

International Journal of Research Publication and Reviews

Journal homepage: www.ijrpr.com ISSN 2582-7421

A Brief Note On Properties And Classification Of Nanomaterials With Their Significant Applications In Photocatalysis

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ABSTRACT:

In recent decades, water environment has been deteriorating owing to the rapid urbanization, industrialization and population. Great volumes of wastewater polluted with organic dye pollutants and microorganisms are discharged into the water bodies not only creating a serious danger to the aquatic and human life but also threatening the eco-environment. Therefore, a pivotal importance to remove these toxic matters from contaminated water. In that view, nanomaterials have gained more attention from researchers towards the cleaning of polluter water. These materials possess special physic-chemical properties which have been successfully implemented to a wide range of applications such as biosensors, catalysis and organic pollutants removal. This review is focused on the nanomaterials with their classification and applications in photocatalysis in sense of dye pollutants removal and inactivation of pathogens.

Keywords : Nanomaterials, semiconductors, photocatalysis, antimicrobial activity.

Introduction to Nanomaterials

Nanomaterials are keystones of nanoscience and nanotechnology. In the past few years, Nanostructure science and technology is a broad and interdisciplinary area of research and development activity that has been growing explosively worldwide. Nanomaterials are typically defined as materials smaller than 100 nm in at least one dimension [1]. A nanometer is one-millionth of a millimeter - approximately 100,000 times smaller than the diameter of a human hair (Fig.1). Nanomaterials are of great interest because at this scale unique optical, magnetic, electrical and other properties emerge. These emergent properties have the potential for the great impacts in electronics, medicine, and used for treatment of water efficiently [2-4] environment and sanitation [5-6].

At nanoscale, materials possess some new size-dependent properties such as large surface to volume ratio, reactivity, rapid dissolution and adsorption which are different from the bulk material. These properties are A promising application of nanotechnology is in water purification [7-9]. What is more, the mobility of nanomaterials in solution is high [10]. Heavy metals [11], organic pollutants [12], inorganic anions [13] and bacteria [14] have been reported to be successfully removed by various kinds of nanomaterials. On the basis of numerous studies, nanomaterials show great promise for applications in water and wastewater treatment.



Fig 1: Examples of materials at different scale [15]

1.2 Classification of Nanomaterials

Depending on the dimension in which the size effect on the resultant property becomes apparent, the nanomaterials can be classified as zerodimensional (quantum dots) in which the movement of electrons is confined in all three dimensions (Fig.2), one-dimensional (quantum wires) in which the electrons can only move freely in the X-direction, two-dimensional (thin films) in which case the free electron can move in the X-Y plane, or three dimensional (nanostructured material built of nanoparticles as building blocks) in which the free electron can move in the X, Y and Z directions [16] (Table 1).

| S.No. | Size in different coordinates | Size (nm) | Examples |
|-------|-------------------------------|-----------|--|
| 1 | 3-dimensions | < 100 | Nanoparticles, quantum dots |
| 2 | 2-dimensions | < 100 | Nanotubes, nanowires, nanofibers |
| 3 | 1-dimension | < 100 | Thin films, coatings |
| 4 | 0-dimension | < 100 | Semiconductor quantum dots (QDs), nanoparticles and colloidal particles |

 Table 1: Classification of nanomaterials



Fig.2: Classification of nanomaterials [16]

1.3 Synthesis routes

Top-down and bottom-up approaches were developed to synthesis of nanomaterials. Copious methods have been developed for the preparation of metal nanoparticles or nanocomposites by both physical and chemical routes. Each method has its own merit and demerits. The methods include sol-gel, hydrothermal, chemical vapour deposition, sonochemical and polymerisation have been developed for the preparation of nanomaterials. Application of hydrothermal in chemical synthesis has initiated a new fascinating field in processing technology (Fig.3). The major advantages of hydrothermal method are increase in reaction speed, more output, efficient energy usage and improvement of particle synthesis.



Fig.3: Schematic representation of the hydrothermal synthesis of nanostructures [17]

1.4 Applications of semiconductors nanomaterials

Semiconductor nanomaterials have interesting physical and chemical properties and useful functionalities when compared with their conventional bulk counterparts and molecular materials. Narrow and intensive emission spectra, continuous absorption bands, high chemical and photobleaching stability, processability, and surface functionality are among the most attractive properties of these materials. The development of "nanochemistry" is reflected in an immense number of publications on the synthesis of semiconductor nanoparticles [18]. For instance, the spatial quantum confinement effect results in significant change in the optical properties of semiconductor nanomaterials. The very high dispersity (high surface-to-volume ratio), with both physical and chemical properties of the semiconductor has a major influence on their optical and surface properties. As a result, semiconductor nanomaterials have been the focus of research for about 20 years and have attracted significant interest in research and applications in diverse disciplines such as solid-state physics, inorganic chemistry, physical chemistry, colloid chemistry, materials science, and recently biological sciences, medical sciences, engineering, and interdisciplinary fields. Among the unique properties of nanomaterials, the movement of electrons and holes in semiconductor nanomaterials is primarily governed by the well-known quantum confinement, and the transport properties related to phonons and photons are largely affected by the size and geometry of the materials [38-39]. The specific surface area and surface-to-volume ratio increase drastically as the size of the material decreases [19-20]. Parameters such as size, shape, and surface characteristics can be varied to control their properties for different applications of interest [21]. These novel properties of semiconductor nanomaterials have attracted significant attention in research and applications in emerging technologies such as nanoelectronics, nanophotonics, energy conversion, non-linear opti

Nanotechnology is thus made up of a broad umbrella covering interdisciplinary research on fabrication of nanomaterials, tuning their properties and applications of these novel properties (Fig.4). Nanotechnology offers an extremely wide range of potential applications in electronics, optical communications and biological systems to new materials. Many possible applications have been explored and many devices and systems have been studied.



Fig.4: An overview of various applications of nanomaterials [22]

Heterogeneous photocatalytic degradation processes gained importance in the area of wastewater treatment since these processes result in complete organics mineralization with operation at mild conditions of temperature and pressure [23]. The photocatalytic activated chemical reactions are characterized by a free radical mechanism initiated by the interaction of photons of a proper energy level with the molecules of chemical species present in the solution, as a semiconductor photocatalyst.

Free radicals released during the photocatalytic mechanism occurring at the surface of a semiconductor, enhances the rates of degradation. A major advantage of the photocatalytic oxidation based processes is the possibility to effectively utilise sunlight or near UV light [24-26] for irradiation, which should result in considerable economic savings especially for large-scale operations.

1.5 Advanced oxidation processes

The development and research in this domain leads to the growth of innovative processes class termed as advanced oxidation processes (AOPs), predominantly in the heterogeneous photocatalysis form, where the chemical energy is formed by the conversion of light energy [27-29]. In heterogeneous catalysis, catalysts and reactants are in different phases, in which catalysts provide a surface for reactants as a support for the chemical reaction to take place. Photocatalysis is a fascinating tool for the conversion of energy, besides that owing to its noticeable nature also used for environment decontamination. In the area of wastewater treatment, heterogeneous photocatalytic degradation processes gained importance, since these processes result in complete organics mineralization at mild conditions of temperature and pressure [28]. Metal-semiconductors as a photocatalyst is an environmental friendly which simulates the approach of photosynthesis to enhance the chemical reactions with the light involvement.

Semiconductors can act as a sensitizer for light reduced reduction-oxidation processes due to their electronic structure [30-31], which is characterized by a valence band (VB) which is filled and conduction band (CB) which is vacant [32-33]. When a photon with an energy of $h\nu$ equal to or greater than the band gap energy (Eg) of the semiconductor irradiates, an electron (e_{cb}) is jumped from the VB into the CB leaving a hole (h_{vb}^+) which are main responsible for the degradation of pollutants into CO₂ and H₂O, the mechanism is illustrated in Fig.5.



Fig.5: Mechanism of semiconductor photocatalysis [29]

The materials used as a photocatalyst must satisfy several pre-requirements with respect to bandgap energy and electrochemical properties under visible light irradiation. The expected conditions are given below:

- 1. Suitable solar visible-light absorption capacity and band gap potentials appropriate for overall water splitting
- 2. Ability to separate photoexcited electrons from holes
- 3. Minimization of recombination of photoexcited charges and energy losses related to charge transport
- 4. Chemical stability to corrosion and photocorrosion in aqueous environment and
- 5. Kinetically stable electron transfer properties from photocatalyst surface to water interface.

Thus, both bulk and surface properties of photocatalyst prove to be important. Also, suitable band structures are required so that water splitting under visible-light irradiation becomes possible.

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