The using of nanomaterials as catalysts for photodegradations

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Abstract. Nanoparticles were physically attached to photodegradation applications. Nanoparticles are particles of sizes within the range of 1 to 100 nm with at least one dimension. Nanoscale structures, for example, nanolayers and nanoparticles, have an extremely high surface-to-volume ratio, making them perfect for employing in different materials for various applications. In general, In case of nanometers, nanoparticles are categorized into organic, inorganic, and carbon-based particles in nanometric scales that have enhanced characteristics in contrast with micrometric or larger sizes of individual materials. The nanoparticles appear upgraded characteristics, for example, surface area, high surface reactivity (bioactive), and high quality, also appeared stable, sensitive, and so on due to their smaller sizes. Different methodologies are used to synthesize the nanoparticle materials for research studies and traditionally utilizes. These techniques are ordered into three principal types to be specific chemical, physical and mechanical procedures that have seen a tremendous improvement after some time. This article covers the fundamentals of nanotechnology, nanoparticle types, synthetic methodologies, the use of metal, metal oxides, and carbon-based nanoparticle in the field of photocatalysis, and the development of using nanomaterials in air purification and environmental protection. Herein, a variety of synthetic strategies for nanomaterials are summarized, including their applications as photocatalysts.

Keywords: Nanoparticle, environmental protection, photodegradation, catalyst, photocatalysis and water purification.

1. Introduction

Nanotechnology has increased enormous consideration after some time. The essential element of nanotechnology is the nanoparticle (NP). A nanoparticle is a particle somewhere in the range of 1-100 nanometers (nm) in size and it mainly comprises carbon, metal, metal oxides, or natural issue [1]. The nanomaterials possess chemical properties like sensitivity to moisture and other factors, reactivity with targets, corrosive and anti-corrosive property, biomedical, toxicity, anti-bacterial, and so on. While the physical properties like light energy penetration, absorption, and reflection, UV absorption on a coated surface, or inside a solution. The material at nanoscale shows chemical and physical properties contrasted with their separate particles at higher scales [2]. This marvel is because of a moderately large ratio of surface area to the volume, raise reactivity or stability in chemical experiments [3], upgraded mechanical quality, and so forth [4]. These properties of nanoparticles have prompted their utilization in different applications [5].
Among others, there are widely recognized nanoparticles utilized for applications in tissue engineering scaffold incorporate bioactive glass [6], titanium oxide (TiO$_2$) [7], tricalcium phosphate [8], and hydroxyapatite (HA) [9] nanoparticles which are essentially counted in the mix with biopolymers. Several investigations have indicated that mixes of a biocompatible polymer and bioactive inorganic material utilizing a nanosized inorganic component are probably going to be progressively bioactive (for example indicating higher surface reactivity) compared to those composites produced using a covenant particle or micron-sized one, for instance, enormous increments in adsorption of protein and osteoblast adhesion when TiO$_2$ and nanophase alumina (Al$_2$O$_3$) were utilized as opposed to micrometric particles.

The nanoparticle possesses a different shape, size, and dimension apart from the whole material [10]. Several dimensional types of nanoparticle, for instance, nanodot, one dimensional which have just a single parameter like graphene, two dimensional where it has length and breadth (for example, carbon nanotubes) or three dimensional which has all the parameters: length, height and expansiveness (gold nanoparticles) [11]. The nanoparticle may be cylindrical, spherical, spiral conic in shape, etc. with either a crystalline or amorphous structure [12]. A few strategies to accomplish process-specific nanoparticles in order to improve their optical, chemical, mechanical, and physical properties. An immense advancement in the instrumentation has prompted an improved nanoparticle portrayal and resulting application. Nanoparticles are presently utilized in each item like from gadgets to sustainable power source and industry. An expansive scope of nanoparticles qualified the medical products have been investigated for clinical applications, involving liposomes, lipid-based nanoparticles, polymeric nanoparticles, micelles, metal oxides, nanocrystals, metal colloids, and numerous others [13]. In Figure 1 shows the essential classifications of nanoparticles and their properties [14]. This article summarizes the types, synthetic procedures and mechanism of formation of nanoparticle materials, in addition to their applications in the field of photo-catalysis.

Figure 1. Two fundamental types of nanomaterial, including organic and inorganic nanoparticles.
2. Methods for synthesis of nanoparticle

Different types of nanostructures can be synthesized and characterized as a structure with one or two dimensions. Nanoparticles can be orchestrated utilizing an assortment of procedures [15]. In liquid dispersion, both of the dry particles and nanoparticles are synthesized mainly by these methods. Nanostructures can be produced by working from the atom or by methods used to diminish microparticle size to the nanoparticle. The synthesis of nanoparticles falls into two categories, the first is called the bottom-up approach, and the second is called the top-down approach [16]. The techniques covered in each approach are listed in the following text with details:

2.1. Bottom up approach

The molecular interactions incorporate noncovalent bonds, making molecules bind to another, making them the basis of dynamic processes, for example, ionic and hydrogen bonds, van der Waals forces, and water-mediated hydrogen bond [17]. The phenomenon of molecular self-assembly [18] is relying on interactions of chemical and physical procedures at the nanoscale at which the bottom-up approaches or as it is known "constructive" approach are relying on this phenomenon [19]. The bottom-up technique is the material building-up from an atom to cluster to nanoparticles. Sol-gel [20], spinning [21], chemical vapor deposition [22], pyrolysis [23], and biosynthesis [24] are the most normally utilized constructive techniques to produce the nanoparticles according to the used material (See Figure 7).

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The simple and cost-effective biosynthesis or as it has known green synthetic technique of the nanoscale particle formation is helpful more than the chemical methods because of its non-toxic and eco-friendly properties [25]. Biosynthesis involves three categories: organic, inorganic, and hybrid. Instead of chemicals, biosynthesis employs the plant extract as a potential precursor, bacteria, fungi, and so on for nanoparticle production [26]. Advances in nanoscience have proven the effectiveness of this approach in the field of medicine and pharmaceutical applications [27]. Superior strong materials of high quality can be synthesized by chemical vapor deposition to create large-area heterostructure as the example is shown in Figure 2 [28]. In the chemical procedure, the water (substrate) exposure to at least one volatile precursor that interact as well as decompose on the substrate to get the required deposit [29]. Also, the volatile precursors will be likewise created and gas flow through the reaction chamber will remove them. Chemical vapor deposition is frequently utilized in industrial applications for thin-film production from a semiconductor material. The main disadvantage of this technique is the high toxic gaseous by-product. Chemical vapor deposition is applicable for nanoparticle synthesize when metal-based material [30] or carbon [31] are used.
Figure 2. Chemical vapor deposition process diagram of molybdenum disulfide (MOS2) shell growth on gold (Au) nanoparticles. Better homogeneity can be achieved by the sol-gel technique of discrete to continuous particle network. The sol-gel method needs low temperature and a small molecule to produce a solid material [32]. The chemical procedure starts with developing the solution (sol) into a gel-like diphasic system that involves both liquid and solid phases (see Figure 3) [33]. Powder of Single and multi-component composition is formed by deposition to produce a high purity nanoscale particle for optical, electronical, sensing, dental, and biomedical applications. The sol-gel method has appeared to be an advantageous route for nanoparticles synthesize. Beginning from using the silica material and now covering metal-oxides [34], mixed metal oxides [35], organic-inorganic materials, and carbon [36].

Figure 1. A schematic diagram of sol-gel method to synthesis nanoparticles. Nanoscale particles can be synthesized by the spinning method "spinning disc reactor"; where the molecules or atoms are fusing, precipitating, collecting, and drying together. As a rule, the reactor is filled with an inert gas such as nitrogen to prevent the undesired chemical reactions, and to drive out the oxygen inside [37]. The rotating disc contained in the reactor holds inside the chamber/reactor in which controlling the temperature parameter. This disc is rotating to pump the liquid in [38]. The different working parameters, for example, the fluid flue rate, disk surface, rotation speed of the disc, ratio of liquid/precursor, feed position, and so on the limit, the attributes of the synthesized nanoparticles from spinning disc reactor methodology from organic polymer use [39]. In this technique, the quality of the synthesis process relies dominantly on the hydrodynamic attributes of liquid films. Three distinguished regions are exhibited in the radical velocity profile on a spinning disk; they are injection zone, acceleration zone, and synchronization zone clearly illustrated in Figure 4 [40]. these films are featured as a free-surface film with a sharp gas-liquid interface.
The nanostructure is obtained by pyrolysis comes in one of the two methods: laser pyrolysis or spray pyrolysis. The first method is laser pyrolysis requires a CO$_2$ continuous laser beam for heating the reactant gases. This step result is a molecular decomposition followed by forming vapors to allow the nucleation to begin and nanoparticles growth. At which the precursor gases absorb the laser energy which leads to decompose the molecules [41]. The second method is spray pyrolysis which requires spraying or injecting a solution carrying precursors onto a hot substrate in the furnace. This process decomposes the precursors to produce the desired substance. The size of the nanoparticle, its shape, and thickness are limited by the spraying energy, the specific temperature of the furnace and substrate, the distance from spray to the substrate, the size of droplets, and the spray duration time [42].

2.2. Top-down approach

Top-down or as it is known "destructive" approach is the process of reducing the bulk into particles on a nanometric scale. Currently, the top-down methodology is predominantly utilized in industry for many man-made materials manufacturing [43]. The top-down methodology focuses on manufacturing by etching away bulk material to accomplish the desired smaller particle structures like in lithographic technique [44]. In general, the most commonly utilized synthesis methodologies to produce nanoparticles are mechanical milling [45], nanolithography [46], laser ablation [47], sputtering [48], and thermal decomposition [49] according to the used material (See Figure 7).

Mechanical milling known also as "mechanical attrition" is considered as the most commercially implemented and the modest technique in the top-down fabrication branch because the chemical reactions are not needed. The mechanical milling principle is to grind a piece of material into numerous small size particles. Nanoparticles creation from mechanical milling can be synthesized at high energy mills, room temperature, or low energy tumbling mills [50].

The method allows us to fabricate one- and two-dimensional nanostructure meaning nanopatterning called nanolithography. Nanolithography replicates the negative and positive patterns into the implied substrates [46]. This process requires a light beam, electron beam, or charged ions to allow the geometric pattern to be transferred from the premade photomask to a photoresist coated layer on a thin film or the substrate bulk. Then the system will suffer a series of treatments for chemical etching or deposition [51]. In laser ablation methodology, nanoparticles are created by nucleation and growth of laser-vaporized species in a gas. When submerging the metal in a liquid, the laser radiation condenses a plume of plasma to produce the pure nanoparticles in a quantum size less than 10 nm [52]. Laser ablation is a technique for synthesizing different sorts of nanoparticles including semiconductor core-shell, quantum dot, nanowires, metal-based [53], and carbon based [54] nanoparticles. An example of using a laser ablation method to produce metal nanoparticle by applying Nd: YAG laser beam of 1064 nm on silver (Ag) as a target immersed in ablation liquid is illustrated in Figure 5.
Figure 3. Laser ablation method diagram; a production of metal nanoparticle.

The sputtering technique refers to the deposition of nanoparticle on a surface when a metal-based is used (see Figure 6). This method starts with the incidence of accelerated high energy inert gas ions on the target at which atoms or small particles are ejected or sputtered from the surface by colliding with ions [55]. Usually, the annealing process follows the nanoparticle deposition. The shape and size of the generated nanoscale particles controlled by layer thickness, annealing duration, and temperature.

Figure 4. Schematic diagram of sputtering method and process for nanoparticle formation.
3. Nanotechnology and basic principle of photocatalysis

Nanotechnology and photocatalysis offer future rules for structuring new semiconductor-based photocatalysts, with minimal effort and high effectiveness, for a scope of items focused on ecological protection. Nanotechnology is used nowadays on a broad scale for finding suitable eco-friendly solutions for the energy issues that threaten the whole life. Applying the nanotechnology idea to catalysis encourages us to know about all the more precisely the changes occurring on the catalyst's surface and manage them [56]. The nanometric dimension facilitates the explanation of reaction mechanisms to design a suitable catalytic system. From the perspective of the materials, photocatalysts require a progression of trademark properties relying upon their applications such as their particles' sizes, surface areas of space between the electronic levels, and so on [36]. The basic principle of photocatalysis is a promotion of a photoexcited electron from the filled valence band to the empty conduction band leaving a hole instead. In this case, the absorbed photon energy "hυ" equals or surpasses the bandgap of the photocatalytic material. Finally, the electron-hole pair (e−–h+) is produced. For example, treating the industrial wastewater by TiO₂-mediated solar photocatalyst explained in Figure 8 [57].

![Figure 5. Nanoparticle categorized according to the nanofabrication method.](image-url)
Figure 6. General mechanism of TiO$_2$ in solar photocatalysis process.

In any application of photocatalysis, the catalyst concentration should be limited before, to maintain a catalyst from being excessed and to make sure of high efficiency photons are absorbed [58]. This is due to undesired light scattering perception and reduce of light penetration into the solution with an abundance of photocatalyst [59]. Because the pace of the photocatalytic response reaction is affected by the concentration of photocatalyst. Heterogeneous photocatalytic reaction shows a proportionate increment in photodegradation with increasing of loaded catalyst [60].

4. Nanoparticles application development as photocatalysis

Water defilement is an overall basic issue for the current society to keep up an eco-friendly situation. Elimination of different contaminations of the overall inorganic and natural mixes from water is the researcher's challenge these days. This purpose requires to employ metal/metal oxide nanoparticles because of the nanoscale size and effective surface area. Additionally, metal/metal oxide nanoparticles-based advancement to improve the expulsions production is presenting some genuine dangers. Herein, a historical survey of some recent reaches about the topic of preparations of catalysis:

In 2017, T. Kamal et al. prepared a porous cellulose acetate fiber by wet spinning technique, and cellulose acetate sheets by doctor blade (tape casting) technique as a material with large surface area. They synthesized silver (Ag) nanoparticles on immobilizing substrate by dipped both of cellulose acetate fiber and sheets in 0.1 M of aqueous AgNO$_3$ and treated them with 0.1 M of NaBH$_4$. The prepared materials were examined and utilized as catalysts. The Ag/cellulose acetate fiber assumed to be better catalysis in the hydrogenation process of 2,6- dinitrophenol when contrasted with the Ag/cellulose acetate sheets [61].

In 2017, S. Toston et al. used super-crucial CO$_2$ to prepare 0.1 wt% Pt-TiO$_2$. as a photo-catalyst for reducing CO$_2$ into methane (the rate of methane production was 0.245 µmol/g-cat/h. The obtained photocatalyst was characterized based on its crystalline structure, large surface area, porosity and ability to absorb visible light [62].

In 2018, G. Liao et al. reported the preparation of a nanocomposite of Ag nanoparticles with poly (styrene-N-isopropyl acrylamide-methacrylic acid). The prepared nanocomposite was examined as a catalyst with good efficiency and stability to reduce and absorb methylene blue dye. Ag NPs possess unique physical and chemical properties due to their high surface area and nanoscale size. . Ag NPs are being used increasingly in wound dressings, catheters and various households’ products due to their antimicrobial activity [63].

In 2018, Lang et al. manufactured an Ag-rGO-TiO$_2$ nanocomposite by depositing Ag nanocubes and TiO$_2$ nanolayers on reduced graphene oxides surfaces. Moreover, they prepared Ag-TiO$_2$ for comparing process. No photocatalytic activities have been detected for Ag-TiO$_2$ and TiO$_2$, while the Ag-rGO-TiO$_2$ nanocomposite had provided a hydrogen rate of 0.53 µmol g$^{-1}$ h$^{-1}$ per mass unit under visible light with
methanol water (20 vol% methanol). Furthermore, a formed Schottky barrier on rGO-TiO$_2$ surface reinforced the hot electron spreading from rGO to TiO$_2$ [64].

In 2019, M. Taherinia et al. prepared a doped-TiO$_2$ nanoparticles by sol-gel method and studied their photocatalytic activity at 450, 550 and 650 °C calcination temperatures. A reduced photocatalytic activity of doped-TiO$_2$ was observed at the higher levels of temperatures. This is due to the fact that the nanoparticles accumulate together, which leads to reduced surface area [65].

In 2019, Q. Gao et al. manufactured a hydrogenated F-doping TiO$_2$ using a two-step facial method. The researchers approved that the F-doping improved the absorption of ultraviolet radiation by TiO$_2$, and it can be increased by hydrogen treatment in visible region. Accordingly, the hydrogenated F-doping TiO$_2$ showed preferred photocatalytic properties over pure, hydrogenated or F-doped TiO$_2$, in either hydrogen generating or organic contaminant degradation [66].

In 2020, Z. Wanga et al. presented an investigation of carbamazepine (CBZ) photocatalytic degradation by neodymium-doped antimony trioxide/titanium dioxide (Nd-doped Sb$_2$O$_3$-TiO$_2$) inside ultrapure water under UVC radiation. They have synthesized the catalyst samples by hydrothermal technique with 0-2% ratios of Nd. The obtained measured surface area at 1% Nd = 9.56 m$^2$g$^{-1}$ and the band gap energy = 3 eV. As a result from this experiment, 1% Nd-doped Sb$_2$O$_3$/TiO$_2$ photocatalyst at catalyst dose of 0.5 g/L demonstrated the best photocatalytic action towards CBZ degradation. Finally, from quenching and trapping tests on each sample, it has been shown that OH radicals and $\cdot$O$_2$ were in charge of CBZ degradation [67].

In 2020, C. Noda et al. synthesized a three component photocatalyst namely C$_3$N$_4$/rGO/C-TiO$_2$ by the in-situ methodology. C$_3$N$_4$/rGO increased the surface contact and C-TiO$_2$ has crystallized over the mentioned surface to get a highly dispersed nanoparticles on C$_3$N$_4$/rGO surface. The most efficient and highest photocatalytic activity was obtained by the samples produced by in-situ method. By measuring the transient absorption, they found that the composite has possessed the longer life time than other components which provides the ability to exhibit higher activity in photocatalytic response [68].

5. Conclusion

Nanotechnology has been attempted to investigate different effective ways for treatment and beating the issue of wastewater. Nanoparticles have monstrous potential that enables them to look into waste water treatment just as water purifying progressions, for instance, adsorption, catalysis and disinfection. Organic contaminants are the most part influence on the water resources. Numerous sorts of organic toxins are found in water bodies, for example, pesticides, industrial solvents, plasticizers, phenolic compounds, pharmaceuticals and another. Many semiconductor nanomaterials such as TiO$_2$, CeO$_2$, ZnO, CdS, Fe$_2$O$_3$ and many others are utilized as photocatalyst for various applications like renewable energy, environment troubles and chemical synthesis processes. Among the promising photocatalysts, high stability TiO$_2$ nanoparticle is chosen as a typical nanomaterial for photocatalysis applications, attributable to its nontoxicity, low expense, optical absorption capacity and eco-friendly. Anatase and rutile phases have commercially got a real interest in field of photocatalytic. Under solar light, few investigations have demonstrated that anatase is more proficient than rutile for catalyzing response, despite its bandgap (E$_g$ = 3.2 eV) which is boarder than that of rutile (E$_g$ = 3.0 eV).

Conflict of interest: The authors declare that no conflict of interest.

6. References

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