Synthesis of fe doped tio2 nanoparticles

Introduction

The synthesis of nanoparticles with controlled size, crystalline structure and shape has been very keenly inspired by the world of Nano-chemistry. Generally the synthesis methods for nanoparticles can be band together into two categories. The Top Down method and the Bottom Up method. The Top down method involves the division of a solid into smaller portions. This method could involve the process of milling or attrition, chemical methods, and volatilization of a solid followed by condensation of the volatilized components.

The second which is the Bottom Up method of nanoparticle fabrication involves the condensation of atoms or molecular units in a gas phase or in solution. This method is far more prevalent in the synthesis of nanoparticles.

This paper will be specified to methods of synthesis of Fe Doped TiO2 nanoparticles. Several researches have been carried out and papers published about the methods of synthesis of Fe doped TiO2.

Titanium dioxide (TiO2) is broadly acknowledged as very promising photo catalysts in the purification and treatment of polluted water and air. This is mainly because of its high activity, relatively low cost, nontoxicity, and chemical stability. Studies have shown that the efficiency of TiO2 photocatalyst depends greatly on its crystal phase, crystallinity, particle size, surface area and its porous structure. It is therefore the most practical semiconductor choice for many environmental clean-up applications.

Most of the dye pollutants have a threat to the environment and they are most resistant to biodegradation. The dye molecules usually have a high solubility in water. The eï¬„ uents discharged from textile and dye manufacturing industries pose an adverse eï¬€ect on the aquatic life and human health. Remediation techniques generally reduce the problem but do not totally eliminate it. There is a large demand for an eï¬€ective and inexpensive means to degrade dye pollutants into a non-toxic compound.

The technique using metal ion doping is one of the likely methods of shifting the band gap of titania. This is achieved by changing its electronic properties, by the formation of ” shallow traps” in the titania. The metal ion dopants generally modify the properties of titania and therefore act as an electron or hole traps which increase the efficiency of its photocatalytic activity.

Among many metal ions, the doping with iron(III) has been widely researched and used because of its unique electronic structure and its size that is very similar to that of titanium (IV). And the energy level of the Fe4+/Fe3+ couple is only just greater than the titania conduction band and the energy level of the Fe3+/ Fe2+ couple is just above the valance band This useful electronic states of iron ions in titania results in formation of efficient trapping sites for electrons and holes.

The Iron(III)-doped titania photocatalyst have been synthesized by various methods such as wet impregnation, chemical coprecipitation, and sol-gel method.

The physical and photocatalytic properties of various preparations methods vary on the synthetic procedure and post processing conditions.

And the adsorption of organic contaminants onto the surface of the nanosized TiO2 is size-dependent and the particle size is a key factor in photocatalytic decomposition of organic contaminants by nanosized TiO2.

Methods of Synthesis

There are several methods of synthesis that have been researched at practised for doping TiO2 nanoparticles. In this essay I shall be covering most of the methods and the ones largely practiced in more detail. The following are the several methods used for the synthesis Fe doped TiO2 nanoparticles.

- Electrochemical anodic oxidation
- Controlled Hydrolysis
- High Pressure Crystallisation
- Ultrasonic
- Solvothermal
- Sol-gel
- Mechanical Alloying
- Microemulsion
- Plasma Oxidative Pyrolysis
- Reactive Magnetron Sputtering
- Solution Combustion Method
- Metal Organic Vapour Deposition
- Sol-gel method with Hydrothermal treatment

- Homogenous Precipitation – Hydrothermal
- Hydro-Alcohol Thermal
- Impregnation

Sol-gel Method

The sol-gel method is one of the more common methods of synthesis. The sol-gel conventional method uses a hydrolytic route that involves the initial hydrolysis of an alkoxide precursor, which is then followed by constant condensations of the hydrolysed particles forming the gel. This process is generally carried out at room temperature, and the preferred properties of the particles are achieved by controlling the conditions under which the synthesis is carried out.

The following describes the synthesis of Fe doped TiO2 using a modified sol-gel process.

Firstly Iron(III)-doped titania photocatalyst are synthesized using a modiï¬ ed sol-gel process under constant sonication. According to literature for a typical synthesis, 200 ml of titanium (IV) n-butoxide alkoxide precursor in 15 ml ethanol is permitted to undergo hydrolysis at room temperature in the presence of 1 ml of water.

A whitle solution is then formed resulting in the formation of hydrolyzed titania particles. Some ethanolic solution of an inorganic precursor Fe(NO3)3. 9H2O is then added to the hydrolyzed titania solution under constant sonication. Then the reaction mixture is left to condensation under sonication for about 30 min. And as the concentration of the Fe(NO3)3. 9H2O

is increased the reaction mixture colour changes from a milky yellow to a dark milky brown.

Later, the precipitate is washed with ethanol and then centrifuged several times to remove excess Fe3+, NO3 and water. The precipitate is then allowed to dry overnight at a temperature of about 100oC in order to remove any organics that were used during the synthesis.

And it is then heat treated in a crucible for up to 5 hours to convert the shapeless titania into crystalline anatase form. The temperature should be kept at 450 oC so as to avoid the development of rutile phase.

Finally the samples are ground into a ï¬ ne powder and are kept in the oven at about 100 oC for further improvement in shape.

UV-Vis absorption spectra of titania and iron(III)-doped titania with increasing amounts of iron content before heat treatment is shown in Figure 1. It can be seen that the iron(III)-doped titania samples show a relatively sharp band-gap transition typical of semiconductors and does not show any absorption characteristic of isolated iron oxide phases in the visible region.

An according to Zhang and Banfied, (2005), by heating the amorphous TiO2 in air, a large quantity of anatase nano-sized TiO2 with average particle size between 7 to 50 nm can be obtained.

Impregnation Method

Another method of synthesis widely used is the impregnation method. In this type of synthesis the doped samples are prepared by the wet impregnation method.

An aqueous solution of TiCl3 with ammonia is added to titanium hydroxide resulting in a precipitation reaction. The white precipitate formed is then washed repeatedly so as to remove residual ions of Cl−. This is then dried for 24 hours at 100oC and finally heated in air for 24 hours at 500 oC.

The TiO2 is then impregnated with an aqueous solutions of Fe(NO3)3. 9H2O. This is then lest to stand at room temperature for 24 hours, during which the water was evaporated by heating the samples to 100oC.

Finally the dried solids are manually grounded with the aid of an agitated motor and calcined in air at 500 oC for 24 hours.

The optimum particle size obtained from this method is between 2 and 4 nm

Hydrolysis Method

The method involves the preparation by a hydrolysis of a Ti precursor in the presence of a Fe(III) ions containing aqueous solution. This is shown graphically by the scheme on figure 2. And figure 3 shows a more improved method.

The samples appear as yellowish powders which can be suspended in water, methanol or in a mixture of both solvents to attain a colloidal suspension transparent in the visible region.

Preparation of iron(III) doped TiO2 nanoparticles.

Solvothermal

The solvothemal method is summarised in the scheme below on figure 4.

200 ml 1, 4-butanedial in a 250 ml flask

Stirring

Addition of TTIP 0. 1mol

Addition of Ferric Nitrate 0. 001mol

Stirring for 1 hr until homogeneous gel

Solvothermal treatment at 300oc for 1h in autoclave (Pressure= 20 atm) – Figure 4

Cooling to room temperature

Separation powder from solution by centrifuge

Washing powder with acetone at 3 times

Drying at 100oc for 24hrs

TiO2 and Fe/Ti oxide powders (weight= 10mg)

The nanosized TiO2 can be produced through the solvothermal method with or without the support of surfactants,. For an example, a nanosized TiO2 with a diameter and length in the ranges of 3 to 5 nm and 18 to 25 nm can be synthesized with the aid of surfactants

Metal Organic Chemical Vapour Deposition

Titanium dioxide (TiO2) nanoparticles can be prepared by a process known as Metal Organic Chemical Vapour Deposition (MOCVD).

Different amount of iron (Fe) dopant was introduced inside the MOCVD reactor along with the precursor to produce different Fe dopant concentrations of TiO2nanoparticles.

The MOCVD setup consists of stainless steel gas flow lines, mass flow controllers, a bubbler and a quartz tube (52 mm o. d. and 800 mm long) in a split tube furnace as the reactor. The heating zone was 300 mm long. The precursor, titanium (IV) butoxide (TBOT) obtained from Aldrich was used as received. The TBOT precursor was stored in a stainless steel bubbler located on a hot plate and maintained at 175°C. To produce different Fe dopant concentration of TiO2nanoparticles, different amount of Fe precursor which was ferrocene (0. 005, 0. 01, 0. 03 and 0. 05 g) was mixed directly with 20 mL TBOT precursor inside the bubbler. The quartz tube was purged by nitrogen (400 mL min-1) during the initial heating step towards reaching the desired deposition temperature (400 and 700°C). Once the reaction temperature was achieved, the precursor was introduced into the quartz tube using nitrogen as the carrier gas (400 mL min-1) along with an oxygen feed (100 mL min-1). Undoped and Fe-doped TiO2nanoparticles would be thermophoretically deposited inside the quartz tube upon thermal decomposition of the precursor gas. After 3 h of reaction time, the flow of the precursor gas and the flow of the oxygen gas inside the reactor were stopped by switching off the carrier gas and oxygen gas valves. The reactor was allowed to cool to room temperature under 400 mL min-1 nitrogen flow. The nanoparticles were then collected from the quartz tube wall using a spatula and kept in a small container.

Figure 6 shows a TEM micrograph (left) and respective nanoparticle size distribution histograms (right) for TiO2 nanoparticle samples deposited by MOCVD at different temperatures.

For 400oC – 0. 01g of Fe dopant, Mean Particle Size = 32. 92nm

For 400oC – 0. 05g of Fe dopant, Mean Particle Size = 30. 53nm

For 700oC – 0. 01g of Fe dopant, Mean Particle Size = 9. 98nm

For 700oC – 0. 05g of Fe dopant, Mean Particle Size = 9. 71nm

Nanosized TiO2 with a diameter of 50 to 100 nm can also be synthesized by the MOCVD method using titanium tetraisopropoxide as the precursor.

Hydrothermal

Hydrothermal method is generally carried out in a steel pressure vessel called an autoclave with or without aTeflon (poly-tetrafluoroethylene) liner. This is carried out under controlled temperatures and pressures in the presence of aqueous solution. There are many advantages associated with this method, such as it yields a high purity nanosized TiO2 at comparatively faster rates under slightly elevated water temperature and vapour pressure with the lowest possible contamination. The moderate temperatures that are used in this method of preparation greatly encourage reduced energy cost and improve the reactivity of the nanosized TiO2.

TiO2 is obtained by the hydrothermal treatment of peptized precipitates of a titanium precursor with water.

The precipitate is prepared by adding 0. 5M isopropanol solution of titanium butoxide into deionized water and then they were peptized at 70oC for 1 hour in the presence of tetraalkylammonium hydroxides.

Then it is treated at 240 oC for 2 hour and is followed by filtration to obtain the TiO2 powder.

The powder is then washed with deionized water and dried at 60oC. The particle size can be decreased with increase of alkyl chain length.

Nanosized TiO2 in the range from 25 to 45 nm of particle size can be obtained by the hydrothermal reaction of titanium alkoxide in an acidic alcoholwater solution.

Application

TiO2 nanosize particles have gained a largely significant interest due to their special properties and have attained a great importance in several technological applications such as photocatalysis, sensors, solar cells and memory devices.

Iron doped TiO2 have the following applications,

Polypropylene packings, coated with the prepared N-Fe co-doped TiO2 nanoparticles, were used as a heterogeneous catalyst for the treatment of micro-polluted source water.

Iron-doped photocatalytic TiO2 sputtered coatings on plastics for self-cleaning applications.

Iron (III)-doped titania is stable, inexpensive photocatalyst with activation in the visible spectral range that can be used for water purification applications.

Optical Properties

Figure 7: Points of Zero charge of the doped samples verses the amount of metal content.

The figure 7 above shows the points of zero charge of the doped samples verses the amount of metal content. As we can see from the figure the pzc changes depending on the dopant metal and metal content per mole%.

Generally, the main objective of doping the nanosized TiO2 with metal ion is to induce a batho-chromic shift, which is decrease of the band gap or introduction of intra-band gap states, resulting more visible light absorption

For an example, an Fe doped TiO2 film prepared by sol-gel dip coating showed improvement in the decomposition of methyl orange. This was possible by the shift in optical absorption of the catalyst in visible region by Fe doping.

Nanosized TiO2 will only absorbs UV light below 400 nm, but Fe doped TiO2 absorbs UV and portion of visible energy hence there is increase in photocatalytic activity.

Doping TiO2 with transition metals such as Fe, V and Cu makes it active higher in photocatalytic conversions. This is explained by the ability of the modiï¬ ed titania samples to reduce the band gap energy value and the

recombination rate of the pair electron-photoinduced hole under sunlight radiation compared to that in the case of pure TiO2

The movement of λ towards the red light area will decrease in the order, V> Cr> Mn> Fe> Ni

Spintronics

Conventional electronic devices depend on the transport of electrical charge carriers which are the electrons in a semi-conductor such as silicon. There is a great interest and research to exploit the ‘ spin’ of the electron in addition to its charge to create a significant new generation of ‘ spintronic’ devices that would be more smaller, more versatile and robust than the ones currently in the market.

Information is stored (written) into spins as a particular spin orientation (up or down)

All spintronic devices follow a simple scheme as shown below.

The spins, being attached to mobile electrons, carry the information along a wire.

The information is read at a terminal.

The spin orientation of the conduction electrons are found to survive for a comparatively long time. i. e nanoseconds, compared to the tens of femtoseconds during which electron momentum decays.

This makes the spintronic devices particularly attractive for memory storage and for the use in magnetic sensors applications.

And eventually be applied for quantum computing where electron spin would represent a bit, which would be called a qubit of information.

The following figure 2 shows the concepts and applications of this technology. Spintronics is also gained attention in semiconductor fields such as spin-FET, spin transistor, spin quantum computer, magnetic semiconductors devices etc. However, these research fields are in basic stage at present.