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Uses of Nanoparticles in Photo Catalysis

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Abstract – The aim of this review paper is to give an overview of the development and implications of nanotechnology in photo catalysis. The topics covered include a detailed look at the unique properties of nanoparticles and their relation to photo catalytic properties.

Keywords: Nanoparticles, Quantum Size, Photo catalysis, Dopants, Sensitization, Nano Crystalline Films

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INTRODUCTION

Organic chemicals which may be found as pollutants in wastewater effluents from industrial or domestic sources must be removed or destroyed before discharge to the environment. Such pollutants may also be found in ground and surface waters which also require treatment to achieve acceptable drinking water quality (Lindner, et. al., 1995). The increased public concern with these environmental pollutants has prompted the need to develop novel treatment methods (Zeltner & Anderson, 1996) with photo catalysis gaining a lot of attention in the field of pollutant degradation. Much of the natural purification of aqueous system lagoons, ponds, streams, rivers and lakes is caused by sunlight initiating the breakdown of organic molecules into simpler molecules and ultimately to carbon dioxide and other mineral products. There are various natural sensitizers that accelerate the process. The utilization of 'colloidal semiconductors' and the introduction of catalysts to promote specific redox processes on semiconductor surfaces were developed in 1976 (Kalyanasundaram, 1983). Since then, laboratory studies have confirmed that naturally occurring semiconductors could enhance this solar driven purification process (Matthews, 1993). The photo catalytic detoxification of wastewater is a process that combines heterogeneous catalysis with solar technologies. Semiconductor photo catalysis, with a primary focus on TiO_2, has been applied to a variety of problems of environmental interest in addition to water and air purification. The application of illuminated semiconductors for degrading undesirable organics dissolved in air or water is well documented and has been successful for a wide variety of compounds (Hoffmann, et. al., 1995).

Organic compounds such as alcohols, carboxylic acids, amines, herbicides and aldehydes, have been photo catalytically destroyed in laboratory and field studies. The photo catalytic process can mineralize the hazardous organic chemicals to carbon dioxide, water and simple mineral acids (Ahmed & Ollis, 1984).

Many processes have been proposed over the years and are currently used to remove organic toxins from wastewaters. Current treatment methods for these contaminants, such as adsorption by activated carbon and air stripping, merely concentrate the chemicals present, by transferring them to the adsorbent or air, but they do not convert them into non-toxic wastes. Thus, one of the major advantages of the photo catalytic process over existing technologies is that there is no further requirement for secondary disposal methods.

PHOTO CATALYSTS

An ideal photo catalyst should be stable, inexpensive, non-toxic and, of course, highly photoactive. Another primary criteria for the degradation of organic compounds is that the redox potential of the H_2O/ •OH couple ($OH^- \rightarrow {}^{\bullet}OH + e^-$; $E^0 = -2.8$ eV) lies within the bandgap of the semiconductor (Hoffmann et al., 1995). Several semiconductors have bandgap energies sufficient for catalyzing a wide range of chemical reactions. These include TiO_2, WO_3, $SrTiO_3$, α-Fe_2O_3, ZnO and ZnS.

TiO_2, the semiconductor most thoroughly investigated in the literature, seems to be the most promising for photo catalytic destruction of organic pollutants. This semiconductor provides the best compromise between catalytic performance and stability in aqueous media. The anatase phase of titanium dioxide is the material with the highest photo catalytic detoxification.

Binary metal sulphide semiconductors such as CdS, CdSe or PbS are regarded as insufficiently stable for catalysis, at least in aqueous media as they readily undergo photo anodic corrosion. These materials are also known to be toxic.

The iron oxides are not suitable semiconductors as they readily undergo photocathodes corrosion . The band gap for ZnO (3.2 eV) is equal to that of anatase.

ZnO however, is also unsta- ble in water with $Zn(OH)_2$ being formed on the particle surface. This results in catalyst deactivation.

NANO PHOTO CATALYSTS

Nano crystalline Photo catalysts are ultra-small semiconductor particles which are a few nanometers in size. During the past decade, the photochemistry of nano semiconductor particles has been one of the fastest growing research areas in physical chemistry. The interest in these small semiconductor particles originates from their unique photo physical and photo catalytic properties.

Nano sized particles, with diameters ranging between 1 and 10 nm, possess properties which fall into the region of transition between the molecular and the bulk phases (Bahnemann, et. al., 1993). In the bulk material, the electron excited by light absorption finds a high density of states in the conduction band, where it can exist with different kinetic energies. In the case of nanoparticles however, the particle size is the same as or smaller than the size of the first excited state. Thus, the electron and hole generated upon illumination cannot fit into such a particle unless they assume a state of higher kinetic energy.

ACTIVITY OF NANO-PHOTO CATALYSTS

Size quantization in semiconductor particles leads to drastic changes in numerous important properties of the material. Firstly, size quantization affects the electronic properties of the semiconductor particle, with the ultra- small crystallites composed of a few molecular units maintaining their discrete HOMOs (Highest Occupied Molecular Orbitals) and LUMOs (Lowest Unoccupied Molecular Orbitals) . This in turn affects charge-carrier dynamics. Secondly, in the Q-size regime, the chemical and physical properties, which are related to electronic properties, strongly depend on the size of the nanoparticles.

One of the main advantages of the application of Q-sized particles is the increase in the bandgap energy with decreasing particle size. As was mentioned earlier, as the size of a semiconductor particle falls below the critical radius, the charge carriers begin to behave quantum mechanically and the charge confinement leads to a series of discrete electronic states. As a result there is an increase in the effective band gap and a shift of the band edges. Thus by varying the size of the semi- conductor particles, it is possible to enhance the redox potential of the valence-band holes and the conduction- band electrons.

However, the solvent reorganization free energy for charge transfer to a substrate remains unchanged. The increasing driving force and the unchanged solvent reorganizational free energy are expected to lead to an increase in the rate constants for charge transfer at the surface. Thus, the use of size-quantized semiconductor particles may result in increased photo activity for systems in which the rate-limiting step is interfacial charge transfer.

Hence Nano sized semiconductor particles can possess enhanced photo redox chemistry, with reduction reactions, which might not otherwise proceed in bulk materials, being able to occur readily using sufficiently small particles. Another factor which could be advantageous is the fact that the fraction of atoms that are located at the surface of a nanoparticle is very large. Q-sized particles also have high surface area to volume ratios, which further enhances their catalytic activity. One disadvantage of Nano sized particles is the need for light with a shorter wavelength for photo catalyst activation. Thus a smaller percentage of a polychromatic light source will be useful for photo catalysis.

Fu, et. al., 1997, demonstrated that there exists an optimal particle size in Nano crystalline TiO_2 systems for maximum photo catalytic efficiency. In their experiments which involved the decomposition of chloroform, they observed an improvement in activity when the particle size was decreased from 21 to 11 nm, but the activity decreased when the size was reduced further to 6 nm. They concluded that for this particular reaction the optimum particle size was about 10 nm.

CONCLUSIONS

Considering the topics covered in this review, it is evident that the emergence of nanotechnology is bound to have significant implications in the research field of photo catalysis. The nanostructure their remarkable properties will prove invaluable in the development of novel Photo catalysts and the enhancement of existing ones. In areas such as doping, coupling, capping and sensitizing, benefits have already been seen with enhanced photo catalytic and optical properties.

Secondly, the use of Nano crystalline thin films in electrochemically assisted photo catalytic processes is another area where nanoparticles will be very useful. Finally, the use of nanoparticles for providing mechanistic information will continue to make significant contributions in enhancing the understanding of photo- initiated processes in semiconductor materials.

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