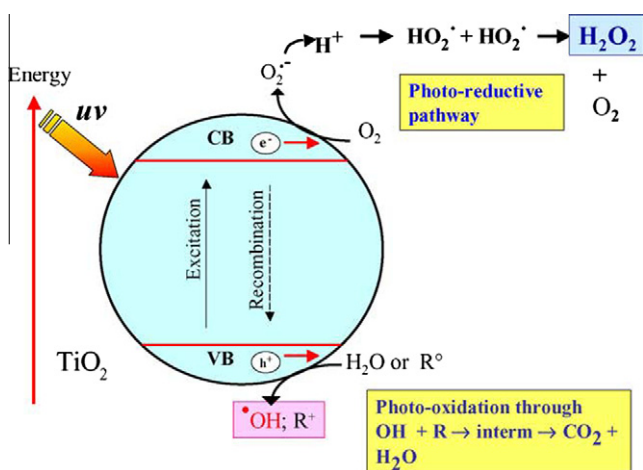
can be adsorbed on the very large surface, but also for two additional reasons: (a) they allow the semiconductor small particles to become almost totally depleted upon immersion in the electrolyte (allowing for large photovoltages), and (b) the proximity of the electrolyte to all particles makes screening of injected electrons, and thus their transport, possible (Cahen et al., 2000). Ordered mesoporous  $TiO_2$  nanocrystalline films showed enhanced solar conversion efficiency by about 50% compared to traditional films of the same thickness made from randomly oriented anatase nanocrystals (Zukalova et al., 2005). Higher efficiencies of solar cells were achieved with  $TiO_2$  nanotube-based electrodes due to the increase in electron density in nanotube electrodes compared to P25 electrodes (Ohsaki et al., 2005). Nanoporous electrodes in a core-shell configuration, usually a  $TiO_2$  core coated with  $Al_2O_3$  (Fabregat-Santiago et al., 2004),  $MgO$  (Kumara et al., 2004),  $SiO_2$  (Palomares et al., 2003),  $ZrO_2$  (Chen et al., 2001), or  $Nb_2O_5$  (Chen et al., 2001), could improve the performance of dye-sensitized solar cells. Doped  $TiO_2$  nanomaterials also show a good promise in the application of DSSCs. For the best N-doped  $TiO_2$  electrodes, the photoinduced current due to visible light and at moderate bias increased around 200 times compared to the behavior of pure  $TiO_2$  electrodes (Lindgren et al., 2003) (Figs. 1–5).



**Figure 3** Preparation of  $TiO_2$  and 10.0 mol%  $Bi/TiO_2$  nanometer particles by solvothermal method.



**Figure 4** Concept chart of the nano-composite of  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2\cdot\text{TiO}_2$ .



**Figure 5** Classical scheme for the production of highly oxidative species by  $\text{TiO}_2$  under light irradiation with wavelengths  $< 400$  nm.

### 3.6.6. Photo catalytic degradation of phenol

Nanoparticle catalysts are highly active since most of the particle surfaces can be available to catalysis. Many of the nanocatalysts have found applications in ammonia synthesis, environmental protection, photocatalysis, waste removal, fiber and mechanical industries. Mohamed et al. (2007) studied the use of nanocatalyst for photocatalytic degradation of phenol. Phenol and substituted phenols are widely distributed at low concentration in natural waters, including algal secretion, hydrolyzable tannins and flavonoids and humification processes, and at high concentrations in some industrial wastewater discharge and agricultural activities (Sobczynski et al., 2004). Treating phenolic wastewater to harmless level is an arduous process for many biological and chemical processes due to its high solubility and stability in water. Although a wide range of catalyst has been tested, titania ( $\text{TiO}_2$ ) seems to be the most widely used catalyst because of its photocatalytic, conservative nature, low cost, low toxicity, corrosion resistant (Moonsiri et al., 2004) and high stability to light illumination. A way to increase photocatalytic activity is the

preparation of a nanostructural to get a high surface area that is directly related with catalytic activity (Hwu et al., 1997). Moreover, photocatalysis of nanocrystalline  $\text{TiO}_2$  has many of advantages on wastewater treatment, such as high catalysis efficiency, energy-saving, non-pollution and can degrade all kinds of organic pollutants from water effectively. All of these merits make photocatalysis of  $\text{TiO}_2$  a fine and attractive method in the research of water treatment and it is supposed to be used widely in future. The prepared nano  $\text{TiO}_2$  catalyst is uniform and spherical particles with an average nanoparticles size of 11.50 nm. In order to evaluate photoactivity of prepared nano  $\text{TiO}_2$  catalyst, the photocatalytic degradation of phenol in a batch reactor was studied. Results revealed that the photoactivity of the prepared nano  $\text{TiO}_2$  catalyst and commercialized  $\text{TiO}_2$  powder (Degussa P25). The figure obviously indicates that the phenol concentration decreases with the increase of reaction time. The degradation of phenol using prepared nano  $\text{TiO}_2$  is higher than the Degussa P25. It is well known that the higher efficiency of prepared nano  $\text{TiO}_2$  is influenced by many factors such as particle size and surface area. In this study, the findings show that the prepared nano  $\text{TiO}_2$  has larger surface area, higher porosity and is of smaller particle size than the Degussa P25. This is the reason why the prepared nano  $\text{TiO}_2$  is more active than the commercialized  $\text{TiO}_2$  powder for photocatalytic degradation of phenol (Table 1).

**Table 1** Sample labels and treatment condition.

Sample	Treatment condition plasma electrolytic oxidation	Chemical treatment
nPEO	√ <sup>a</sup>	–
PEO	√ <sup>b</sup>	–
CT-nPEO	√ <sup>a</sup>	√
CT-PEO	√ <sup>b</sup>	√

“√”: With treatment; “–”: without treatment.

<sup>a</sup> The oxidized coating formed in an electrolyte without addition of HA.

<sup>b</sup> The oxidized coating formed in an electrolyte with addition of HA.

### 3.7. In solid rocket propellants

The use of aluminum particles of sub-micrometer size in the combustion of composite solid propellants has gained recent attention. Several facets of this application have been reported, such as production (Lee et al., 2003; Mench et al., 1998), thermal decomposition (Kwok et al., 2002; Kwon et al., 2004; Johnson et al., 2008) in combination with ammonium perchlorate (AP) (Liu et al., 2004; Kwok et al., 2007), surface coating of aluminum particles (Bocanegra et al., 2007; Trunov et al., 2005), ignition (Trunov et al., 2006) and oxidation or combustion of aluminum particles (Kwon et al., 2003; Huang et al., 2007) including bimodal blends of micrometer and sub-micrometer sized particles (Romonadova and Pokhil, 1970), combustion of pressed pellets of aluminum and AP with additives (Dokhan et al., 2002), aluminized composite propellants (De Luca et al., 2005; Galfetti et al., 2006, 2007; Jayaraman et al., 2009), and collection of aluminum agglomerates formed during the combustion of aluminized propellants (Galfetti et al., 2007). Jayaraman et al. (2009) studied nano-aluminum particles of  $\sim 50$  nm size are added to composite solid propellants based on ammonium perchlorate and hydroxyl-terminated poly-butadiene binder that exhibit plateau burning rate trends and those including burning rate catalysts. The nano-aluminized propellant burning rates are compared with corresponding micro-aluminized and non-aluminized ones in the 1–12 MPa pressure range. The mid-pressure extinction of the matrixes containing the fine-sized ammonium perchlorate particles in the propellant along with the binder is investigated in all the cases to understand the mechanism of plateau-burning. The non-aluminized propellants show plateau burning wherein the mid-pressure extinction occurs in the corresponding matrixes. Plateau burning regime occurs in the micro-aluminized propellants too, but not always at the same pressures as the corresponding non-aluminized propellants. Replacement of micro-aluminum by nano-aluminum increases the propellant burning rate by  $\sim 100\%$  regardless of the other parameters considered in this paper. These burning rates always show low pressure-exponents in the elevated pressure range. On the other hand, the plateau burning rate trends observed in the non-aluminized and micro-aluminized formulations are washed out in the corresponding nano-aluminized formulations. These results show that the nano-aluminized propellant burning rate is controlled by the near-surface ignition and diffusion-limited combustion of nano-aluminum agglomerated to  $\sim 5$   $\mu\text{m}$  in size, at elevated pressures. The increase in plasticizer content in the propellants leads to shift in the plateau burning regime to lower pressures. The increase in nano-aluminum size decreases the burning rate but the opposite effect is observed with micro-aluminum. The burning rate monotonically increases with nano-aluminum content in bimodal aluminized propellants. Addition of micron-sized catalysts does not contribute to burning rate enhancement in nano-aluminized propellants, although they increase the burning rate by  $\sim 100\%$  in non-aluminized and micro-aluminized propellants, as expected. Nano-sized catalysts increase the burning rate by  $\sim 5\%$  in nano-aluminized propellants, however. Agglomeration is observed in self-quenched matrixes with nano-aluminum to the extent of  $\sim 1$ – $5$   $\mu\text{m}$ , but this could still be too small to offer two phase flow losses in rockets.

Singh et al. (2008, 2009a,b,c) studied catalytic properties of several compounds like mono oxide, ferrites, metal alloys etc.

on thermal decomposition of ammonium perchlorate (AP) which is main oxidizer of composite solid rocket propellant (CSPs). Investigation results showed that in presence of nano sized catalyst thermal decomposition of AP enhanced many fold. Due to small size of catalyst and their large surface area extent of adsorption increased which enhanced the percentage of thermal decomposition of AP. Burning rate of CSPs also enhanced in presence of these nano catalysts as compared to their macro size.

### 3.8. $\text{TiO}_2$ in energy application

Titanium dioxide ( $\text{TiO}_2$ ) is a biocompatible and environmentally benign and has been widely used as a pigment (Salvador et al., 2000; Zallen and Moret, 2006; Braun et al., 1992; Reck and Richards, 1999). Recent enormous research efforts dedicated to  $\text{TiO}_2$  materials have been most fascinated with the discovery of the phenomenon of photocatalytic splitting of water on a  $\text{TiO}_2$  electrode by the researchers (Fujishima and Honda, 1972; Fujishima et al., 2000; Tryk et al., 2000). An exponential growth of research activities has been seen in nanoscience and nanotechnology in the past decades (Burda et al., 2005; Chen et al., 2005a,b; Chen and Mao, 2006, 2007; Cozzoli et al., 2006, 2006; Millis and Hunte, 1997; Grätzel, 2000, 2001).  $\text{TiO}_2$  nanomaterials, including nanoparticles, nanorods, nanowires, and nanotubes, are widely investigated for various applications in photocatalysis, photovoltaics, batteries, photonic crystals, sensors, ultraviolet blockers, smart surface coatings, pigment, and paints (Salvador et al., 2000; Zallen and Moret, 2006; Braun et al., 1992; Reck and Richards, 1999; Fujishima and Honda, 1972; Fujishima et al., 2000; Tryk et al., 2000; Burda et al., 2005; Chen et al., 2005a,b; Chen and Mao, 2006, 2007; Cozzoli et al., 2006; Millis and Hunte, 1997; Grätzel, 2000, 2001; Lan et al., 2005; Holland et al., 1998, 1999; Mor et al., 2003; Hwang et al., 2003; Meilert et al., 2005; Pfaff and Reynders, 1999; Hagfeldt and Grätzel, 1995; Linsebigler et al., 1995). Various methods, such as sol-gel, sol, hydrothermal/solvothermal, physical/chemical vapor deposition, electro-deposition, etc., have been successfully used in making  $\text{TiO}_2$  nanomaterials. In the nanometer scale, new physical and chemical properties emerge and they vary with the sizes and shapes of the nanomaterials. The movement of electrons and holes in semiconductor nanomaterials is governed by the well-known quantum confinement, the transport properties related to phonons and photons are largely affected by the size and geometry of the materials, and the specific surface area and surface-to-volume ratio increase dramatically as the size of a material decreases (Burda et al., 2005; Chen et al., 2005a,b; Chen and Mao, 2006, 2007; Cozzoli et al., 2006; Millis and Hunte, 1997). The high surface area brought about by small particle size is beneficial to most  $\text{TiO}_2$ -based devices, as it facilitates reaction/interaction between the devices and interacting media, which mainly occurs on the surface and depends on the surface area. As the size, shape, and crystal structure of  $\text{TiO}_2$  nanomaterials change, not only does surface stability vary, but the transitions between different phases of  $\text{TiO}_2$  under pressure or heat become size dependent as well.

### 3.9. Photochemical activity of $\text{TiO}_2$

Matsunaga et al. (1985) reported the novel concept of photochemical sterilization. Microbial cells were killed

photoelectrochemically with semiconductor powder (platinum-loaded titanium oxide, TiO<sub>2</sub>/Pt). Coenzyme A, (CoA) in the whole cells was photo-electrochemically oxidized and, as a result, the respiration of cells was inhibited. Inhibition of respiratory activity caused death of the cells. *Lactobacillus acidophilus*, *Saccharomyces cerevisiae* and *E. coli* (10<sup>3</sup> cells/ml, respectively) were completely sterilized when they were incubated with TiO<sub>2</sub>/Pt particles under metal halide lamp irradiation for 60–120 min.

Another study of Matsunaga et al. (1988) reported a novel photochemical sterilization system in which *E. coli* cells were sterilized with photoconductor powders (titanium oxide). For sterilization that could be used in practice, it was necessary to separate the TiO<sub>2</sub> powders from the cell suspension. Therefore, semiconductor powders were immobilized on acetylcellulose membranes. We constructed a continuous-sterilization system consisting of a TiO<sub>2</sub>-immobilized acetylcellulose membrane reactor, a mercury lamp, and a masterflex pump. As a result, under the various sterilization conditions examined, *E. coli* (10(2) cells per ml) were sterilized to less than 1% survival when the cell suspension flowed in this system at a mean residence time of 16.0 min under irradiation (1800 microeinsteins/m<sup>2</sup> per s). We found that this system was reusable.

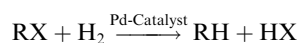
### 3.10. Thin film solar cell

Many nano-structured materials are now being investigated for their potential applications in photovoltaic, electro-optical, micromechanical and sensor devices (Whitesides and Grzybowski, 2002; Duan et al., 2003; McAlpine et al., 2003). Advantage of the benefits is also to make inexpensive and efficient solar cells on a large scale. To this end, nanostructured layers in thin film solar cells offer three important advantages. First, due to multiple reflections, the effective optical path for absorption is much larger than the actual film thickness. Second, light generated electrons and holes need to travel over a much shorter path and thus recombination losses are greatly reduced. As a result, the absorber layer thickness in nano-structured solar cells can be as thin as 150 nm instead of several micrometers in the traditional thin film solar cells (Ernst et al., 2003). Third, the energy band gap of various layers can be tailored to the desired design value by varying the size of nano-particles. This allows for more design flexibility in the absorber and window layers in the solar cell. In particular nano-structured CdS, CdTe and TiO<sub>2</sub> are of interest as window and absorber layers in thin film solar cells (Singh et al., 1995, 2004; Singh and McClure, 2003; Linam et al., 2001; Calixto et al., 2000; Mathew et al., 2000). Singh et al. (2004a,b) used the self-assembly process to fabricate a variety of nano-structured films including CdTe and CdS on ITO-coated glass substrates. In addition nano-porous CdS and TiO<sub>2</sub> films were fabricated on a plastic substrate with a view to making devices on a lightweight, flexible substrate. The results indicated a blue shift in the absorption with an effective band gap of 2.8 eV: This opens the possibility of using nano-crystalline *n*-type CdTe as a window layer in an *n*-CdTe/*p*-CdTe homo junction solar cell. Nano-crystalline CdS films on ITO-coated glass substrates exhibited particle sizes of 15 nm and an effective band gap of 2.98 eV as compared to the 2.4 eV value for the band gap of bulk CdS. This makes nano-crystalline CdS a better window material in an *n*-CdS/*p*-CdTe hetero

junction solar cell. Porous CdS and porous TiO<sub>2</sub> films were deposited on plastic substrates by a self assembly method. Typical pore sizes were 80 and 70 nm, respectively. These can be used in nano-structured solar cell configuration where the pores are filled with a *p*-type absorber material. Due to the nano-structured character of the absorber, the transport path for the light generated electrons in the absorber is reduced. At the same time, the optical path for photon absorption is increased due to multiple reflections.

### 3.11. Waste water treatment

Halogenated organic compounds (HOCs) are among the most widely distributed water pollutants in industrialized countries. These organic molecules play an important role as solvents and additives in different industries such as the pharmaceutical production or in the IT branch. HOCs are mostly hazardous and toxic compounds which have very often a high persistence and may cause serious health problems such as cancer or mutagenic damage. Therefore, a complete destruction of these compounds is aspired or even mandatory. Ordinary wastewater treatment works cannot handle the problem. Thus, high priced and energy-intensive methods still have to be employed to solve this problem. Common practice to dispose of industrial wastewaters contaminated with threshold load of organic solvents and only traces of HOCs is incineration. However, organic compounds such as alcohols could be removed by bacterial treatment in a wastewater treatment plant. The critical component leading to cost-intensive disposal is frequently the HOC. Current detoxification techniques such as adsorption on activated carbon or oxidation of the wastewater components do not lead to an environmentally friendly and economically priced solution. For example huge amounts of activated carbon would be necessary in order to remove HOC traces from water loaded with other sorption-active components. In the case of oxidation, excess amounts of oxidant are required because all reduced water components would be oxidized. The risk derives when insufficient amounts of oxidant are applied, that even more toxic components can occur if the oxidation is not complete. The last and often practiced consequence is an excess-priced incineration. However, the incineration of aqueous waste is a waste of energy. Therefore, for a medium-sized enterprise a decentralized selective dehalogenation treatment of wastewater can give a significant economic advantage. Hildebrand et al. (2008) suggested an idea to detoxify the water by a selective destruction of the HOCs using the method of HDH on palladium-containing nanocatalysts. Detoxification means that persistent HOCs are converted into organic compounds which can easily be removed by biodegradation in a wastewater treatment plant. Reductive hydrodehalogenation reactions are very efficient and selective. That means, only the toxic and harmful halogenated compounds are affected by the catalytic reaction following the presented reaction type.



For this reaction H<sub>2</sub> or a hydrogen source as reducing agents are required. The products are predominantly non-toxic organic molecules and small amounts of HX. There are, however, some exceptions such as benzene formed by dechlorination of chlorobenzene. Palladium containing catalysts in the

form of catalyst pellets are commonly used in fixed bed reactors in technical processes such as hydrogenation. For environmental applications such as ex-situ groundwater treatment, Pd catalysts have been tested already (Lowry and Reinhard, 2000; Mc-Nab et al., 2000). Kopinke et al. (2003) defined the specific catalytic activity  $A_{Pd}$  as measure of the Pd efficiency. Extremely active catalysts for cyclic batch or continuous flow-through reactor applications can be produced on the basis of ferromagnetic nano-sized carrier colloids (magnetite,  $Fe_3O_4$ ) containing only traces of Pd (0.1 wt.%). Nano-sized Pd catalysts have been successfully tested for selective hydrodehalogenation of wastewater pollutants at the laboratory scale. Dehalogenation using Pd on nano-scale supports shows the true inherent activity of Pd clusters which is several orders of magnitude higher than reached in fixed-bed arrangements due to minimized mass-transfer limitations. Magnetite particles are suitable catalyst carriers because of their rather high resistance against milieu parameters. Their magnetism allows the extraction of the nano-particles from the treated water by means of magneto-separation which makes a reuse of the catalyst possible. Alternative H-donor such as formic acid was successfully tested. Beside the study of the opportunities and the high potentials of such catalyst systems, the evaluation of their potential environmental risks is in progress.

Mackenzie et al. (2007) showed two different examples for *ex situ* and *in situ* water treatment using nano-sized materials. Two novel colloidal particles have been developed and tested in initial studies for (i) the *in situ* generation of sorption/reaction barriers based upon zero-valent iron on sorption-active carbon carriers (carbo-iron) for application in subsurface water treatment and (ii) the selective catalytic elimination of halogenated hydrocarbons using Pd on magnetic carriers as agent for *ex-situ* waste water treatment. The common ground for both applications is the utilization of nano-particles for dehalogenation reactions in the aqueous phase in order to minimize mass transport limitation and therefore permit high decontamination rates. These water treatment applications have been selected for presentation in order to show the wide applicability of nano-sized materials in environmental technology. With carbo-iron (20 wt.% Zero-Valent Iron {ZVL}), a novel material is provided which forms stable colloidal solutions up to high concentrations and  $Ca^{2+}$  concentrations. Stabilizers such as polyanionic substances can help to keep the particles mobile under aquifer conditions. Humic acid as a natural product can act as stabilizer; however, carboxymethyl cellulose is able to stabilize much higher particle concentrations of carbo-iron and facilitates long transport distances. Carbo-iron has proved its dehalogenation activity for chlorinated and brominated C1- and C2-hydrocarbons in aqueous solution. Furthermore, the hydrophobic nature of carbo-iron permits its distribution in NAPL phases where dehalogenation can be performed without the application of additives. This is a great advantage over pure nano-sized ZVI, which requires additives for source treatment. Extremely active catalysts for cyclic batch applications can be produced on the basis of ferromagnetic nano-sized carrier colloids containing only traces of Pd (0.1 wt.%). Nano-sized Pd catalysts have been successfully tested for waste water problems at the laboratory scale. Dehalogenation using pure Pd colloids or Pd on colloidal supports shows the true inherent activity of Pd clusters which is several orders of magnitude higher than reached in fixed-bed

arrangements due to minimized mass-transfer limitations. Magnetite particles are suitable catalyst carriers because of their high resistance against milieu parameters. Their magnetism allows a complete extraction of the nanoparticles from the treated water by magneto-separation.

Water treatment using  $TiO_2$  semiconductor as a durable heterogeneous photocatalyst has been the focus of environmentalists in recent years. Liu et al. (2006a,b) developed an inexpensive and highly efficient approach for synthesizing nitrogen-doped  $TiO_2$  with lower band-gap energy that can respond to visible light. Doping on the molecular scale led to an enhanced nitrogen concentration of up to 21.8%. Reflectance measurements showed the synthesized N-doped  $TiO_2$  nanoparticles are catalytically active with the absorbance that extends into the visible region up to 600 nm. The water purification potential of this new class of compound was evaluated by studying the photodegradation of Acid Orange 7 (AO7) and *E. coli*. Experiments were conducted to compare the photocatalytic activities of N-doped  $TiO_2$  nanocatalysts and commercially available Degussa P25 power under identical solar light exposure. N-doped  $TiO_2$  demonstrated superior photocatalytic activities in both chemical compound degradation and bactericidal reactions. The result of this study shows the potential of applying new generations of catalyst for wastewater purification and disinfection.

### 3.12. In environment protection

Sulfate radical-based advanced oxidation technologies (SR-AOTs) are attracting considerable attention due to the high oxidizing ability of SRs to degrade organic pollutants in aqueous environments. Yang et al. (2009) studied current concerns and challenges in SR-AOTs, including (i) need of heterogeneous activation of sulfate salts using transition metal oxides, (ii) nanoscaling of the metal oxide catalysts for high catalytic activity and promising properties with respect to leaching, and (iii) easy removal and recovery of the catalytic materials after their applications for water and wastewater treatments. In this study a novel approach of using Fe-Co mixed oxide nanocatalysts for the heterogeneous activation of peroxy-mono-sulfate (PMS) to generate SRs targeting the decomposition of 2,4-dichlorophenol was introduced. Ferromagnetic  $Co-Fe_2O_4$  composites formed by thermal oxidation of a mixed phase of Fe and Co exhibited significant implications for the efficient and environmentally friendly activation of PMS, including (i) the cobalt species in  $CoFe_2O_4$  are of Co(II), unlike  $Co_3O_4$  showing some detrimental effects of Co(III) on the PMS activation, (ii)  $CoFe_2O_4$  possesses suppressed Co leaching properties due to strong Fe-Co interactions (i.e., Fe-Co linkages), and (iii) Fe-Co catalysts in form of  $CoFe_2O_4$  are easier to recover due to the unique ferromagnetic nature of  $Co-Fe_2O_4$ . In addition, the presence of Fe was found to be beneficial for enriching hydroxyl group content on the Fe-Co catalyst surface, which is believed to facilitate the formation of Co(II)-OH complexes that are vital for heterogeneous PMS activation.

### 3.13. In fuel

Gas to liquids (GTL) process is considered as an alternative process to produce liquid fuels from natural gas due to high oil price. GTL process consists of synthesis gas production,

Fischer–Tropsch synthesis, and product work-up. In GTL process, the capital cost of synthesis gas production is about 60% of total capital cost (Rostrup-Nielsen, 1993; Ross et al., 1996; Aasberg-Petersen et al., 2001; Yagi et al., 2005; Peña et al., 1996; Armor, 1999; Tsang et al., 1995). It is very important to adjust a  $H_2/CO$  ratio for Fischer–Tropsch synthesis. In practical syngas production, representative reforming processes such as steam reforming of methane (SRM), carbon dioxide reforming of methane (CRM) have some drawbacks because both reforming reactions require the additional process to adjust  $H_2/CO$  ratio (Beurden, 2004; Roh et al., 2002, 2004; Chin et al., 2006; Wang et al., 1996). Partial oxidation of methane (POM) can be considered as an alternative due to the suitable  $H_2/CO$  ratio for Fischer–Tropsch synthesis. However, it is difficult to control the POM process due to the hot spot and explosion danger (Ashcroft et al., 1991; Roh et al., 2001a,b; Koh et al., 2007; Song and Guo, 2006). On the contrary, combined steam and carbon dioxide reforming of methane (CSCRM) is a feasible process for the direct control of the  $H_2/CO$  ratio by adjusting the feed ratio of steam and carbon dioxide. Thus, CSCRM is an adequate reforming process to produce syngas for Fischer–Tropsch synthesis (Qin et al., 1996; Jing et al., 2004; Bhattacharyya et al., 1998; Zhang et al., 2004; Choudhary and Mondal, 2006; Jeong et al., 2006). In general, it is necessary to develop economical catalysts with high activity and stability for CSCRM. Ni catalysts have commercially been applied for SRM because they are economical compared to noble metal based catalysts (Sehested, 2006; Pompeo et al., 2005). However, supported Ni catalysts have some problems such as Ni particle sintering and coke deposition, resulting in catalyst deactivation (Oh et al., 2003). To prevent coke formation in SMR, excess steam is usually employed, which results in  $H_2$  enriched syngas (Hou et al., 2006; Roh et al., 2007). However, excess steam cannot be used in CSCRM to adjust a  $H_2/CO$  ratio for Fischer–Tropsch synthesis. Therefore, it is necessary to develop catalysts with high coke resistance for CSCRM. It has been reported that Ni catalyst supported on nano-particles of  $ZrO_2$  could be highly active and stable for CRM (Sehested; 2006). It is also reported that nano-sized Ni–Ce– $ZrO_2$  catalyst could be active and stable in CRM (Roh et al., 2004). Therefore, it is inferred that the crystallite size of Ni and support plays an important role in catalytic activity as well as stability in methane reforming reactions under severe conditions. Very recently, Liu et al. (2006a,b) reported that Ni/MgO– $Al_2O_3$  catalyst exhibited the highest activity as well as stability among supported Ni catalysts. While Kee et al. (2008) investigated the effect of Ni crystallite size and SMSI on the coke resistance to suppress coke deposition. Pre-calcination temperature of the support plays a significant role in determining the crystallite size of both Ni and support and metal to support interaction. With increasing the pre-calcination temperature, Ni crystallite size increases and BET surface area decreases due to the collapse of support. In general, large Ni particles have a weak interaction with support, while highly dispersed Ni particles have a SMSI, resulting in high resistance to coke deposition. As a result, the Ni/MgO– $Al_2O_3$  catalyst pre-calcined at 800 °C exhibits the highest coke resistance due to the smallest Ni crystallite size and SMSI, resulting in the highest catalytic activity and stability. Thus, the Ni/MgO– $Al_2O_3$  catalyst will be a promising catalyst in CSCRM for the GTL process.

### 3.14. Alcohol oxidation

Methanol and ethanol are the most studied alcohols for Direct Alcohol Fuel Cell (DAFC) application (Wasmus and Kuwer, 1999; Vigier et al., 2004a,b; Batista et al., 2004; Xia et al., 1997; Lamy et al., 2004). Use of ethanol as fuel in DAFCs provides many advantages over methanol due to its re-newability, low toxicity, safety, high energy density, and its easy production in great quantities from biomass (Delime et al., 1999; Coutanceau et al., 2008; Wang et al., 1995). The main problems of DAFCs are poor performance of electrocatalysts, especially anode catalysts at lower temperatures and the severe fuel crossover from anode to cathode, which leads to poisoning of cathode catalyst (Arico et al., 2005; Baglio et al., 2007; Lamy et al., 2001). The activity improvement of anode catalysts is helpful to reduce fuel permeation through electrolyte. Pt has been demonstrated as the only active and stable noble metal for alcohol oxidation, particularly in acid medium. However, it is well known that pure platinum is readily poisoned by CO-like intermediates of methanol or ethanol electro-oxidation (Lamy et al., 2000). On the other hand, the high cost of the platinum limits its use. One of the grand challenges in DMFC development is to reduce the usage of Pt precious metal. One approach to cost reduction is to use the Pt-based alloys to reduce the Pt loading. Another effective approach is to increase the utilization efficiency of Pt electrocatalysts by exploring the high surface area supports such as high surface area carbon. Methanol or ethanol oxidation on Pt is only possible at potentials where adsorbed CO and other poisoning intermediates are effectively oxidized, leading to a significant overpotential and hence loss in efficiency. Kadirgan et al. (2009) investigated the effect of Pt–Pd/C nano-sized electrocatalysts on oxidation of alcohols. The experiments confirm that Pt–Pd/C nano-particles synthesized lead to synergistic effect toward methanol and ethanol oxidation, particularly important than that of commercial Pt/C ETEK. Pt–Pd binary catalyst was more active toward oxidation of methanol than ethanol because not only strongly adsorbed intermediate (e.g., CO) but also other oxidation reaction intermediates, such as acetaldehyde and acetic acid may be adsorbed after dissociative chemisorptions of ethanol molecule during electro-oxidation process. Although an enhancement of the reaction kinetic for both alcohols was observed increasing the working temperature, apparent activation energy values were smaller for methanol oxidation than ethanol oxidation reaction on Pt–Pd/C electrode indicating easier oxidation kinetic for methanol.

Recently, there is a growing concern about the damage done to the natural environment due to the human activity. Industry is usually blamed for the introduction of pollutants to the environment. However, the changes in agriculture bring about similar problems. For example, application of fertilizers and pesticides leads to the pollution of soil and ground water. Some of them are resistant to environmental degradation and have the tendency to accumulate in the food chain. Therefore, there is an interest in development of innovative, efficient, cheap and environment friendly techniques for the degradation of these pollutants. Among such poorly exhausting pesticides, organophosphorus insecticides have been most heavily consumed in agriculture and horticulture. Hence, a lot of researches have been engaged in the mineralization technology of organophosphorus insecticides. For example, the method

of high power ultrasonic irradiation is usually used to treat some dyestuff wastewaters owing to its advantages, such as cleanness, high efficiency and non-secondary pollution (Tezcanli-Guyer and Ince, 2003; Ge and Qu, 2003; Ince et al., 2001). As known to all, under the function of ultrasonic irradiation, the dissolved vapors and gases in the liquid become cavitations bubbles and then entrap the organic pollutants, which attain very high temperatures that the organic pollutants are directly decomposed or indirectly oxidized by formed hydroxyl ( $\cdot\text{OH}$ ) radicals during momentary collapse of cavitations bubbles (Suslick et al., 1990; Okitsu et al., 2005; Sivakumar and Pandit, 2001; Pétrier and Suslick, 2000). However, the degradation of organic pollutants by high power ultrasound usually needs lots of energy, costly treated equipment and long reaction time (Taghizadeh and Mehrdad, 2003). Previously, in order to overcome these drawbacks of mere ultrasonic irradiation, the anatase titanium dioxide ( $\text{TiO}_2$ ) powders were used as the sonocatalysts combined with low power ultrasonic irradiation to treat methyl parathion solution (Wang et al., 2006). Because of the slightly narrow energy gap and appropriate adsorbability, the rutile  $\text{TiO}_2$  powder was used after heat treatment as sonocatalyst in this work and satisfying results were obtained. The influences of reaction parameters were established on sonocatalytic degradation of methyl parathion. In addition, both micron-sized and nano-sized rutile  $\text{TiO}_2$  powders were used to compare their catalytic activities. The results indicated that the degradation of methyl parathion sonocatalytically progressed more rapidly in the presence of micron-sized rutile  $\text{TiO}_2$  powder than in the presence of nano-sized rutile  $\text{TiO}_2$  powder, which is different from the case, where micron-sized and nano-sized anatase  $\text{TiO}_2$  powders were used. In the degradation, the  $\text{TiO}_2$  powder was used as sonocatalyst because of its unique photochemical, photostable, inexpensive and non-toxic characters (Karcher et al., 1999; Poullos et al. 1998). Here, the ultrasonic irradiation instead of ultraviolet light was used to degrade the methyl parathion in aqueous solution in the presence of micron-sized and nano-sized rutile  $\text{TiO}_2$  powders. In conclusion, the method of sonocatalytic degradation for organic pollutants is expected to be promising as an inexpensive and environment-friendly technology of wastewater purification with huge industrialization prospect on the basis of further research works. Wang et al. (2007) experimental result showed that the sonocatalytic performance of micron-sized  $\text{TiO}_2$  powder is obviously better than that of nano-sized rutile  $\text{TiO}_2$  powder. The research results demonstrated the feasibilities of sonocatalytic degradation of methyl parathion and other organic pollutants in wastewater. Especially, this method is applicable to the non- and low-transparent wastewater. The degradation of methyl parathion depends on the amount of rutile  $\text{TiO}_2$  catalysts, initial concentration of methyl parathion solution, acidities, temperature and ultrasonic frequency and intensity. The optimal conditions for obtaining high degradation percentage of methyl parathion are considered to be initial methyl parathion concentration of  $50 \text{ mg L}^{-1}$ , micron-sized rutile  $\text{TiO}_2$  catalyst amount of  $1000 \text{ mg L}^{-1}$ , and ultrasonic frequency of  $40 \text{ kHz}$ , output power of  $50 \text{ W}$ , pH 10.0 and at  $20 \text{ }^\circ\text{C}$  for about 80 min.

### 3.15. Nanotoxicology

Several works are reported in the literature in field of nanotoxicology which will be one of the major applications in near fu-

ture. Some of the nanoparticles are used like Silver nanoparticles (Ag-np) are being used increasingly in wound dressings, catheters, and various household products due to their antimicrobial activity. The toxicity of starch-coated silver nanoparticles was studied by AshaRani et al. (2009) using normal human lung fibroblast cells (IMR-90) and human glioblastoma cells (U251). The toxicity was evaluated using changes in cell morphology, cell viability, metabolic activity, and oxidative stress. Ag-np reduced ATP content of the cell caused damage to mitochondria and increased production of reactive oxygen species (ROS) in a dose-dependent manner. DNA damage, as measured by single cell gel electrophoresis (SCGE) and cytokinesis blocked micronucleus assay (CBMN), was also dose-dependent and more prominent in the cancer cells. The nanoparticle treatment caused cell cycle arrest in  $G_2/M$  phase possibly due to repair of damaged DNA. Annexin-V propidium iodide (PI) staining showed no massive apoptosis or necrosis. The transmission electron microscopic (TEM) analysis indicated the presence of Ag-np inside the mitochondria and nucleus, implicating their direct involvement in the mitochondrial toxicity and DNA damage. A possible mechanism of toxicity is proposed which involves disruption of the mitochondrial respiratory chain by Ag-np leading to production of ROS and interruption of ATP synthesis, which in turn cause DNA damage. It is anticipated that DNA damage is augmented by deposition, followed by interactions of Ag-np to the DNA leading to cell cycle arrest in the  $G_2/M$  phase. The higher sensitivity of U251 cells and their arrest in  $G_2/M$  phase could be explored further for evaluating the potential use of Ag-np in cancer therapy.

At present, nanofilaments are not exclusively based on carbon atoms but can be produced from many inorganic materials in the form of nanotubes and nanowires. It is essential to systematically assess the acute toxicity of these newly synthesized materials since it cannot be predicted from the known toxicity of the same material in another form. Magrez et al. (2009) studied the cellular toxicity of  $\text{TiO}_2$ -based nanofilaments in relation to their morphology and surface chemistry. These structures produced by hydrothermal treatment were titanate nanotubes and nanowires with a  $\text{Na}_x\text{TiO}_{2+\delta}$  composition. The cytotoxic effect was mainly evaluated by MTT assays combined with direct cell counting and cytopathological analyses of the lung tumor cells. This work clearly demonstrated that the presence of  $\text{Na}_x\text{TiO}_{2+\delta}$  nanofilaments had a strong dose-dependent effect on cell proliferation and cell death. Nanofilament internalization and alterations in cell morphology were observed. Acid treatment performed to substitute  $\text{Na}^+$  with  $\text{H}^+$  in the  $\text{Na}_x\text{TiO}_{2+\delta}$  nanofilaments strongly enhanced the cytotoxic action. This effect was attributed to structural imperfections, which are left by the atom diffusion during the substitution. On the basis of these findings, it is concluding that  $\text{TiO}_2$ -based nanofilaments are cytotoxic and thus precautions should be taken during their manipulation.

Given the emergence of nanotherapeutics and nanodiagnostics as key tools in today's medicine, it has become of critical importance to define precisely the interactions of nanomaterials with biological systems and to characterize the resulting cellular response. Hutter et al. (2010) reported the interactions of microglia and neurons with gold nanoparticles (GNPs) of three morphologies, spheres, rods, and urchins, coated with poly(ethylene glycol) (PEG) or cetyl trimethylammonium bromide (CTAB). Microglia are the resident immune

cells of the brain, primarily involved in surveillance, macrophagy, and production of cytokines and trophic factors. Analysis by dark-field microscopy and by two-photon-induced luminescence (TPL) indicates that the exposure of neural cells to GNPs resulted in (i) GNP internalization by both microglial cells and primary hippocampal neurons, as revealed by dark-field microscopy and by two-photon-induced luminescence (TPL), (ii) transient toll-like receptor 2 (TLR-2) up-regulation in the olfactory bulb, after intranasal administration in transgenic mice, *in vivo*, in real time, and (iii) differential up-regulation *in vitro* of TLR-2 together with interleukin 1 alpha (IL-1 $\alpha$ ), granulocyte macrophage colony-stimulating factor (GM-CSF) and nitric oxide (NO) in microglia. The study demonstrates that GNP morphology and surface chemistry strongly influence the microglial activation status and suggests that interactions between GNPs and microglia can be differentially regulated by tuning GNP nanogeometry.

### 3.16. Production of hydrogen for fuel cell

The cleanliness of hydrogen and the efficiency of fuel cells taken together offer an appealing alternative to fossil fuels. Implementing hydrogen-powered fuel cells on a significant scale, however, requires major advances in hydrogen production, storage, and use. Splitting water renewably offers the most plentiful and climate-friendly source of hydrogen and can be achieved through electrolytic, photochemical, or biological means. Whereas presently available hydride compounds cannot easily satisfy the competing requirements for on-board storage of hydrogen for transportation, nanoscience offers promising new approaches to this challenge. Fuel cells offer potentially efficient production of electricity for transportation and grid distribution, if cost and performance challenges of components can be overcome. Hydrogen offers a variety of routes for achieving a transition to a mix of renewable fuels.

Aluminum, one of most reactive metals, rapidly corrodes in strong acidic or alkaline solutions but passivates at pH of about 5–9. Czech and Troczynski (2010) has determined that the passivation of aluminum in this range of pH, and in particular in regular tap water, can be substantially prevented after milling of aluminum with water-soluble inorganic salts (referred to as “WIS”), such as KCl or NaCl. Ensuing corrosion of Al in tap water, with accompanying release of hydrogen and precipitation of aluminum hydroxide, at normal pressure and moderate temperatures ( $\sim 55$  °C) is rapid and substantial. For example,  $\sim 92\%$  of the Al in the Al–WIS system when milled for 1 h and  $\sim 81\%$  when milled for 15 min, corrodes in 1 h, with the release of 1.5 mol of hydrogen per each mole of Al consumed in the reaction. Besides gaseous hydrogen, only solid aluminum hydroxides were formed as the reaction byproducts, opening up the possibility of straightforward recycling of the system.

Mahmoodi and Babak Alinejad (2010) work to enhance hydrogen generation rate in aluminum–water reaction by improving the activity of aluminum particles and using the heat released during the reaction. This was accomplished by developing fresh surfaces by milling aluminum particles together with salt. Salt particles not only serve as nano-millers, but also surround activated particles and prevent re-oxidation of bare surfaces in the air. Therefore, the activated powder can be easily stored for a long time. Immersing the powder in warm water, the salt covers are washed away and hydrogen be-

gins to release at a high rate until efficiency of 100% is achieved. The rate of reaction depends crucially on initial temperature of water. Hence, the mass of water was reduced to employ released energy to increase water temperature and, consequently, to increase hydrogen production rate. The optimum value of salt-to-aluminum mole ratio for achieving high activation, air-storage capability and 100% efficiency was obtained to be 2. When immersed in water, at initial temperatures of 55 and 70 °C, the powder lead to average hydrogen generation rate of  $\sim 101$  and  $\sim 210$  ml/min per 1 g of Al, respectively. To increase the rate of corrosion, three different alloys/composites of aluminum were prepared by mechanical alloying and activated with optimum salt-to-aluminum mole ratio. The alloys/composites formed galvanic cells after being immersed in water. In the case of aluminum–bismuth alloy, the average hydrogen generation rate increased to  $\sim 287$  and  $\sim 713$  ml/min per 1 g of Al, respectively.

## 4. Conclusion

The field of nanocatalysis (the use of nanoparticles to catalyze reactions) has undergone an explosive growth during the past decade, both in homogeneous and heterogeneous catalysis. Nanoparticles have a large surface-to-volume ratio compared to bulk materials, they are attractive to use as catalysts. Catalysts daily accelerate and boost thousands of different chemical reactions, and thereby form the basis for the multibillion dollar chemical industry worldwide and indispensable environmental protective technologies. Research in nanotechnology and nanoscience is expected to have a great impact on the development of new catalysts. The detailed understanding of chemistry of nanostructures and the ability to control materials on the nanometer scale will ensure a rational and cost efficient development of new and more capable catalysts for a chemical process.

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