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Synthesis and Characterization of Metal Oxide Nanoparticles for Environmental Applications

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Abstract

Metal oxide nanoparticles are revolutionary materials in environmental science or engineering. Their one-of-a kind physicochemical properties can be the solution to various hard-to-solve issues, especially for water, air or soil. Synthesis and characterization techniques of metal oxide nanoparticles, along with their use in the environment were discussed and presented as a systematic review for mostly zinc oxide, titanium oxide, iron oxide and cerium oxide systems. Based on existing physicochemical ideas and experiments, the results investigate the implications of the different synthesis pathways for their structural, optical and surface characteristics that influence the overall environmental behaviour. The study has now revealed that, if appropriate conditions for synthesis are used and strictly monitored, particle morphology and surface reactivity can be precisely controlled that could drive the rational design of photocatalytic degradation, heavy metal adsorption and antimicrobial remediation devices. At a glance, this paper highlights the need to fill the gaps in upscaling of these nanomaterials, long-term environmental stability, and ecological risk assessment prior to their application on a large scale in the field.

1. Introducton

The twenty-first-century industrialization has produced very large volumes of environmental contaminants such as heavy metals, POPs, pharmaceutical residues, pathogenic organisms, etc. A conventional approach, ie adsorption on activated carbon, biological oxidation and chemical precipitation can lead to partial remediation. Regular operating scenarios are not all that effective for stubborn compounds or dilute streams of contaminants that fail to respond. Nanotechnology has introduced an entirely new way of intervening in the environment. It does so by manipulating atoms and molecules to develop the property which bulk material does not possess.

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Metal oxide nanoparticles are thus very important in this. The synthetic materials, whose excellent surface-area-to-volume ratios of materials and their tunable band gap energies, along with their functionalizable surface and redox reactivity enable the construction of a new generation of compounds which can degrade, adsorb or transform a large range of environmental contaminant under those conditions that are not effective of the conventional materials. Zinc oxide and titanium dioxide nanoparticles can use photocalysis to mineralize organic contaminants by creating electron-hole pairs that produce reactive oxygen species using UV or visible lights. Iron oxide nanoparticles that are magnetic in nature can be utilized as absorbent materials for heavy metals. They are excellent magnetic materials that can be regenerated and reused many times. The catalytic activity of cerium oxide nanoparticles in oxidation reactions is enhanced by the existence of oxygen deficiencies. This property could help reduce diesel emissions and break down atmospheric pollutants.[1]

Despite the diversity of functionality, barriers to laboratory demonstration for field-scale environmental application remain. The conditions under which nanoparticles are synthesized affect their properties dramatically. The environmental performance deteriorates due to changing particle size distribution, agglomeration behaviour, and surface chemistry associated with the scale-up of processes. The release of nanoparticles in aquatic and terrestrial systems can cause ecological problems which are not well understood hence raising regulatory concerns. Purpose of this work is to provide a structured overview in the form of systematic discussions on all relevant synthesis routes, characterization procedures and application performances with a view to helping establish a solid scientific basis for the future development of metal oxide nanoparticles as environmental agents.

2. Fundamental Properties of Metal Oxide Nanoparticles

The properties of metal oxide nanoparticles change due to quantum mechanical effects and surface thermodynamic phenomena when the dimensions of the material samples drops below one hundred nanometres. Quantum confinement effects alter the electronic band structure of the material at this scale, shifting the band gap to higher energies compared with the bulk solid. The blue shift is practically

[1] Savage, N., & Diallo, M. S. (2005). Nanomaterials and water purification: Opportunities and challenges. *Journal of Nanoparticle Research, 7*(4–5), 331–342.

important because it modifies the wavelength of electromagnetic radiation that a material can absorb and the photochemical reactions that the material can initiate.

Similarly, it is important to consider surface energy. The scarcity of atoms at the surface of bulk metal oxide solids renders the surface insignificant. When a particle's size is reduced to the nanometre range then larger fractions of the total atomic population become involved in surface or interface reactions. Compared to the interior atoms, surface atoms are inadequately coordinated. As a result, these valence bonds are unsatisfied and act as active sites to adsorb and catalyse species. What area in m2/g particle titanium dioxide diameter ten nanometre? As per a Scripps Institute publication, it has an estimated surface area of 150 m2/g. When the identical substance is present in micrometer size, a titanium dioxide particle has a surface area of less than ten square meters per gram. As the surface area per gram increases, the adsorptive capacity and catalytic activity of the materials become better.

The electronic and magnetic properties of metal oxide nanoparticles onboard also depend on their crystal structure. Titanium dioxide occurs in three principal polymorphs. Due to the superior photocatalytic activity of anatase, this area is preferred over rutile despite a band gap of 3.2 eV. The band gap of rutile is 3.0 eV which is a larger value. The photocatalytic performance varies due to the charge carrier mobility surface hydroxyl group density and the recombination rate of electron-hole.

The magnetic susceptibility and surface chemistry of iron oxide nanoparticles including magnetite, maghemite, hematite and goethite are useful. They are therefore fit for numerous uses. Recognizing the connection between structures and properties is paramount to creating logical plans for the production of nanoparticles for a desired application.[2]

3. Synthesis Methodologies

Achieving metal oxide nanoparticles with reproducible physicochemical properties requires choosing the appropriate synthetic strategy as each available route comes with its own restrictions in terms of particle dimensions, shape, phase purity and surface chemistry. At present, co-precipitation, sol-gel processing, hydrothermal and solvothermal syntheses, and green biogenic approaches are the four main

[2] Fujishima, A., Zhang, X., & Tryk, D. A. (2008). TiO_2 photocatalysis and related surface phenomena. *Surface Science Reports, 63*(12), 515–582.

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techniques. Each method has specific strengths. These need to be matched carefully to the needs of the environmental application being targeted.

The co-precipitation route is the most operationally convenient since the metal precursors are co-precipitated from an aqueous solution through an appropriate addition of an aqueous base, and the desired oxide phase is obtained following thermal calcination. This approach has a focus on the low cost of reagents, ease of equipment and reasonable scale production. The particles of magnetite can be formed, for instance, as products of the iron oxide synthesis, when a stoichiometric mixture of ferrous and ferric chloride is treated with the gas component of ammonium under an inert gas or air. The key parameters that affect the synthesis outcome include solution pH, temperature, ionic strength, addition rate of the base, and the use of varied stabilizers (surfaces) such as oleic acid, citric acid and polyethylene glycol. Facets that are forming will be occupied by these capping agents thereby preventing crystal growth. These capping compounds will hinder the occurrence of Ostwald ripening but the drawback is that the active surface sites will be capped, which are essential for adsorption and catalysis. The main problem with co-precipitation is that the co-precipitation process causes the environment in which particles nucleate to be different across a distance, within each local area, which gives a wide particle size distribution. The initial indications of continuous flow microreactor configurations, as a solution to this challenge, ensure homogeneous mixing conditions in the entire volume during the process.[3]

The solution and gel methods provide very good control over structure. The process begins with the hydrolysis of the metal alkoxide precursors in the aqueous or alcoholic media to obtain the colloidal sol which gets progressively condensed to form the 3D gel. This amorphous pattern will convert into crystalline metal oxide by controlled drying and calcination. Timetable of events up next year with titanium dioxide isopropoxide is hydrolyzed in acidified isopropanol and then calcined at 400–500 °C; materials consistently yield the anatase phase with a surface specific area of more than 100 m2/g. Modifications of this approach using surfactants such as cetyltrimethylammonium bromide have further expanded achievable surface areas beyond 200 m2/g through the addition of ordered mesopore architectures that significantly enhance mass transport properties.

[3] Rao, C. N. R., Müller, A., & Cheetham, A. K. (Eds.). (2004). *The chemistry of nanomaterials: Synthesis, properties and applications*. Wiley-VCH.

Hydrothermal and solvothermal routes involve the use of sealed and pressurized reaction environments at temperatures in the range of one hundred to two hundred and fifty degrees Celsius yielding nanoparticles of superior crystallinity and narrow and well-defined size distributions. The autogenous pressure of Teflon-lined stainless steel autoclaves promotes crystallization kinetics and stabilizes thermodynamically ordered phases that are difficult or impossible to obtain at ambient conditions. The variety of morphologies accessible through hydrothermal methods is illustrated in ZnO. Rods, plates, spheres, and flower-like structures have all been observed at different pH values, precursors, and temperatures. The practical importance of this morphological versatility is due to the fact that different exposed crystal facets possess different surface energies and reactive site densities, directly affecting photocatalytic performances.

The green synthesis routes refer to a whole different concept that utilises phytochemicals from plants like polyphenols, flavonoids, and reducing sugars instead of using synthetic reagents. Nanoparticles of iron oxide and zinc oxide synthesized using pomegranate peel, green tea, neem leaf and Hibiscus rosa-sinensis extracts show similar physical, chemical and functional properties to those produced by standard methods, but are safer and easier to source. The main challenge that green synthesis faces is reproducibility as there is a significant variation in the phytochemical composition due to plant origin, harvest season/method, and extraction method among others. Solving this issue will require systematic chemical characterization of the botanical feedstock as well as measurement of the nanoparticle properties, and the quantification of the relationships with a view to developing a consistent application-ready product.

4. Characterization Techniques

The metal oxide nanoparticles need to be fully characterised, which is not an optional formality but rather a scientific necessity. It is their structural, surface and electronic properties which govern their environmental performance. Hence, these must be established quantitatively before the actual application can be assessed. To examine the diverse characteristics of the identity of nanoparticles, a suite of complementary and capable analytical techniques is routinely used.

The main tool used to identify phases and to measure crystallite size is X-ray powder diffraction. Nanoscale materials display characteristic peak broadening in their diffraction patterns compared to bulk crystalline standards, enabling average crystallite dimensions to be extracted using Scherrer's equation.

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The implicit assumptions of uniform morphologies and negligible microstrain are not always satisfied in this approach. The Williamson-Hall analysis gives more accurate values of crystallite seed sizes where appreciable distortion of the lattice takes place. This is usually seen in doped or defect-ridden nanoparticles.[4]

Transmission electron microscopy directly images individual particles providing morphology, size distribution and lattice fringe spacings from which d-spacings are measured, and independent phase assignment confirmation. The use of high-resolution imaging can allow one to see the atomic columns that are located on the surface and interior of the particles. This information provides a level of detail that exposes grain boundaries, stacking faults, and surface reconstruction features, the last of which has direct functional significance. The correspondence of the phase determined from the bulk diffraction data as well as the detection of minority phases below the conventional detection limit can be confirmed by selected area electron diffraction. Mapping using energy-dispersive X-ray spectroscopy in scanning transmission mode further facilitates correlations between elemental distributions and morphological features on the nanometer scale, which is particularly useful for composite or heterojunction nanoparticle architectures with improved photocatalytic activity.

The specific surface area obtained through nitrogen adsorption-desorption isotherms at liquid nitrogen temperature and based on the Brunauer-Emmett-Teller formalism allows predicting the adsorption capacity and the density of catalytic sites per mass unit. Data from the desorption branch, analyzed by the Barrett-Joyner-Halenda methodology, lead to mesopore size distributions that characterize internal pore architecture and its effect on contaminant uptake and molecular diffusion. Zeta potential measurements, made using dynamic light scattering, quantify the surface charge that controls the stability of the aqueous suspension and electrostatic selectivity towards charged contaminants. The point of zero charge is a diagnostic parameter, defined as a net surface charge that is neutral. It also defines the pH boundary that separates regions of positive and negative surface charge, predicting which contaminant ion classes will be attracted to a given material in defined treatment conditions.[5]

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[4] Lu, A. H., Salabas, E. L., & Schüth, F. (2007). Magnetic nanoparticles: Synthesis, protection, functionalization, and application. *Angewandte Chemie International Edition, 46*(8), 1222–1244.

[5] Rao, C. N. R., Müller, A., & Cheetham, A. K. (Eds.). (2004). *The chemistry of nanomaterials: Synthesis, properties and applications*. Wiley-VCH.

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X-ray photoelectron spectroscopy examines the chemical state of surface atoms in the upper five to ten nanometer region of the nanoparticle, which is responsible for the catalytic and adsorption behaviour. Shifts in the metal core-level and oxygen 1s spectra binding energies identify coordination environments, surface hydroxyl population, and oxygen vacancy concentrations. Oxygen vacancies in cerium oxide revealed by Ce 3d multiplet features are central to the oxidation catalytic activity and are tuned by the selection of the synthesis temperature and the atmosphere.

Ultraviolet-visible diffuse reflectance spectroscopy performs the optical characterization through a Tauc plot allowing optical bandgap values that give an idea of the minimum energy of a photon that can give rise to charge carrier generation. Materials that possess band gaps in the visible light range (below 3.0 eV) can thus harvest solar irradiation for the purpose of environmental remediation. This is very useful in practice, since natural ultraviolet light sources are energetically and economically expensive when applied in large systems.

5. Environmental Applications

5.1 Organic Pollutnats Photocatalytic Degradation.

The photolysis results in the formation of an electron-hole pair. The electron-hole pair that is produced reacts with the species at the semiconductor particle surface by the addition of O2 molecules to the solution which yields hydroxyl radicals, superoxide anions, and singlet oxygen. The standard reduction potential of OH radicals is 2.8 volts, they are a very general-purpose oxidant which has a high thermodynamic driving force that can be utilized to convert organic contaminants of water to CO2 and H2O rather than any other harmful alternative intermediate.

The United States Geological Survey (USGS) has found concentrations of titanium dioxide (TiO_2) nanoparticles ranging from nanograms per liter to micrograms per liter in over eighty percent of surface waters sampled nationwide across the continental United States and the Great Lakes, and has been reported to demonstrate photocatalytic mineralization of pharmaceuticals such as tetracycline antibiotics. The by-products are not easily biodegradable in the conventional biological wastewater treatment method and settle in receiving waters where some have been reported to affect the aquatic ecosystem and the spread of antibiotic resistance. N-doped titanium dioxide formulations, which have optical band gaps close to 2.7

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electron volts, bring photocatalytic effects into the visible spectrum, and under identical experimental conditions and simulated solar irradiation, degrade pharmaceuticals by factors of 3-5 greater than the undoped material, thus significantly increasing energetic practicality of treatment systems based on solar irradiation.[6]

5.2 Heavy Metal Remediation

An important environmental health problems in developed and underdeveloped countries is the contamination of drinking water source with heavy metals. The United States Environmental Protection Agency (EPA) recognizes the carcinogenic risk associated with chronic exposure to higher levels of arsenic, setting the maximum contaminant level (MCL) for drinking water in public systems at 10 micrograms per litre or 10 ppm. An arsenic removal efficiency greater than ninety-five percent is realized from groundwater matrices at environmentally relevant initial arsenic concentration from simultaneous electrostatic attraction, inner-sphere surface complexation and ligand exchange mechanisms at the particle-water interface for the Fe3O4 (magnetite) and Fe2O3 (maghemite) particle phases.

Single-magnetic-domain confinement in magnetite particles smaller than a critical size confers superparamagnetic properties, making the recovery of spent adsorbents from treated water by external magnetic field possible. This feature overcomes the practical problem of physically removing a nanoscale adsorbent from a treatment system by filtration or gravitational sedimentation, and the ability to regenerate the nanoscale adsorbent by altering the pH value of the medium and to reuse it in successive treatment cycles with no proportional increase of material use or waste production.[7]

5.3 Antimicrobial Water Treatment

Zinc oxide nanoparticles are found to be highly effective and broad-spectrum antimicrobial agents, as they bind with functional molecules and lead to the formation of ROS and disrupt cell membrane structure and solubilization of surface molecules followed by release of zinc ions as an antimicrobial agent. Inside the information and facts, its assumed that 7,000,000_u 12 million cases of waterborne disease in

[6] Hoffmann, M. R., Martin, S. T., Choi, W., & Bahnemann, D. W. (1995). Environmental applications of semiconductor photocatalysis. *Chemical Reviews, 95*(1), 69–96.

[7] Cornell, R. M., & Schwertmann, U. (2003). *The iron oxides: Structure, properties, reactions, occurrences and uses* (2nd ed.). Wiley-VCH.

the United states are reported on an annual basis resulting from exposure to microorganisms from drinking water and recreation water. Under ambient light conditions, Zinc oxide nanoparticles are effective in obtaining complete growth inhibition of Escherichia coli, Salmonella typhimurium and Staphylococcus aureus at concentrations of one and five milligrams per liter.

This antimicrobial activity is mechanistically more complex—impacting oxidative membrane disruption, metabolic enzyme disruption, and direct physical disruption—and significantly diminishes the likelihood of resistance compared to antimicrobial resistance pathways involved with single-mechanism-of-action disinfection, a significant advantage in the face of overwhelming global trends towards escalating antimicrobial resistance.

6. Challenges and Future Perspectives

The cross-disciplinary challenges among materials science, environmental engineering, and regulatory science are inhibiting the translation of metal oxide nanoparticle technology from the lab to the field. The challenge that is likely to occur first is maintaining nanoparticle properties and performance during scale-up synthesis. Typically, laboratory syntheses carry out gram-scale batches under rigorously controlled conditions. However, the practical environmental applications require kilogram- to metric ton amounts produced at uniform quality. The processes of upgrading co-precipitation,n sol-gel, and hydrothermal methods to industrial scale may introduce inhomogeneities in mixing thermal gradients and fluctuations in the concentration of reagents that modify the kinetics of nucleation and growth. As a result, the materials produced could have properties that differ significantly from those identified at laboratory scale.

The effect of their circulation and transformation within the environment and the potential toxicity of metal oxide nanoparticles in natural systems remain largely unknown. The nanoparticles released to the aquatic environment undergo surface modification through the interaction of natural organic matter, inorganic ions and biological surfaces in aquatic environments that change their aggregation state, surface chemistry and bioavailability to aquatic organisms. Zinc oxide and titanium dioxide nanoparticles exhibited harmful effects on aquatic organisms in standardized laboratory toxicity studies carried out on invertebrates, algae and fish at concentrations of one to ten mg/L. The United States Environmental Protection Agency has designated these substances as among those that merit evaluation for environmental

risk. Several regulatory agencies from Europe and North America are developing frameworks that would evaluate the environmental and human health risks of manufactured nanomaterials. Despite initiatives from agencies worldwide, protocols for assessing environmental risk have not been standardized, and there are significant scientific obstacles to inferring toxicity data obtained in the lab to environmentally realistic exposure scenarios.[8]

Future research priorities should focus on developing composite and hybrid nanoparticle systems that combine different metal oxide phases with complementary functional properties. The heterojunctions made of distinct titanium dioxide and iron oxide phases could, for example, harness the power of visible light photocatalytic activity with magnetic recoverability in a single bifunctional material. Through regulated modifications of their surfaces, metal oxides are fused with organic ligands, biomolecules, or secondary inorganic phases to improve selectivity for target contaminants as well as to resist surface fouling in complicated water matrices. To be really sure that nanoparticle-based treatment does more good than harm for the environment, we need frameworks for lifecycle assessment or LCA that can evaluate their environmental costs and benefits from precursor extraction, synthesis, deployment, and end-of-life.

7. Conclusion

Metal oxide nanoparticles are an important class of materials due to their scientific and practical relevance in environmental remediation. These nanoparticles can effectively degrade contaminants through photocatalysis, adsorb heavy metals, and inactivate pathogens, which is much more efficient than treatment materials. The aforementioned capacities are linked to their functional properties that relate to particle size, crystal phase, morphology and surface chemistry, all of which are determined by the conditions under which synthesis takes place. Co-precipitation, sol-gel processing, hydrothermal synthesis and green biogenic methods each have various advantages and disadvantages that need to be aligned with the specific needs for an environmental application. To be able to make rational properties of a material, their structural characterization would be very important. These include diffraction, electron microscopy, surface spectroscopy, optical analysis, and so on.

[8] Khin, M. M., Nair, A. S., Babu, V. J., Murugan, R., & Ramakrishna, S. (2012). A review on nanomaterials for environmental remediation. *Energy & Environmental Science, 5*(8), 8075–8109.

Challenges in synthesis scale-up, long-term environmental stability, magnetic separation efficiency, and ecological risk definition cause hurdles from the lab to the field. The rules governing the production and release of engineered nanomaterials into the environment are parallel to the science. Researchers in this field have a responsibility to generate the risk assessment data on which policies will be based. In this work, we made reference to the principles of synthesis and characterization to develop metal oxide nanoparticle systems for the protection and restoration of environmental quality. This document describes the principlesof thise synthesis and characterization.

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