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REVIEW

Lanthanide Oxide Nanoparticles for Environmental Remediation: A Review

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ABSTRACT: The lanthanide oxide nanoparticles were used for the removal of pollutants towards environmental remediation. The enhanced properties and effectiveness of nanotechnology based materials makes them particularly suitable contender in detection of pollutants. The used particles synthesized by facile and easy method with additional standard modification. The origin of pollutants, their toxicity and influential effect of respective pollutants on the environment, humans and ecological system studied in details. The prepared nanoparticles as highly efficient probes, with novel methodology utilized for detection and removal of pollutants. The easy, cost effective and efficient technologies were performed for sensing of these pollutants. This article deals with mainly detection of pollutants present in water, air and soil by using nanomaterial. Further, these nanoparticle is utilized in degradation of various types of pollutants present in the environment.

Keywords: Lanthanide Oxide, Nanoparticles, Environmental Pollution, Environmental Remediation

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1. INTRODUCTION

The environment is degrading continuously which is due to the vulnerable exploitation of funds, unplanned application of synthetic chemicals, uninterrupted exploitation of resources and increasing population load [1–4]**.** Therefore, it is necessary the proper planning, management and utility strategies. World is going through problem of water scarcity [5]. The shortage of drinking, moderate and sever water in various parts of world is due to the overexploitation of ground water and a rapid increase in population [6,7]. The waste released from various industries and textiles contains organic and inorganic toxic compounds [8,9]. The phenols, azo dyes, hydrocarbons, pesticides, chlorinated phenols and polychlorinated phenols are the toxic organic compounds which contaminant the environment due to their direct release in water, air and soil (Figure 1). Additionally, some pollutants like polyaromatic hydrocarbons, inorganic pollutant including chromium (Cr), cadmium (Cd), arsenic (As), mercury (Hg) and lead (Pb) also affect environment quality [10]. The quantity of waste water increasing day by day and availability of fresh water decreased [11]. The trace amount of pollutants can produced acute toxicity [12]. The United State Environment Protection Agency (USEPA) has assigned the pesticides acts as prior pollutant due to unabated and harmful environmental impact.

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2. ENVIRONMENTAL POLLUTION

2.1. Water Pollution

In today world, it is a great challenge to provide the excellent technique for purification of water. On earth, 70% of water is in form of frozen as eternal ice and 2.5% of water is available as fresh water in forms of world's ocean, rivers and atmosphere [13]. Around the world, drinking water is available in less than one percent [14]. Million people do not have access for potable water and this problem increasing in developing nations. Due to water quality deterioration, population growth and global climate change demand of fresh water is decreasing [15]. The great importance in present time is to provide the quality of fresh water, air and soil because we interact daily with natural resources.

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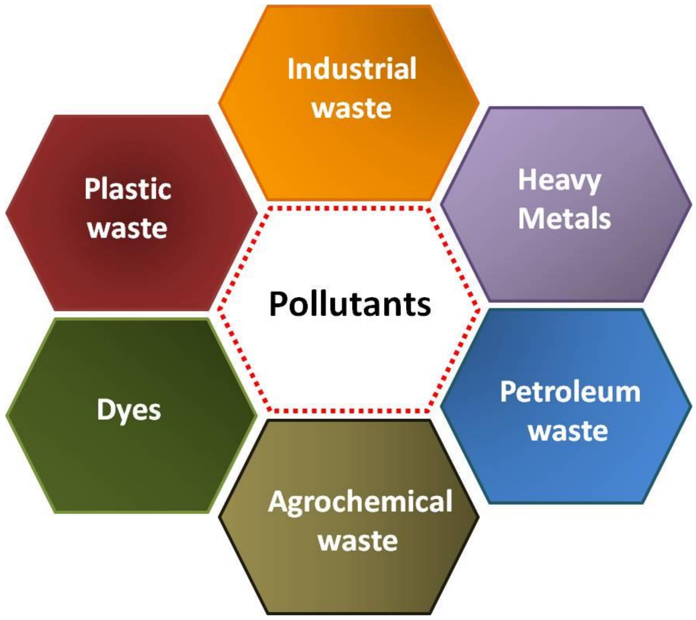

Fig. 1. Several types of environmental toxins affecting human being.

Now a day, it is necessary to explore the excellent techniques for the purification of water with efficient recyclability and reuse [16]. Therefore, due to increase in the pollution of fresh reservoirs, a lot of countries do not have available fresh water for domestic purpose also. The pollution of water by various chemicals, plastic waste, industry waste etc. is main cause of environment destruction [17]. Therefore, researchers have gained the attention towards treatment of waste water with appropriate developing technique in growing countries. The carcinogenic chemicals meet in the water resources affect badly ecosystem and environment [18]. A number of organic pollutants like phenols, pesticides, fertilizers, detergents, grease, hydrocarbon meet in soil, water and atmosphere which a reason for pulling down the environment (Table 1) [19].

Various chemicals dissolved in water such as toluene, benzene, xylenes when exposed to atmosphere then these substances evaporate to contaminant the environment. The ground water, surface water and industrial water mostly contaminated by heavy metals, inorganic substances like metal ions, ammonia, other gases, organic compounds phenols, plants material, nitrates and other compounds which are dangerous and toxic to environment and living beings [20]. Several water born diseases are arising from microbes. These organic pollutants cannot remove out at lower concentrations by available procedures of purifications (flocculation, filtration and sedimentation). Therefore, the removal of pollutants from contaminant water is necessary to provide a better health to the humans.

2.2. Air pollution

Various material employed to detect respective pollutants for environmental sustainability with a wide spread approaches which can be exploited for this thrust. The removal and degradation of these environmental pollutants is a great challenge due to the high volatile, low reactive and complexity of different compounds [21]. The destruction of environment is due to presence of the pollutants present in environment like nitrogen dioxide (NO_2), ammonia (NH_3), carbon dioxide and carbon monoxide (CO_2 & CO), methane (CH_4), sulphurous oxides (SO_x), volatile organic compounds (VOCs), heavier metals and hydrocarbons [22]. Exposure of ammonia creates skin irritation, throat nose irritation which is a serious concern to human health. Even the skin, eyes and respiratory system also affect by the presence of lower level of ammonia [23]. Nitrogen oxides and carbon monoxide also affected the environment and human health from the release of exhaust from vehicle, industrial process and various chemical plants during combustion [24]. The VOCs released form combustion of automobiles exhaust, petrochemical products and fossil fuels generally located around natural gas and petroleum deposits (Table 2).

2.3. Soil destruction

Various pollutants are exposed routinely by population in the environment, through air we breathe, water we drink and food we eat. Pesticides have several routes to contaminate the environment. During spraying the pesticides residues reached to the plant and then released into soil with litter breakdown [25]. Soil may also affected by dissipation of pesticides and it may happen with number of ways such as drainage, leaching, evaporation, dilution, biotic and abiotic degradation, plant uptake and run off. There are many factors like soil temperature, pH, air temperature etc. which affect the dissipation and degradation of pesticides in soil. Accumulation of trace heavy elements in soil has confined their function, contaminate the food chain and toxicity to plants [26].

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Table 1. Different sources of water pollution

Sources	Example	Effect
Agricultural runoff	Pesticides & herbicides	Carcinogen effect on living beings
Household waste	Plasticizers	Affecting central nervous system
Hospital waste	Pharmaceuticals by prodcuts	Imparting harmful effect on living beings
Industrial waste	Heavy metal ions	DNA damaging effect

Table 2. Different sources of air pollution

Sources	Example	Effect
Industrial effluents	Oxides of nitro compounds	Adverse effect on lungs
Volatile effluents	CO or CO_2	Irritation of eyes and skin
Automobile waste	Smog	Skin cancer
Petro industrial waste	SO_2	DNA damaging effect, glucoma

3. CHALLENGES

3.1 Population growth

It is a major cause because human is spreading a lot of contaminant in the environment. With regular increase in population, a lot of load is increased on the water treatment resources [27].

3.2 Waste plastic

Use of plastic is increasing every year and pollution from it called 'white pollution' becomes a great challenge. Plastic debris is accumulated in the environment due to the inappropriate waste and unsustainable use of plastic. It was assumed that the production of plastic will be 630 million tons by 2050 and effect of this plastic not be experienced [28].

3.3. Sludge management

Sludge is generally contaminated by various pollutants. Treatment of sludge before dispose is necessary for the environment sustainability. It is a great challenge to treatment the sludge because of high footprint demand [29]. The solid waste and municipal waste is generally consist of waste release from home, waste food, plastics, demolition waste, garden waste, markets waste, vehicle, glass and electrical appliances [30]. The waste is dumped into an open place without any management which has adverse effect on the environment and life cycle. Therefore, the ground water has been polluted by these landfills which become a major threat to surface and ground water resources. These landfills also generate various greenhouse gases like methane, CO_2 and other trace gases. Generally waste dump is left in open which have serious impact on human health, create major public health threats and environmental threats in environmental surroundings in urban cities.

3.4. Industrial waste

Dyes, heavy metals are main cause of environmental pollution. It is highly challenging to remove these pollutants. Industrial growth rate increased in last every year. Safe dispose off is the great matter to concern towards environment remediation [31–34]. In addition, the pesticides have been widely used in agriculture and forestry to increase the yields of crops and destroy the unwanted plants [35]. Generally, pesticides used to kill the target pests. The continuous increasing usage of pesticides reveals their toxicity and its affect non-target species and human beings also. These affect the environment badly and its poisoning lead to death and chronic illness. Pesticides not only affect the food sources for humans but also life of birds, wildlife, fish and domestic animals. Animal can be affect by pesticides generally in two ways by direct exposure or indirect effect with reduction of essential sources and food chain for their healthy growth and population. In last decade, detection of pesticides were experimented in lot of sources like soil, sediments, ground water, seawater and other various water sources. Misuse of pesticides is dangerous to environment. All pesticides can be carcinogenic and hazardous to humans and other living beings. The soil affected by direct spraying of pesticides, herbicides, bactericides and fungicides and these spraying also affect the beneficial microbes of soils. The regular uses of pesticides significantly affect the various species and microbes of soil. These pesticides reached in our body by exposure through ingestion, inhalation and dermal. The use of pesticides risky to life and create various diseases like endocrine disorders, increasing incidence of cancer, affect immune system, neurological and behavioral disorders. Pesticides have been classified into various categories such as herbicides, insecticides and fungicides which is used for high growth of crops in excellent manner and to control fungi, weeds. Various pesticides contain the organic group which is

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major cause for the contamination of soil and water, living beings. The oldest class of pesticides is Lindane (organochlorine) which create problem in environment and soil by their contamination. It has been counted under the category of persistent organic pollutants. A lot of industries in various countries of the world produce persistent organic pollutants every year. Lindane is particularly used for louse control and wood preservatives. It has been detected in blood, fatty tissue and breast milk of human beings. The lindanes affect the humans and other living beings by interruption through variety of mechanism. The lindanes have carcinogenic effect on the human like headache, vomiting, dizziness, nausea, irritability and muscle weakness.

As a result, the water resources, agriculture products and soil getting polluted [36]. These pollutants associated with various household and food products (Figure 2) which create harmful effects like cancer and damage to central nervous system [37]. The toxicity effect of pesticides is due to the compounds such as phenols, dioxins and cyanides remains unaffected by conventional techniques. In today world, clean and affordable drinking water become a great challenge for lot of developing countries. The plastic also affect the environment badly as it becomes more and more significant. The inappropriate use of plastic and toxic substance released from plastic during deterioration greatly affects the environment. The detrimental effect of toxins on human beings is well documented. However, the exact quantification effect of plastic on environment cannot be easily evaluated. Therefore, it is necessary to detect trace amount of pollutants, accurately, rapidly and quantitatively in the environment (water, air and soil).

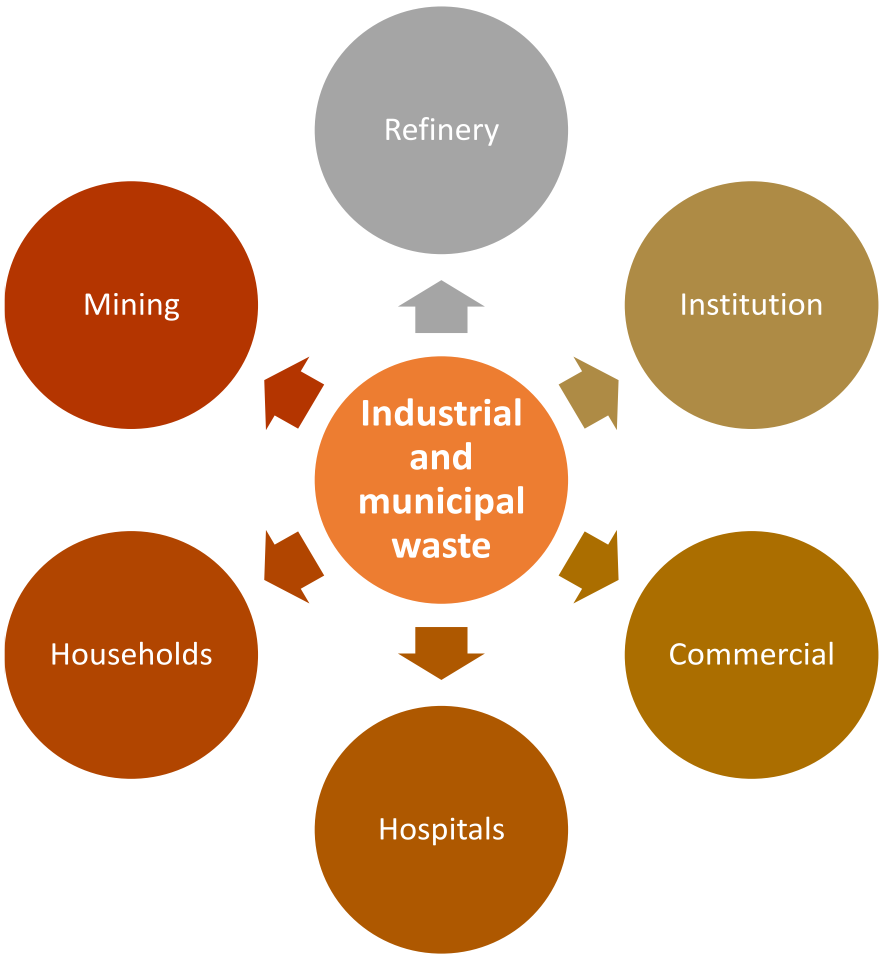

Fig. 2. Industrial and municipal waste sources affecting living beings.

We compare the role of industrial sectors in developing the country, most of the economic usage is employed for the treatment of pollution generated from different sources used in production of raw material. The chemical used in industries are highly toxic and used for processing of raw material to find the good quality product in short time period. The industrial waste water released in river, ponds and ocean contains hazardous organic and inorganic solvents which cause major environmental detrimental effect and human hazards [38]. The man made products possessed higher level pollution which has adverse effect on the environmental surrounding. The pollutant released in environment create various health problem due to contamination and bad effect on fauna, flora. The water pollution generates several

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problems not only to humans but to animals and birds also and has adverse effect on environment and human health [39]. Thus, it has is become a great challenge to biodegrade and remove respective inorganic substance and organic pollutants from industrial waste which is a major question for safe environment and diseases free life. A lot of efforts have been performed for the purification of water. The available methods are screening, anion exchange, filtrations, reverse osmosis, crystallization, ultra violet filtrations, sedimentation, coagulation, distillation, adsorption, electrolysis, deionization centrifugal, setting-out, reduction and oxidation, neutralization and re-mineralization, membrane separation and so on [38]. But these methods are not effective for complete removal of pollutants at lower concentration level. Therefore, it is necessary a suitable technique to detect the pollutants in environment for purify the water and also for fresh air and soil.

3.5. Organic pollutant

The use of organic pollutant like pesticides, herbicides, biphenyl, plasticizers, hydrocarbon, detergent etc. become common in the environment which affect ecosystem badly. Volatile organic compound easily evaporate in the environment when water is reveal [40]. The organic pollutant containing petroleum hydrocarbon like hexane, naphthalene, fluorene, anthracene etc. have serious impact on the ecological system and environment remediation [41]. These hydrocarbons enter in the soil, and polluted the surface and ground water which affect the human beings [42].

The dyes are confined with various groups such as azo dyes, benzodifuranone, quinophthalones and anthraquinone. Dyes are used to color the things to give the better and fantastic look. The major sources are textiles, plastic industries, leather, and paint acrylic for the release of dye in environment. But their use carried without extract the carcinogenic chemicals which has attached with the dyes. In recent era dyes has not been degraded with proper and techniques and resistant to humans and nature [26]. The dyes reached through contaminated water and colored products in environment which affect the ecosystem, create disease, health hazards, vomiting, liver and kidney damage and skin irritating in humans and animals [43]. Dye released from textiles, industries contaminated the water. After industrialization revolution, the dyes from textiles industries released in the environment without treating them which badly affect the water bodies by reduction of photosynthesis rate of algae and adversely effect on aquatic ecosystem. The erythrosine (xanthene dye) dye significantly affects the human body, cause allergy, DNA damage, cancer, neurotoxicity on animal also. Dyes and textile effluents affect the plant cell growth procedure with strong genotoxicity effects. The toxic effect of dyes has been shown on the root cells of *Allium cepa*, detrimental effect on the natural bacterial luminescence and inhibits algae growth.

The other toxins including phenolic compounds are considered to be toxic to human beings. It generally release in water stream during production and preparation of organic compound and pesticides [43,44]. Phenols and chlorinated phenols have adverse effect on the living beings. This release in the environment and highly concentration can cause obstruction in circulating system of lungs, central system disorder.

All inorganic heavy metal ions such as Cd, Cr, As, Pb and Hg are toxic in nature. The toxicity of respective metals has carcinogenic effect on environment and humans [45]. Cadmium affects the human body by cell damage through reactive oxygen species (ROS) and cause DNA damage. Arsenic toxicity leads to the CNS bone marrow depression, disturbance of cardiovascular, polyneuropathy and high exposures lead to death. Lead (Pb) found in various daily usage things like batteries, paint, pesticides, organic evolution activities, industrial waste etc. The efficacy of lead takes place in plants through inhibition of enzymes which cause reduction in chlorophyll, increase production of ROS and causes oxidative stress and photosynthesis. Lead is very toxic metal to humans as it causes injury to CNS, loss of memory, confusion, irritability, cause headache, dullness and adverse effect on the kidneys, endocrine system, livers and reproductive system. Inorganic mercury (Hg) metal has adverse effect on the environment and ecologic system. The main sources from which it releases in environment are thermometer, fossil fuel emission, dental amalgam, batteries and thermometer. The mercury has major threat on the ecological system, human, animal and plants. It destroy the cellular metabolism and lipid and cause mental retardation, neurological defects, loss of hearing, blindness, abnormal muscle tone [45,46].

The mercury poisoning from Minamata bay of Japan had reached to humans by consumption of fishes in their body. Heavy metals have toxic property and increasing metal concentration affect the environment through soil and water pollution [47]. These metal have carcinogenic effect to the environment and creates many diseases cancer, liver and kidney damage, skin lesions etc. It becomes a great challenge to remove hazardous metals which left the significant threat for the life on earth in humanity [48]. These heavy metals adversely affect the land, air and aquatic system, ecological system through industries and human activities [49]. The main origin of heavy metal contamination is from industrial waste, agriculture run off and occupational exposure [50]. Some metals are also essential to the world like iron but its high concentration act as a heavy metal. Sometimes metal also affect the metabolic process of human beings to cause the sickness. Toxic metals also affect the essential element present in our body by resembling their action.

4. REMEDIATION USING NANOTECHNOLOGY

Nanotechnology is a rapidly expanding area involving different type of nanomaterials. It manipulates matter on an atomic and molecular scale. The particle size below 100 nm and have at least one dimension in nano range called nanoparticle [51]. At nanoscale, the particle possessed unique chemical, physical and biological properties, high surface area, new size dependent properties etc. The enhanced

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properties and effectiveness of nanotechnology based materials makes them particularly suitable in various fields like nano-medicine, nano-biotechnology, energy application and many more [50,51]. Nanotechnology has gained a lot of attention in the past decades due to the unique physical properties. Nanomaterials offer the potential to leverage unique surface chemistry as compared to traditional methods as they can be functionalized so that they can target specific molecules of interest. The method of nanotechnology for detection and purification are cost effective, more efficient and less time consuming than the traditional methods. The potential applications of nanomaterials are very attractive in many industrial sectors including biomedical, defense, energy and storage, pharmaceutical, food, agriculture and environmental remediation (Figure 3). The applications in environmental remediation include waste water treatment, soil treatment, sensors and energy storage.

4.1. Lanthanide based nanomaterials

Lanthanides also known as rare earth elements and play a key role in applied sciences due to benefit of sharp band emission, multiple emission bands from ultra violet to infrared by single wavelength excitation and long fluorescence lifetime and therefore have large range of applications in drug delivery, bio-sensing, super resolution microscopy [52]. Amongst various nanoparticles, lanthanide oxide nanoparticles has gained the interest of the scientists due to their potential luminescent centers as the inner 4f orbitals are shielded by 5s and 5p valance orbitals, interaction with the surrounding and results in interesting photoluminescence properties [53,54]. Apart from their optical properties, they have unique catalytic, magnetic and electrical properties which make them suitable for industrial applications (Figure 4).

One lanthanide nanoparticle contain multi lanthanide atoms, thus one nanoparticle contain multi photons, which results in the excitation of multi lanthanide atoms at the same time. This feature makes lanthanide nanoparticles as effective material with improved sensitivity [52]. Lanthanide doped nano material are used for the development of a new generation of energy conversion devices and systems (lasers, photosensor, light emitting diodes, solar cells) [55].

Fig. 3. The diverse range of applications of nanomaterials in envrionmental remediation.

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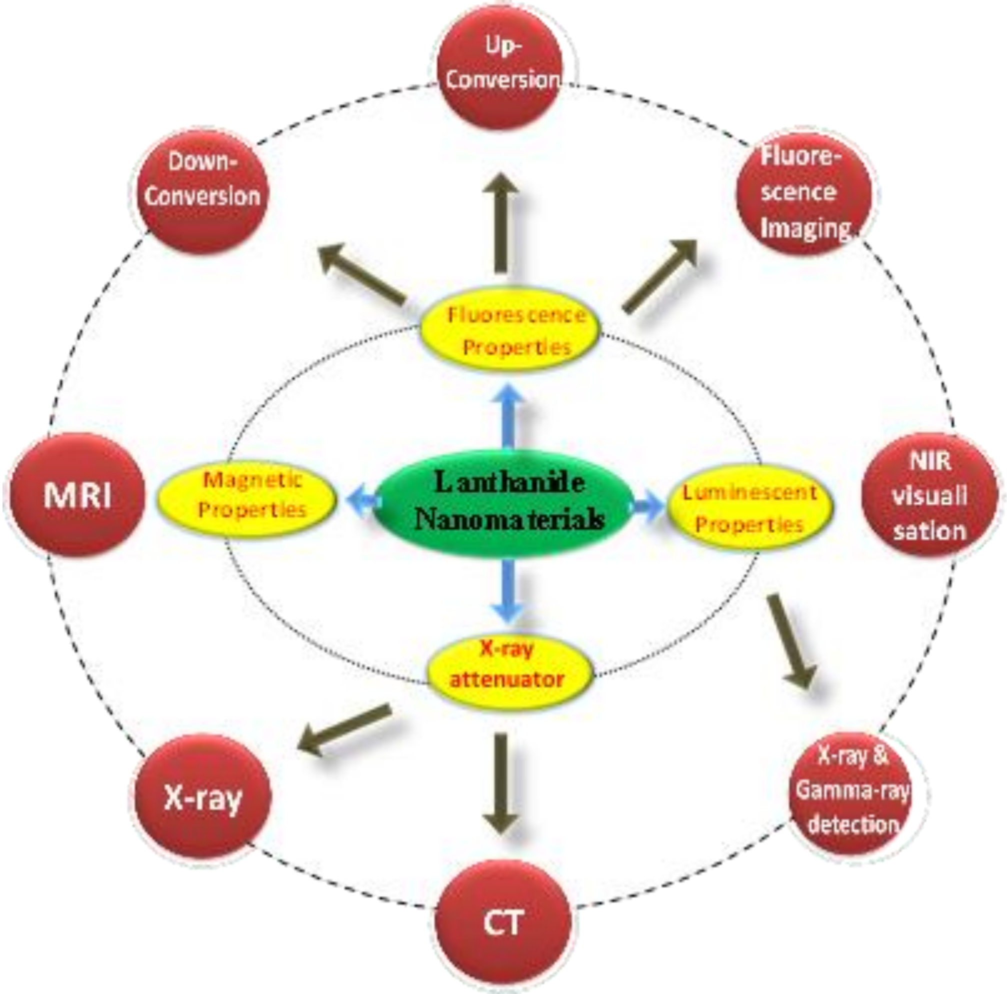

Fig. 4. Properties and applications of Lanthanide nanomaterials.

Currently, lanthanide chemistry is a very active area of research, because of the electronic structure of these elements, have various properties which makes them applicable in organometallic synthesis, catalysis, electronic and luminescent materials. [Xe]$4f^n$ is general electronic configuration of lanthanide (n=0-14) which generate a lot of variety energy levels and have well defined levels because 4f is shielded by filled $6s^2 5p^6$ sub shells. In last year's, it is found that lanthanide doped nanomaterials have magnificent features like long luminescence lifetime, excellent photo-stability, sharp-band emission and large anti-stoke shift due to their intra 4f or 4f-5d transitions [56]. Lanthanide doped upconversion nanoparticles have gained the much attention because of their anti-stoke photoluminescent shifting properties [57,58] . The transition in lanthanide involving the redistribution of electrons in 4f orbital and transition only in 4f orbital is contradict to Laporte rule i.e. allowed transition must have change in parity. Therefore, these ions show small molar absorption coefficients. Lanthanide-doped upconversion nanoparticles (UCNPs) offer promising applications in sensing and bioimaging due to their large anti-Stokes shift, non-autofluorescence from biosamples, high tissue penetration, and resistance to photobleaching (Figure 5). These properties enable efficient detection, minimize background noise, and support long-term imaging without signal degradation, making UCNPs valuable tools for biomedical research and clinical diagnostics [57].

Lanthanides have the remarkable properties and make them suitable for various applications like electronic, catalytic and luminescent. The size of lanthanide ion makes it to form a stable compound with high coordination number and geometric flexibility. Lanthanides behave as Lewis acid and therefore it form stable complexes with more electronegative donor atoms. Lanthanides have 4f electrons from which the optical and magnetic properties make them useful in MRI and fluorescence imaging (FI) and due to magnetic and fluorescence properties and unaffected by ligands. Therefore, it was shown that the lanthanide with ligands coated NPs are biocompatible, water soluble and highly stable. The NPs strongly conjugated with various functional group (-COOH, -OH, $-NH_2$ etc.) by electrostatic interaction [59, 60].

The lanthanide based nanomaterial has gained the efficient advantage in remediation of environment remediation. The photocatalyst treatment of wastewater using lanthanide based nanoparticles is one of the efficient

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methods to monitor toxins. The dyeing wastewater treatment was improved by lanthanide doped ZnO NPs as a photocatalyst for degradation of methylene blue [61]. The different lanthanide element were used for doping and degradation efficiency obtained for various photocatalyst in following manner Er doped ZnO (94.32%), Ce doped ZnO (93.01%), La doped ZnO (72.16%) and Pr doped ZnO (67.67%) [61]. This suggest that Er and Ce doped ZnO NPs are highly efficient photocatalyst for today and promising for future.

The lanthanide stannate ($Ln_2Sn_2O_7$) and its composite used as photocatalyst with highly efficient response in visible light through environment-friendly method. The reported $Nd_2Sn_2O_7$-SnO_2 composite synthesized by pineapple extract (natural source of sugar (fructose and glucose)) and act as novel, non-toxic biofuel nanocomposites used as photocatalyst [62, 63]. The sugar present in pineapple extract has a good impact in fabrication of nanocomposite. The nanocomposite were successfully used in photocatalyst degradation of environment contaminant and found very effective, easy, less time consuming and energy efficient in degradation of Rhodamine B with visible light. The organic dyes used in various industries like textile, paper, leather and pulp and have different ecological impact on the ecosystem. The removal of dyes from water is a major challenge for environment sustainability. The Gd-doped (4%) CdSe NPs were successfully synthesized by hydrothermal treatment and further used in sonocatalytic degradation of Acid Blue 5 (AB5) [64]. It was found that the NPs have 86% degradation efficiency in reaction time up to 90 minutes. The results demonstrated that the decolorization of water in presence of various inorganic ions proved attack of radicals which is responsible to degrade the dye [64].

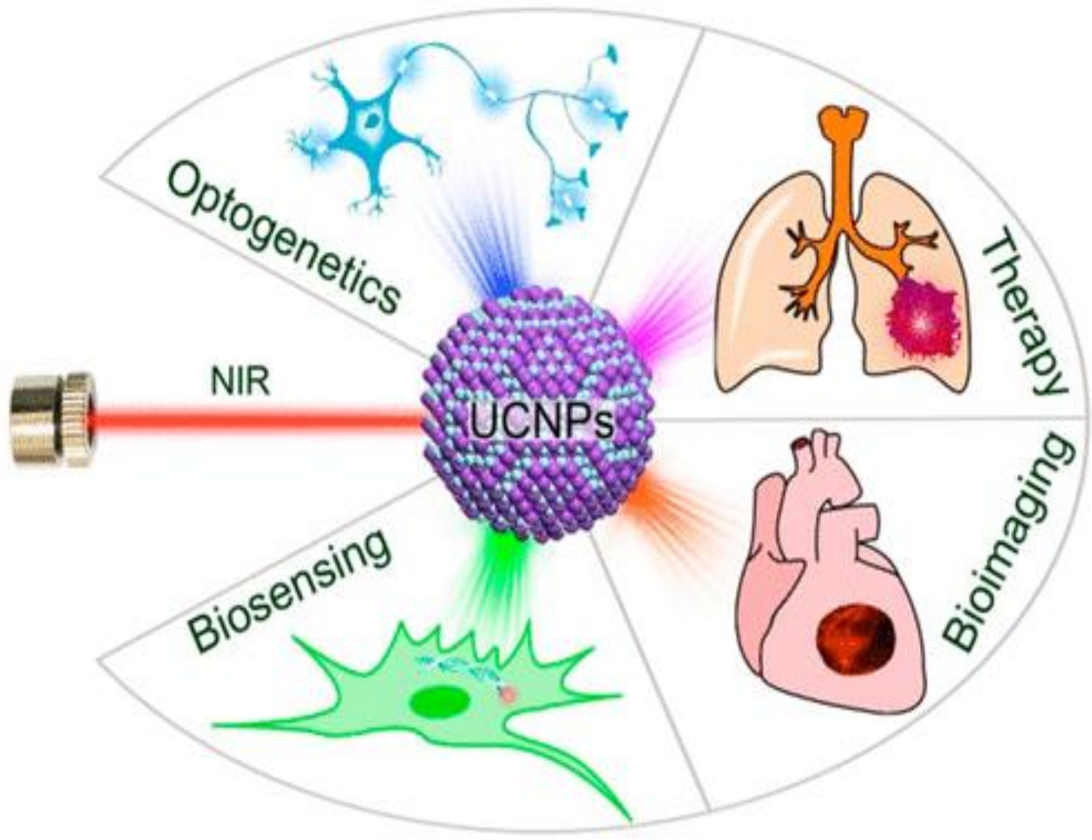

Fig. 5. Applications of Lanthanide based UCNPs. "Reprinted with permission received from reference [58] Zhang, X. *et al.* 'Ultrathin lanthanide oxides nanomaterials: synthesis, properties and applications', *Science Bulletin*, 61(18), pp. 1422–1434. Copyright @ ACS publications (2016).

For instance, Ln^{3+} (Yb^{3+}, Tm^{3+}) doped $BiPO_4$ and $BiVO_4$ nanocomposite for photocatalyst applications under UV-visible light illumination [65]. The photocatalytic probe was highly efficient in three regions UV, visible and NIR. The photocatalyst nanocomposite shows excellent degradation rate of better from last previous reports. The lanthanides doped in $BiPO_4$ make it upconversion nanocatalyst which has emission in visible region after excitation with near infrared laser (980). When the solar light is incident on nanocomposite photocatalyst, the holes and electrons generate in valence and conduction band (Figure 6). The electron generated in conduction band react with oxygen and hole in valence band react with water molecule which further produce $\dot{O}_2^-$ and $H\dot{O}$ respectively [65]. These reactive species further oxidized the dye molecules which produce CO_2 and H_2O after degradation. The surface area increased catalytic efficiency. In this paper, 30% area increase after composite formation than that of BiPO4:Yb^{3+}, Tm^{3+} nanocatalyst. The

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photocatalyst was very efficient in degradation the 98% of methylene blue in 100 min.

The europium containing compound polyoxometalates was design for fluorescent enhancement solution by the interaction of a cationic component (tetramethylammonium bromide) and anionic clusters (europium containing polyoxometalates) using ionic self-assembly strategy [66]. This sensor shows a great fluorescence sensing behavior towards detection of Cu^{2+} and it could detect with a limit of detection 0.15 µM. The sensor is highly efficient, real, selective and sensitive towards the detection of copper (II). The result prove that the fluorescent material have a lot of potential in optoelectronic sensing and application.

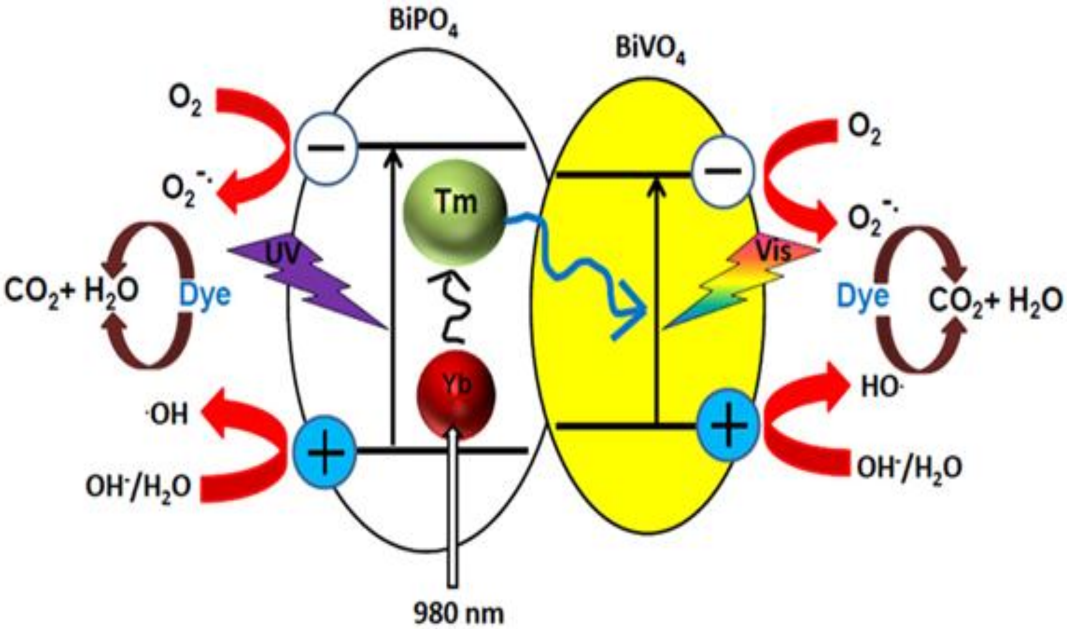

Fig. 6. Schematic representation of photocatalytic mechanism of BiPO4:Yb^{3+}, Tm^{3+} /$BiVO_4$ nanocatalyst. "Reprinted with permission received from reference [65] Ganguli, S. *et al.* 'A Highly Efficient UV–Vis–NIR Active Ln^{3+}-Doped $BiPO_4$ /$BiVO_4$ Nanocomposite for Photocatalysis Application', *Langmuir,* 32(1), pp. 247–253. Copyright @ ACS publications (2016)".

CeO_2-biochar nanocomposite by hydrothermal treatment for the sonocatalytic degradation of textile dye [67]. The nanomaterial further characterize by various technique like DLS, XRD, SEM, TEM and BET for obtain the size, morphology and area of the particles which conclude that 10-20 nm size particle with porous and rough surface. The degradation of reactive Red 84 (RR) was depending upon the CeO_2-H@BC amount, solution pH, ultrasonic power and amount of RR. The degradation of RR improved by enhance the amount (1g/L) and ultrasonic power (450 W), pH 6.5 for solution and 10mg/L initial concentration of RR which then lead to the 99% efficiency. Nd-TiO_2/bentonite and Ce-TiO_2/bentonite nanocomposite were used for photocatalytic activity and effective adsorption and removing of heavy metals from water. These nanocomposites successfully synthesized by sol-gel method and treated at 500 °C for 3 hours [68]. Then synthesized particles used in adsorption and removal of Cd and Pb. This system show excellent behavior towards degradation 5-20 minutes. The system is used to removing the organic pollutants in absence and presence of light. In presence of light, the nanocomposite Nd-TiO_2/bentonite was highly efficient, repeatability capability and decomposition of organic pollutant with removal of heavy metals also.

The nanoscale Fe_3O_4/CeO_2 composite was synthesized accordingly impregnation method and further applicable in degradation of 4-chlorophenol (CP) using through promotion the Fenton oxidation of CP by H_2O_2 [69]. The catalytic activity was checked by various components like Fe_2O_3 only, CeO_2/H_2O_2 and composite Fe_3O_4/CeO_2 without H_2O_2 but none of them was not able to efficient degradation of CP. The catalytic behavior of Fe_2O_3 was possible to only degrade upto 10% which was due to surface adsorption of Fe_3O_4 NPs and negligible as compared to heterogeneous Fenton reaction. The fast removal of CP from Fe_3O_4/CeO_2 composite using heterogeneous Fenton like catalyst was more efficient and higher removal of CP from pure Fe_2O_3 which demonstrated that introduction of CeO_2 increase the efficiency of catalyst. The dosage of H_2O_2 has also adverse effect on the degradation rate. As the concentration of H_2O_2 increased from 6mM to 30mM the degradation rate constant increased from 0.06 to 0.11 min^{-1}. Therefore the role of CeO_2 and H_2O_2 enhance the ability of heterogeneous Fenton like catalyst for degradation of CP in an excellent manner.

Further, the degradation of amoxicillin (Ax) was accomplished by the amine functionalized MOF@Sm_2O_3-ZnO nanocomposite. The porous NH_2-MOF-53(Al) was used as supporting frame for the Sm_2O_3-ZnO nanoflowers [70].

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The Ax is an antibiotic, widely used in treatment of infection (bacterial) for humans and animals both. So it is a major pollutant which affect the environment because of it low rate of biodegradation. The photocatalytic activity of environment friendly Sm_2O_3-ZnO enhanced by increase the active sites on the composite surface (Figure 7).

The ratio of Sm_2O_3-ZnO and NH_2-MOF play a major role in enhance the activity of synthesized probe. It was found that 7 wt% of Sm_2O_3 in the compound and 30 wt% corresponds to Sm_2O_3-ZnO and NH_2-MOF ratio in an excellent manner in dye degradation at pH=5 along with H_2O_2 as oxidant. In case of ZnO, Sm_2O_3 and Sm_2O_3-ZnO nanomaterials the degradation of Ax was reduced in comparison to NH_2-MOF@Sm_2O_3-ZnO nanocomposite which degraded the Ax 100%. The Ax was completely removed in Uv region to visible light in presence of NH_2-MOF@Sm_2O_3-ZnO nanocomposite before obtaining the natural water. This prove that MOF based probe can use as a potential for photocatalytic application at industry level to degrade the Ax pollutant.

Lanthanide doped upconversion nanoparticles (UCNP) have gained more attention due to the anomalous properties like long lifetimes, low autofluorescence background, large anti-stoke shift, convert the near infrared excitation to UV-visible emission [58]. These are generally consisting of a host, an activator and a sensitizer. Most important part of UCNP is host material because this provides unique optical and essential properties. $NaYF_4$:Yb, Er recently used in a lot of applications including small animal imaging, drug delivery, DNA detection and photodynamic therapy. These nanoparticle were used for the detection of herbicides 2,4-Dichlorophenoxyacetic acid and fenitrothion [71]. The immunochromatographic strips which based on UCNP were used for quantitative and sensitive detection of 2,4-Dichlorophenoxyacetic acid and fenitrothion. This method might be very efficient in detection of low molecular weight pesticides residues. The detection limit was found to be 5ng/ml and 12ng/ml for 2,4-Dichlorophenoxyacetic acid and fenitrothion. Rajaji et al focused on fabricated nanocomposite for detection of nitrite using through electrochemical sensor. The authors have synthesized ecofriendly, cost effective Er_2O_3 nanoparticles decorated with reduced graphene oxide nanocomposite (Er_2O_3 NP@RGO) through ultrasonic assisted synthetic route [72]. The cyclic voltammetry and ampereometric studies were showed excellent and tremendous electro catalytic performance and superior sensitivity towards nitrite. The excellent sensor shows superior sensitivity (24.17 $\mu A \mu M^{-1} cm^{-2}$) with a detection limit of 3.69 nM and also applicable in real sample like cured meet (beef) and water containing. Lanthanide doped titania increase the photocatalytic activity in presence of solar irradiation. Therefore this photocatalyst was used in degradation of organic pollutants. The lanthanide doping is shifted the catalytic activity towards visible spectra (bathochromic shift). Many lanthanides were used for doping and studied for catalytic activity in degradation of organic pollutants. All these photocatalyst were synthesized by easy, simple and facile methods and highly efficient in remove and degrading the organic pollutants. The detection of H_2O_2 is a major challenge. The high level of H_2O_2 would create cellular damage, DNA damage, aging and cell death. Therefore H_2O_2 with high level associated disease Alzheimer's disease, Parkinson's disease, inflammation etc. The Nd^{3+}-sensitized upconversion NPs ($NaYF_4$:Yb,Nd,Er@$NaYF_4$:Nd) was synthesized for detection of H_2O_2 [73] (Figure 8).

Further some modification was done by amphipathic micelles poly acrylic acid octylamine (PAAO) and then adsorbs the dicyano-methylene-4H-pyran (DCM). The sensor is then applicable for sensing of H_2O_2 in tumor bearing mice model. The detection limit of sensor was found to be 0.168 μM at excitation of 808 nm laser.

Zhou et al. prepared the Er-doped $BiFeO_3$ NPs with varying concentration of Er by sol-gel method. The synthesized NPs used for removal of tetracycline hydrochloride (TC) by photocatalyst degradation with visible light [74]. It was found that with increase in concentration of dopant Er optical absorption of $BiFeO_3$ significantly enhance and better.

Experimentally, 3% Er doped $BiFeO_3$ found to give highest photocatalytic efficiency for removal of TC(75.8%) which is approximately three times than that of without doped $BiFeO_3$ prepared samples. The Eu doped $BiFeO_3$ found to be stable, reusable and effective photocatalyst in removal of TC. Pr–doped In_2O_3 macroporous sphere were synthesized with different concentration variation of Pr by pyrolysis ultrasonic spray [75]. The growth of Pr doping into In_2O_3 affect the gas response by macrosphere significantly (Figure 9). As Pr concentration increased, the sensor suppressed the humidity dependent of gas characteristic. It was obtained that the humidity independent gas-sensing phenomenon of synthesized Pr–doped In_2O_3 gas sensor were ascribed to +3/+4 redox pairs of Pr ions. This redox process was attributed towards close approach of surface hydroxyl group which regenerated oxygen adsorption and dissipation of the electrons. The gas sensing ability of sensor was due to electron transfer from In ion to Pr ion and excellent hygroscopicity of Pr [75].

Rong et al. have been successfully synthesized the selective gas sensor based on molecular Ag-$LaFeO_3$ fiber (ALMIPs). Ag-$LaFeO_3$ molecular imprinted polymer were prepared by sol-gel method and then subjecting to calcination according as ALMIPs fiber 1 (filter paper), ALMIPs fiber 2 (silk), ALMIPs fiber 3 (carbon fiber templates) respectively. Experimentally, it was found that ALMIPs gas sensors exhibited higher selectivity towards 5ppm methanol i.e. higher than that other test gases (acetone, ammonia, formaldehyde, ethanol, gasoline and benzene). The response and recovery time of sensor is very less 40s and 60s, 47s and 44s, 44s and 48s for fiber 1, fiber 2 and fiber 3, respectively[76].

The results demonstrated that ALMIPs fibers show excellent sensing behavior towards methanol with high response, low limit and high selectivity. Thin film of La_2O_3 NPs was used for the sensing of CO_2 gas at low operating temperature 498 K [77].

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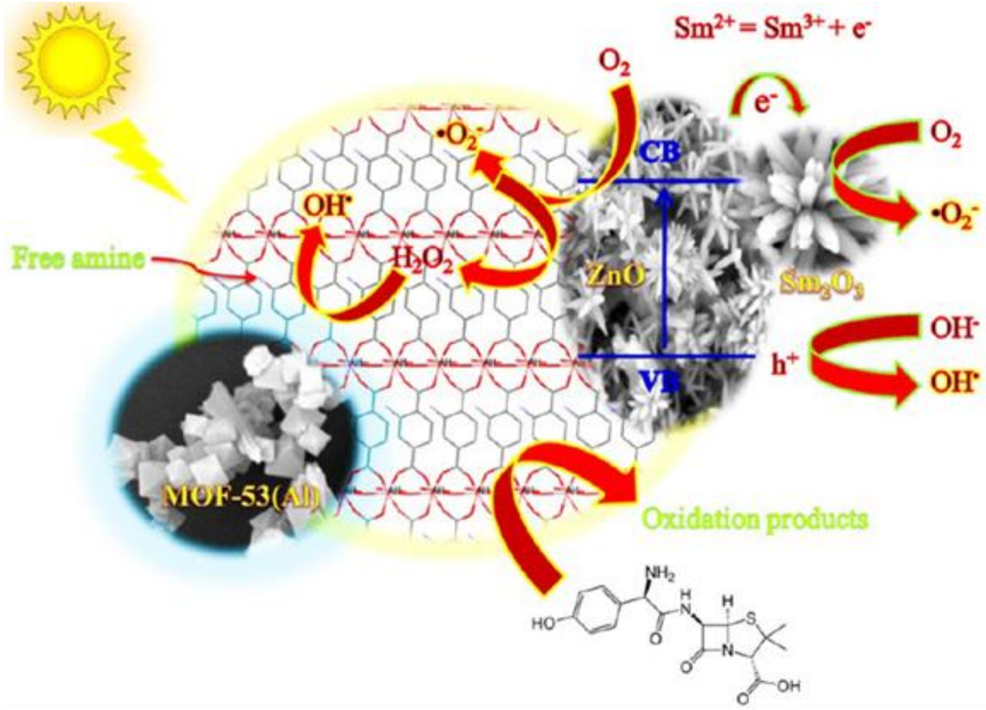

Fig. 7. Mechanism for photocatalyst degradation of amoxicillin (Ax) from MOF@Sm_2O_3-ZnO nanocomposite. "Reprinted with permission received from reference [70] Abazari, R. and Mahjoub, A.R. 'Amine-Functionalized Al-MOF@ ${}^{y}{}_{x}Sm_2O_3$–ZnO: A Visible Light-Driven Nanocomposite with Excellent Photocatalytic Activity for the Photo-Degradation of Amoxicillin', *Inorganic Chemistry*, 57(5), pp. 2529–2545. Copyright @ ACS publications (2018)".

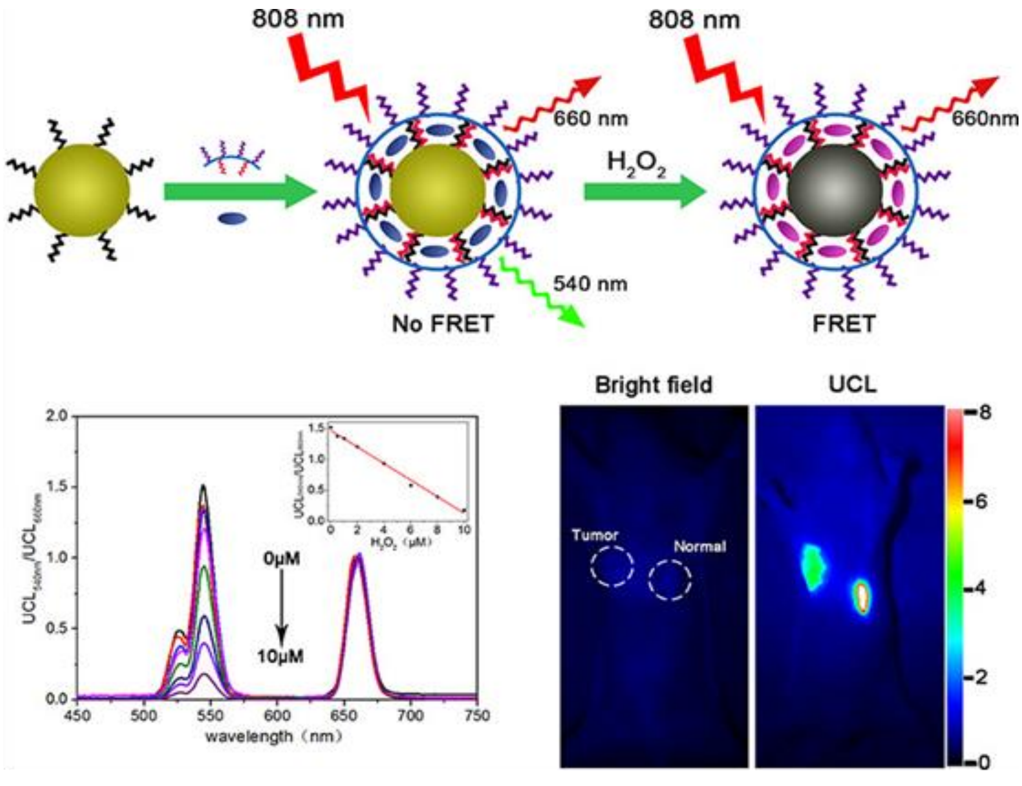

Fig. 8. Mechanism for detection of H_2O_2 by using Nd^{3+}-sensitized upconversion NPs ($NaYF_4$:Yb,Nd,Er@$NaYF_4$:Nd) with emission spectra. "Reprinted with permission received from reference [73] Wang, H. *et al.* 'FRET-Based Upconversion Nanoprobe Sensitized by Nd^{3+} for the Ratiometric Detection of Hydrogen Peroxide in Vivo', *ACS Applied Materials & Interfaces*, 11(7), pp. 7441–7449. Copyright @ ACS publications (2019)".

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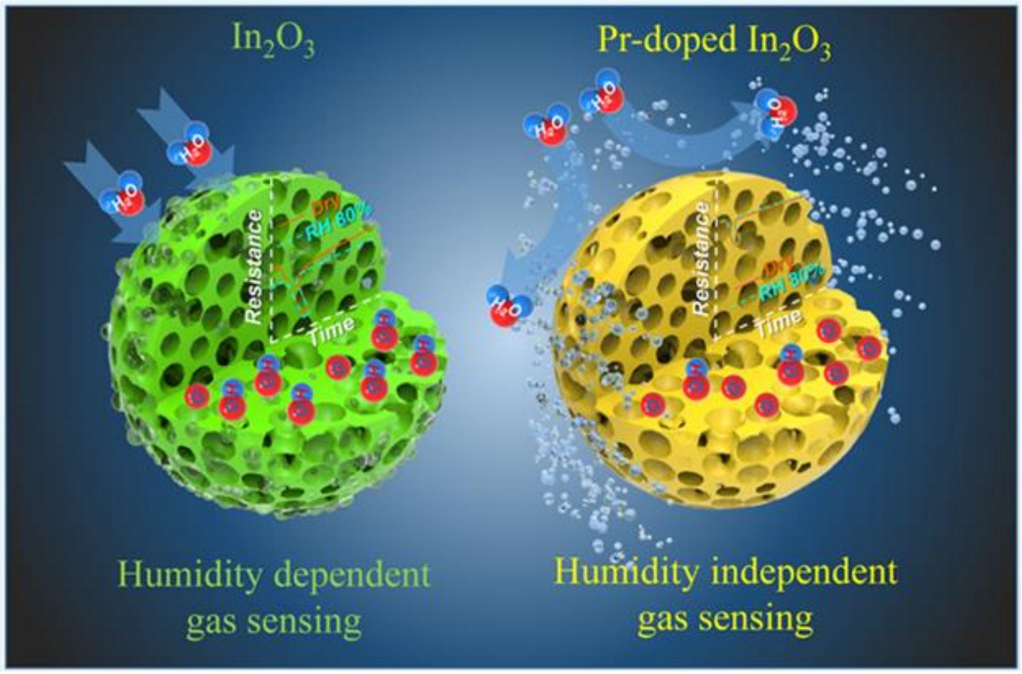

Fig. 9. Humidity gas sensing phenomenon from Pr–doped In_2O_3. “Reprinted with permission received from reference [75] Kim, J.-S. *et al.* ‘Humidity-Independent Gas Sensors Using Pr-Doped In_2O_3 Macroporous Spheres: Role of Cyclic Pr^{3+}/Pr^{4+} Redox Reactions in Suppression of Water-Poisoning Effect’, *ACS Applied Materials & Interfaces*, 11(28), pp. 25322–25329. Copyright @ ACS publications (2019)”.

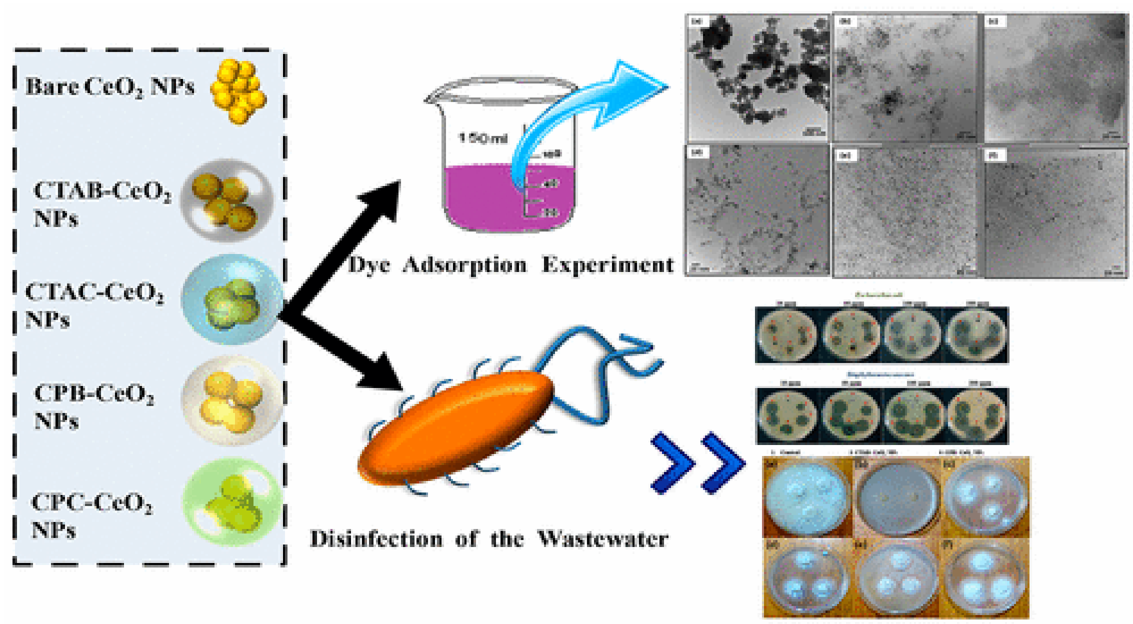

Fig. 10. Pictorial representation of procedure to follow the waste water treatment by surfactant functionalized CeO_2 NPs. “Reprinted with permission received from reference [79] Chaudhary, S. *et al.* ‘Chemical and Pathogenic Cleanup of Wastewater Using Surface-Functionalized CeO_2 Nanoparticles’, *ACS Sustainable Chemistry & Engineering*, 5(8), pp. 6803–6816. Copyright @ ACS publications (2017)”.

The La_2O_3 thin film is subjected to stable for electrical resistance for 30 minutes. The sensors shows maximum selectivity towards CO_2 gas and it was stable for a long for a long time period to detect CO_2. The sensor was also good response and recovery time period for CO_2 i.e. 80s and 141s, respectively.

Rahman synthesized the Ln doped TiO_2 NPs by hydrothermal treatment. The doping elements enhance the properties of complete probe and minimize the distortion [78]. The photoluminescence spectra for Ln doped TiO_2 NPs was

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temperature dependent in forming the gas (5% H_2 + 95% Ar) at 520 °C which is because of NPs modifications by doping and hydrothermal treatment. PL spectrum with varying distinguishable feature at low and high NIR wavelength region shows that the contribution from oxygen vacancies and trapped electrons. Chaudhary et al. synthesized bare and functionalized (CTAC, CTAB, CPC and CPB) CeO_2 NPs by aqueous precipitation method [79]. The NPs further used for wastewater treatment in dyes removal (Figure 10). The results of experiment confirmed that synthesized NPs exhibited efficiently lower the pollutant concentration, chlorine-free disinfection of water, less turbidity and significant reduction of chemical and biological oxygen demand, total dissolved solids and pathogenic load. The functionalized CeO_2 NPs were very effective in dye removal (99%) by adsorbents varied from 112.4 to 171.3 mg/g of dye which is excellent as compared to other nanoadsorbents studied. The antimicrobial and antimold activities of functionalized NPs have explained for their disinfective nature. The dye removed and adsorption performance was due to high surface area of functionalized CeO_2 NPs. The system is efficient in regeneration of adsorbent, adsorbate and better for several spike samples.

5. CONCLUSIONS

The modification of nanomaterial provides an advance approach towards monitoring of pollutants and their removal. Several types of nanomaterial has been used for detection and degradation of pollutants present in the environment from last decades. But lanthanide doped and modified nanomaterial showed excellent performance to achieve this goal. The used nanomaterial offer high stability, narrow absorption/emission bands and bright photoluminescence. Their modification and enhanced properties increase their potential in sensing and photo catalytic activity. The reported approach offer a straightforward, energy-efficient and environment friendly method for large production on lanthanide based nanomaterial with superior photo catalytic property.

6. FUTURE PROSPECTIVES

In last, there are urgent requirements to develop such types of materials which are advance and improved technology for environmental pollution control. The use and applications of nanotechnology in environment remediation has considerable probable. Therefore, the lanthanide nanomaterials would have a better option to resolve the challenges of environment. The potential of lanthanide nanomaterials has been exploring in sensing and environment remediation. The properties of lanthanides, detection and degradation of various pollutants discussed above widen the scope of respective particles in environmental applications. The modification and functionalization of materials give a new approach towards environmental remediation. The challenges must be overcome from lanthanide nanomaterials towards environmental remediation.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests.

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