Introduction and Object of Investigation

IA. Introduction

Growing water demand and increasing contamination remain significant challenges worldwide. Current water treatment processes to remove organic contaminants such as membrane filtration, activated carbon adsorption, biological treatment and advanced oxidation processes are often energy and capital intensive, **(Nakata et al. 2013; Gumy et al. 2006; Danion et al. 2004).**

Photocatalysis is an attractive technology because it can use solar energy to degrade organics and inactivate pathogens. Photocatalytic oxidation operates at ambient conditions without high temperature or high pressure, and many recalcitrant organic contaminants can be degraded without addition of chemical oxidants, (**Elbanna et al. 2016; Wang et al. 2015; Ismail et al. 2015; Narayanan et al. 2005; Torrell et al. 2010).**

ZnO-based photocatalytic process has shown a great potential as a low-cost, non-toxic, stable chemical structure, Eco friendly and sustainable treatment technology to remove various organic dyes in sewage to overcome the shortcomings of the conventional technologies, **(Faisal et al. 2015; Zhou et al. 2013;Klubanuan et al. 2016; Zhang et al. 2015; Chang et al. 2016).**

Although, the low quantum yield and the limited photo-responding range, which is mainly caused by its large band gap, still limit its utilization and commercialization. It should be emphasized that the photocatalytic reactivity of ZnO is improved by incorporation of noble metals such as Pt, Ag, or Au due to the role of these metals in improving electron–hole separation and promoting the interfacial electron transfer process that in turn increases the surface reactivity, **(Ren et al. 2010; Chen et al. 2016; Lee et al. 2015; Senthilraja et al. 2015).**

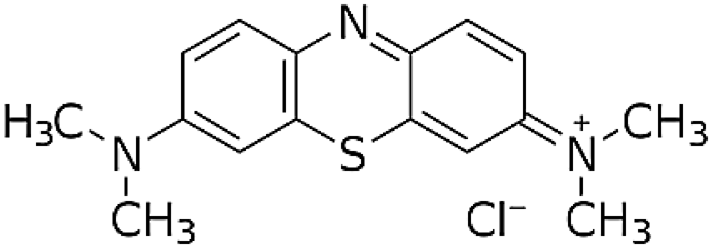
Au is a popular choice that is considered as a key material for newer technologies in the twenty-first century because of its high chemical stability and its ability to generate surface plasmons at the desired wavelength. In recent years, there has been an increasing interest in catalysis by gold nanoparticles which are active in the selective and the non-selective oxidation of hydrocarbons, in hydrogenation reactions, and in pollution control. Au nanoparticles dispersed on TiO_2 surface exhibit extraordinary high activity for photocatalytic degradation of undesirable chemical contaminants. It has been the focal point of numerous investigations, particularly because of the reduction of hole–electron recombination in Au–TiO_2 composites. In earlier studies, Au–TiO_2 composite powders were widely investigated. However, one major drawback, i.e. large cost of separating Au–TiO_2 powder from water after treatment, hinders the practical application. To overcome this obstacle, many investigations are oriented towards immobilization of Au–TiO_2 composites on various supports. The adjustment of synthesis of Au/TiO_2 composite samples will extend its technological application and improve its photocatalytic efficiency. Sol-gel method had proven to be a powerful method for production of nanoparticles. This method has many advantages over other production techniques including ease of processing, control over the composition and purity and homogeneity of the obtained materials. Indeed, the existence of surfactant as pore directing agent will be a key factor in tailoring the size and shape of the catalyst, **(Sharma et al, 2016).**

Moreover, Au can protect ZnO and TiO_2 from light corrosion due to the high stability under UV- irradiation. In fact, gold in its bulk state is regarded as a noble metal and is very unreactive because of its completely filled d-band, **(Lu et al. 2016).**

However, at nanoscale, it is proved to be an important material for catalysis owing to its shape, size, and crystal structure arrangement. The design of the composite material is expected to extend the photoexcitation response to visible region and boost the hot electron injection from the Au nanocrystals into the conduction band of ZnO and TiO_2 leading to a considerably enhanced photocatalytic reactivity of the material under ultraviolet and visible light. Various recent works have been devoted to investigate the influence of gold size and structure, incorporated on zinc oxide surface, on the photocatalytic degradation of organic pollutants. It was generally accepted that gold particle size and shape are considered the key factors that significantly influence the catalytic efficiency of zinc oxide. Many synthetic routes and strategies have been developed to yield a wide diversity of materials of various frameworks with different chemical compositions and pore structures. Sol–gel synthesis approach is considered a promising method that produces highly homogeneous, pure, and strong materials with great compositional flexibility. Agglomeration of particles during the sol–gel route or through calcinations progress is considered a negative factor that restricts the development of nanoparticles and limits their applications in many industrial fields. Surfactants or block polymers are usually involved in the synthesis of various metal- and metal oxide nanoparticles, where they only act as stabilizers or protecting agents. PVP is considered a powerful non-toxic template that can be involved in manipulating metal nanoparticles due to its large hydrocarbon chain that can disperse between metal oxide nanoparticles and prevent their agglomeration. The novelty of the present work is related with the simple and straightforward preparation method for Au/ZnO and Au/TiO_2 nanoparticles by sol-gel route using PVP as structure and pore directing agent and microwave method. The proper adjustment of the preparation route is concerned with anchoring gold nanoparticles on the top of the pore system and prevents their agglomeration on the catalyst surface. The influence of the existence of metallic Au nanoparticles on the structural, morphology, crystalline, and photocatalytic features of the solid catalyst on the degradation of methylene blue as organic pollutant model dye was investigated. The nature of the reactive species that responsible for dye degradation was investigated using various scavengers, (**Ismail et al. 2016; Lee et al., 2015).**

IA.1 Methylene blue (MB)

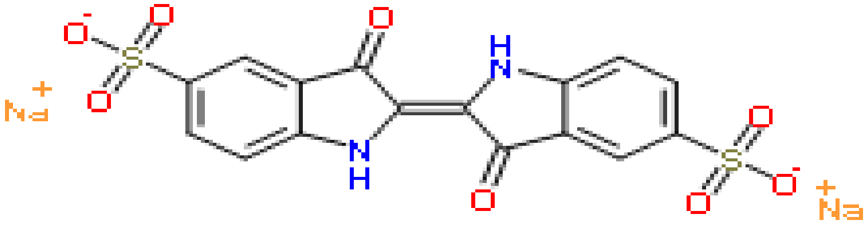
Methylene blue (or MB) is classified as cationic dye with the molecular formula $C_{16}H_{18}N_3SCl$. At room temperature, it appears as a solid, odorless, dark green powder that yields a blue solution when dissolved in Water.



Many manufacturing industries such as paper, plastics, cosmetics, textile and food use dyes for colouring their products. The discharge of effluents from these industries contain large amount of dyes, not only damage the aesthetic nature of receiving water bodies, but also may be toxic to aquatic life. Methylene blue (MB) is considered cationic dye, has wide applications which includes colouring paper, dyeing cottons, wools, silk, leather and coating for paper stock. Although methylene blue is not strongly hazardous, it can cause some harmful effects, such as heartbeat increase, vomiting, shock, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans the treatment of effluents containing this dye is of great interest due to its harmful impacts on receiving waters, (**Yi and Zhang, 2008**).

IA.2 Indigo carmine dye

Indigo carmine, or 5,5′-indigodisulfonic acid sodium salt, is an organic salt derived from indigo by sulfonation, which renders the compound soluble in water. It is approved for use as a food colorant



Several million tons of different types of synthetic dyes are manufactured every year across the world. The characteristic features of the synthetic dyes can be altered by substituting a suitable functional group to the dye. Textile, paper and pulp, food processing and technology, dye sensitized photovoltaics, leather processing and tanning industries utilize large quantities of synthetic organic dyes as colourants. During the synthesis and application of dyes, large quantities of untreated dyes are discharged into the environment. Indigo carmine is one of the most common dyes used in textile, medical and pharmaceutical applications. Discharge of indigo carmine into the environment is hazardous and causes skin related diseases, affects the cornea and exhibits cytotoxicity. It has been found that a majority of the dyes cannot be practically treated effectively prior to their release into the environment, (**Barka et al, 2008; Donaldson and Khan, 2009).**

IA.3 ZnO nanoparticles

Zinc oxide (ZnO) is a wide band gap (3.37 eV) semiconductor with a high-exciton binding energy of 60meV. Because of its unique properties, researchers have studied its potential applications in optoelectronic devices, field emitters, solar cells, sensors and transparent electrodes. Many types of one-dimensional (1D) ZnO nanostructures, such as nanorods, nanowires, nanobelts and nanotubes, have been synthesized. Primary synthesis methods include chemical vapor deposition (CVD), metal organic CVD, thermal evaporation, the template method, electrochemical deposition and the hydrothermal method. However, these methods involve a strictly controlled synthesis environment, complicated procedures, and expensive equipment. In addition, high-temperature synthesis processes consume more energy. Using catalysts to grow aligned ZnO nanorods may leave some catalyst impurities into the nanostructures, possibly contaminating the purity of ZnO nanorods and influencing their properties. Another method of fabricating 1D ZnO nanostructures is the polymer-assisted method, (**Hu et al, 2003; Park et al, 2005; Zhang et al, 2005; Zheng et al, 2002**).

Tao et al (2004), successfully prepared ZnO nanorods using polyvinyl pyrrolidone (PVP) and zinc acetate using a complex process and a long reaction time. High-purity single crystal ZnO nanowires were synthesized by the thermal decomposition of zinc acetate dihydrate at 300°C in air for 3h without a catalyst. The zinc acetate dihydrate was characterized by thermogravimetric-differential scanning calorimetry and mass spectrometry (TG–DSC–MS) to determine the thermal decomposition and crystallization temperature.

3D flower like ZnO microstructures composed of nanosheets have been prepared on a large scale through a sol gel-assisted hydrothermal method using $Zn(NO3)_2$ $6H_2O$,citric acid, and NaOH as raw materials .The product has been characterized by X-ray powder diffraction(XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and scanning electron microscopy(SEM). The optical properties of the product have been examined by room temperature photoluminescence (PL) measurements. A possible growth mechanism of the 3D flower-like ZnO is proposed based on the results of experiments carried out for different hydrothermal treatment times. Experiments at different hydrothermal treatment temperatures have also been carried out to investigate their effect on the final morphology of the ZnO. The photocatalytic activities of the as-prepared ZnO have been evaluated by photodegradation of reactive blue 14 under ultraviolet (UV) irradiation. The experimental results demonstrated that self-assembled 3D flower-like ZnO composed of nano sheets could be obtained over a relatively broad temperature range (90-150^{o}C) after 17h of hydrothermal treatment. All of the products showed good photocatalytic performance, with the degree of degradation of KGL exceeding 82% after 120 Min. In particular the sample prepared at 120^{o}C for 17h exhibited superior photocatalytic activity to the ZnO samples and commercial ZnO, and it almost completely degraded a KGL solution within 40min , (**Zhao et al, 2014**).

Due to various applications of metal oxide nanoparticles in research and health-related applications, metal oxide nanoparticles are increasingly being developed through cheaper and more user-friendly approaches. **Khan et al (2014),** reported a simple route to synthesize zinc oxide nanoparticles (ZNPs) by a sol–gel method at near-room temperatures 25°C, 35°C, 55°C, and 75°C. The results are analyzed by X-ray diffraction, scanning electron microscopy with energy-dispersive X-ray spectroscopy, and ultraviolet-visible absorption spectroscopy. The effect of different temperature conditions (25°C–75°C) on the particle sizes (23.7–88.8 nm), pH levels (11.7–11.9), and morphologies (slender needle–broad arrow) of flower-shaped ZNP colonies is studied. The values of λ_{max} (293–298 nm) suggest that ZNPs prepared at 55°C are the most effective ultraviolet B absorbers, and that they can be used in sunscreens. Highly significant antimicrobial activity against medically important Gram-positive (Staphylococcus aureus) and Gram-negative (Escherichia coli) bacteria and fungi (Candida albicans) by these ZNPs was also revealed. As S. aureus and C. albicans are responsible for many contagious dermal infections such as abscesses, furuncles, carbuncles, cellulitis, and candidiasis, we can postulate that our fabricated ZNPs may be useful as antimicrobial agents in antiseptic creams and lotions for the treatment of skin diseases.

Fabrication of photocatalysts and photoreactors for treatment of industrial effluents has become vital to harness solar energy for environmental cleanup. Treatment of dye industry effluent by heterogeneous photocatalysis with prepared nano ZnO in falling film photoreactor under natural solar light has been investigated by . Different weight proportions of slurry comprising fevicol and homemade ZnO were prepared and the fevicol-ZnO (F-Z) film on acrylic sheet was obtained by brush coating. Coating of ZnO with 10 wt% fevicol was found to be more adherent and efficient for dye degradation. This F-Z catalyst in the falling film photoreactor was tested for the treatment of dye effluent. F-Z catalyst prepared from nano-ZnO is more efficient than the catalysts made by commercial ZnO and TiO_2-P25. The effects of operational parameters such as the amount of F-Z, effluent concentration, and initial pH on treatment process by F-Z coating as well as by suspended nano-ZnO slurry have been analyzed. Nano-ZnO is advantageous as its maximum efficiency occurs at neutral pH of 7. This pilot scale solar photocatalytic process can be widely applied at industrial scale.

IA.4 TiO_2 nanoparticles

In recent years, investigations of the photocatalytic application of TiO_2 and its composite material are intriguing interest, due to the small crystal size, high specific surface area and highly porous structure of mesoporous titanium dioxide. Many researchers worked on the TiO_2 photocatalytic oxidation of pesticides and phenolic compounds and degradation of organic dyes in wastewater treatment. Also, its mechanism and activity in presence of UV light have been reviewed, (**Ismail et al., 2015; Ahmed et al., 2011).**

TiO_2 nanoparticles was synthesized by **Dhavalkumar et al, 2016** via microwave assisted method in a short time (~10 minutes) to be used as photoanode of dye-sensitized solar cell giving large specific surface area and high dye loading compared with commercial P25 TiO_2 nanoparticles.

Nano-needle titania was fabricated from sol–gel reaction using titanium butoxide (TBO) as titania precursor and acetic acid (HAc). The wet gel after the sol–gel reaction was dried in supercritical carbon dioxide at 313 K and 10.4 MPa for the production of titania powder. The minor-axis of the nano-needles were measured by a scanning electron microscope and evaluated with respect to the effect of the initial molar ratios of HAc to TBO and reaction time in the sol–gel reaction process. A higher molar ratio of HAc in the sol–gel reaction results in a smaller minor axis of the nano-needle. The minor-axis of the titania nano-needle increases with increasing sol–gel reaction time. From these results, the minor-axis size of titania nano-needle could be controlled by the molar ratios of HAc to TBO and reaction time in the sol–gel reaction. The nano-needle titania was also applied to the fabrication of a thin film by a casting and solvent evaporation method. The surface roughness of the titania thin film from the nano-needle with various minor-axis was evaluated and compared with that from the nano-sphere titania. A smaller minor-axis of the nano-needle titania resultsin a larger roughness of the surface on the thin film. It is found that the roughness of the nano-needle film was larger than that using the nano-sphere, (**Shimoyama and Sugamura, 2016).**

Anatase TiO_2 nanoparticles with high surface area has a great importance in the field of energy materials. **Joshi and prasath et al (2016),** reported low temperature and rapid synthesis of direct anatase phase mesoporous TiO_2 by microwave (MW) assisted sol-gel process for the application in Dye Sensitized Solar Cell (DSSC). Highly stable and monodisperse TiO_2 nanoparticles are synthesized by varying parameters like reaction time, temperature, catalyst concentration, etc. The synthesized TiO_2 nanoparticles were characterized by Dynamic Light Scattering (DLS), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Brunauer-Emmett-Teller (BET) analysis and Raman analysis. The average particle size of TiO_2 nano-aggregates (TiO_2-NAgs) of ~300-400 nm with the surface area ~135 m^2/g, and the average pore-size of 2-4 nm were observed. The XRD data found to be in good agreement with standard JCPDS, which clearly confirms anatase phase of TiO_2. Photovoltaic property of the DSSC fabricated using TiO_2 nanoaggregates were studied and compared with the standard P25 TiO_2 nanoparticles. Power Conversion Efficiency (PCE) of 6.16% has achieved for the DSSCs fabricated with TiO_2-NAgs as photoanode as compared to 4.36% observed for DSSCs fabricated using P25 TiO_2 nanoparticlesas photoanode.

A simple in-situ synthesis of reduced graphene oxide (RGO) supported TiO_2 nanostructures by microwave assisted reduction of graphene oxide (GO) in the presence of TiO_2 is discussed. The prepared sample (RGO-TiO_2) was characterized by X-ray diffraction spectroscopy, Raman