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A Study of Novel Metal Nanomaterials and Their Catalytic Applications

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Abstract – Nanomaterials have elevated the importance of science and innovation. Their advancement has substantial impact on a wide range of applications, from catalysis to electronics & data storage. Properties and synthesis of different kinds of nanomaterials are also reviewed with special emphasis on the semiconductor-noble metal and noble metal–noble metal hybrid nanomaterials. Variation of properties of nanomaterials with the modification of shape, size and dimension is also described along with their potential field of applications in this part. This article will serve as initial point for the development of noble metal nanomaterials, which will bring new possibilities in nanocatalysis.

Key Words – Nobel Nanomaterial, Hybrid Nanomaterial, Nanoparticle, Catalysis

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INTRODUCTION

Study of nanoscience & nanotechnology started with the challenge “to write the entire twenty four volumes of Encyclopaedia Brittanica on the head of a pin”. The idea was brought to light by Prof. Richard Fynmann in his legendary lecture ‘there’s plenty of room at the bottom’ in the year 1959. This lecture opened up a new door to scientists to think about ‘small’ particles which was believed to be the first step towards ‘nanoworld’. Since then, nanoscience and nanotechnology evolved as an interdisciplinary branch of science where the knowledge of physics, chemistry, biology and engineering were equally important to synthesize new kind of nanomaterials, to understand their properties and assembling them in a proper way to build up a particular device. The word ‘nano’ comes from the Latin word ‘nanus’ which means ‘dwarf’ or ‘very small’. Thus nanoparticles are small particles which have atleast one dimension in the range of 1- 100 nm and possess dissimilar physical & chemical properties than their bulk counterpart.

These two factors result in prominent and effective properties of nanomaterials for several technological uses in the field of electronics, metallurgy, optics, non-linear optical devices, catalysis, photocatalysis, solar cell, photonic band gap materials, information storage and processing, sensors, fuel cell, water purification, photonics, super plastic ceramics, adsorbent, biomedical applications, and even in the regular house-hold products. Better performance and small size are the main advantages of using nanomaterials at different fields.

General approaches towards the synthesis of nanomaterials: Here are 2 general approaches towards the synthesis and fabrication of nanostructures- i) top-down approach and ii) bottom-up approach. Top-down approach starts with larger (macroscopic) initial structure which is broken into smaller pieces in the nanoscale. Typical examples of this approaches are- ball milling, laser-beam induced chemical etching through mask and different lithographic techniques.

On either side, bottom-up approach starts with atoms or molecules which assemble to form nanostructure. Chemical and physical forces are responsible for this kind of assembly. The bottom-up approach has categorized into two methods, namely liquid phase method and gaseous (vapour phase) phase method. Co-precipitation method, sol-gel method and solvothermal methods etc. are well-accepted liquid phase method, whereas chemical vapour deposition method (CVD) and physical vapour deposition methods (PVD) etc. are well known gaseous phase methods. The bottom-up approach becomes more suitable approach for chemists as it develops nanostructure by the arrangement of atoms or molecules in a regular fashion. In bottom-up approach, nucleation and growth are the two main steps for the synthesis of nanoparticles. Nucleation is the initial step for the creation of NPs where small seeds are formed which act as template for crystalline nanoparticles. The seeds can generate either homogeneously or heterogeneously. Classical nucleation theory explains the steps in terms thermodynamic assumptions. Qualitatively it explains the synthesis of colloidal sulfur from sodium thiosulfate. Decomposition of thiosulfate results in the generation of sulfur monomer which proceeds at a high rate. This step continues until a threshold concentration is reached. After the limiting concentration of monomer, nucleation step ceases and the growth process comes into play. Seeds of sulfur monomer get diffused to the other monomer surface forming nanoparticles of larger size and this step continues until all the monomers are consumed or the particular size depending upon the thermodynamic parameter is reached. Rate of this growth process is dependent on the rate of diffusion of the monomer to the surface and the rate of reaction on the surface. Initially the rate of reaction on the surface is the rate determining step, but when the concentration of monomer decreases, the rate of diffusion becomes the rate determining step. Among the various growth mechanisms of nanoparticles, Ostwald ripening is some of the popular methods. According to this growth mechanism, solubility of nanoparticles changes with the variation of the dimension of the nanoparticles. Smaller nanoparticles have high solubility as well as high surface area which results generation of seeds and re-dispersed in solutions as seeds. This increases the concentration of seeds and helps the growth of nanoparticles of larger size. If sufficient times are provided, the particles may even lost the nano dimensionality.

CLASSIFICATION OF NANOPARTICLES:

Based upon dimension: Since the properties of the nanomaterials are highly dependent on the size, shape and dimension, nanomaterials has classified into 4 categories according to the dimension: i) zero dimensional (0-D), ii) one dimensional (1-D), iii) two dimensional (2-D) and iv) three dimensional (3-D). With decrease in dimensionality of the nanostructure, the movement of the carrier becomes confined. This quantum confinement is in three dimensions for zero dimensional quantum dots (QDs). Nanowires, nanotubes and nanorods are example of 1-D nanostructure where quantum confinement occurs in two dimensions. 2-D nanostructure shows plane like structure and hence made up with thin films, nanolayers and nanocoatings. Nanocubes, spheres, nanoflowers or any other nanostructure can be considered as 3-D nanostructure. Confinement of the movement of the electrons results in generation of discrete energy levels. This has been schematically shown in Fig. where, 3-D bulk semiconductor has continuous energy states, quantization starts with decrease in dimensionality and for 0-D QDs the energy levels become discrete.

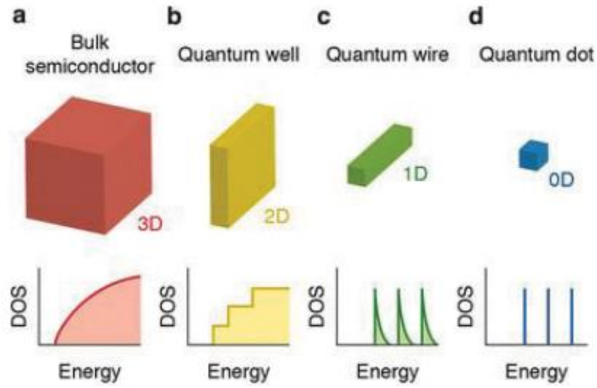

Fig: Schematic presentation of energy level configuration of semiconductor nanomaterials of different dimensionality, such as (a) 3-D, (b) 2-D, (c) 1-D and (d) 0-D.

Noble metal nanoparticles: The metal nanoparticles which are not susceptible to corrosion as well as oxidation in moist air are called noble metal nanoparticles. Gold (Au), silver (Ag), palladium (Pd), platinum (Pt), ruthenium (Ru), osmium (Os) and iridium (Ir) fall into this category. Among these noble metals, properties of Au & Ag nanoparticles have been studied extensively due to their wide applications. Out of several important properties of noble metal nanoparticles, optical property is the most fascinating one. Their distinctive optical properties engender due to surface plasmon resonance (SPR) which make them potential substance in the field of biological imaging, chemical and biochemical sensing and hence medical diagnostics. When tiny metal particles are exposed to electromagnetic wave, the free electrons oscillate forming a dipole in the material due to interaction with the electromagnetic wave. To minimize the displacement of the electron with respect to the nuclei, a restoring Coulombic attractive force originates and the electrons migrate in the material to restore its initial state. As a result electron clouds oscillate with respect to the nucleus. Thus when free electrons in oscillate with the similar frequency of the electric field of the electromagnetic wave SPR takes place. This is schematically shown below.

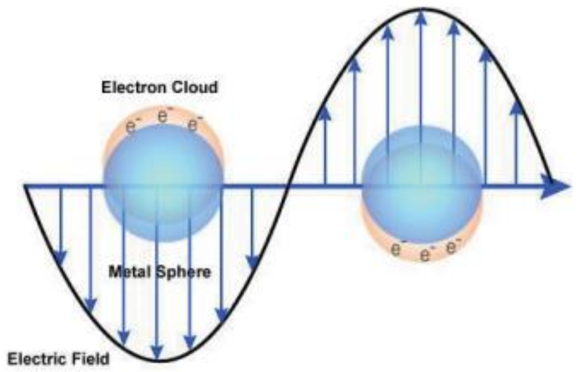

Fig: Graphic representation of surface plasmon resonance.

This oscillation frequency is controlled by the shape and size of the charge distribution, density as effective mass of the electrons. Due to this phenomenon, noble metal nanoparticles, specifically Au, Ag and Cu, exhibit bright and fascinating colors since their SPR fall in the visible region of electromagnetic radiations. It can easily be tuned with size and shape of a particular nanomaterial. For example, change of color of the colloidal silver sol with the change in size of the nanomaterials is shown below.

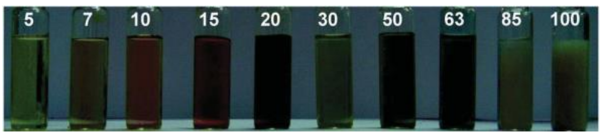

Fig: Variation of color of Ag nanoparticles with the variation of size as shown on the respective test tube in nm.

Magnetic nanoparticle: Iron (Fe), cobalt (Co) and nickel (Ni) nanoparticles are example of magnetic nanoparticles which manifest magnetism. Stability of these magnetic nanoparticles with respect to aerial oxidation is the main obstacle to obtain such high magnetic moment nanomaterials. Apart from metallic nanoparticles, there are several oxide nanoparticles which exhibits magnetic property. Nanoparticles of iron oxides, ferrites etc. show interesting magnetic properties in the nano size region. Magnetic nanomaterials are particularly useful for magnetic resonance imaging, data storage applications, targeted drug delivery as well as catalysis.

Semiconductor nanomaterials: For a semiconductor material, the energy gap (Eg) amongst the highest occupied molecular orbital (HOMO) & lowest unoccupied molecular orbital (LUMO) (usually less than 4 eV) lies in between that of metal and insulator. Flow of electrons result the generation of current for metals, while movement of either electrons or holes can trigger the formation of current for semiconductors. When movement of electrons is responsible for the generation of current, the semiconductor is termed as n-type semiconductor. While movement of holes creates current, the semiconductor is called p-type semiconductor. Group 14 elements like Si, Ge are elemental semiconductors. Compound semiconductor materials can be made with the combination of III-V, II-VI, IV-VI and even I-VI elements. GaN,GaP, GaAs, InP, and InAs are example of III-V semiconductor; ZnS, ZnSe, CdS, CdSe and CdTe are II-VI semiconductors; GeS, GeSe, SnS, SnSe and SnTe are IV-VI semiconductors; Ag2S, Cu2S are I-VI semiconductors. There are some metal oxides like Al2O3, ZnO, TiO2, CeO2 etc.

Hybrid nanomaterials: Advancement of technology requires the development of multifunctional materials. It is quite difficult to obtain different functionalities from single component nanomaterial. Combination of different nanomaterials onto a single nanostructure is a general approach to achieve this goal. These combinations of different nanoparticles to form a single nanostructure which may contain the property of individual materials or may exhibit different from that of the individual materials are called hybrid nanomaterials. Depending upon the nature of interaction between the individual components, the property of the hybrid nanostructure varies. When optical or electrical property obtained from the hybrid nanostructure, is just the addition of that of the component materials, interaction between the components is small or negligible.

Applications of hybrid nanomaterials: Nanomaterials are often combined with a definite composition according to their applications in diverse fields. Among this wide range of possible applications, this work focuses on different types of catalysis as conversed in the subsequent sections.

Catalysis: Usually, catalysis is the method by which activation energy of a chemical reaction decreases in presence of a substrate which remains in its initial state after the completion of reaction, called catalyst, resulting the formation of target molecule at an ease than that is required in absence of the catalyst. Most often, a catalyst reduces the activation energy by forming an activated complex of lower energy and regains their initial state after the completion of the reaction. In short, an efficient catalyst reduces the cost of formation of the desired product. To catalyze a particular reaction, the catalyst must have some definite property depending upon the reaction mechanism. That is why a particular reaction is catalyzed by a particular type of materials.

Photocatalysis: A special type of catalysis which is initiated in the occurrence of light is called as photocatalysis. Degradation of industrial toxic waste into non-toxic materials with the help of photocatalysis is a well-known phenomenon.

Several strategies have been used to enhance the photocatalytic activity among which synthesis of semiconductor-metal hybrid nanostructure serve quite handy.

- Click reaction for the synthesis of 1, 4 disubstituted 1, 2, 3 triazole
- Carboxylation of terminal alkynes
- Preferential oxidation (PROX) of CO in presence of excess H2:
- Surface Enhanced Raman Spectroscopy (SERS):

Miscellaneous application: Several other applications in the field of photophysics, photovoltaics, dye-sensitized solar cells, optics, optoelectronics, non-linear optics, sensing, light emitting diode (LED), other kinds of catalysis as well as in daily households, makes the synthesis of hybrid nanostructure of different functionalities as their proper assembly essential for the betterment of mankind. Hybrid nanoparticles have already shown their potentiality in the field of biomedical imaging, therapeutic applications, detection of several disease at an early stage which helps to cure the disease at an ease

LITERATURE REVIEW

Alain Roucoux et al. (2021) this book gives a comprehensive overview on the recent advances and current trends in the engineering of metal nanoparticles – including their design, synthesis, and characterization by state-of-the-art techniques – together with their various applications in catalysis. A collection of short chapters is proposed to make the reading of the whole book easier and more dynamic, while providing the main key aspects of the use of metal nanoparticles in catalysis today. Coming from a large range of institutions in different countries, the authors have been chosen for the originality of the synthesis method or of understanding approach or/and the interest toward a target catalytic application that they develop.

This book brings together the most new accomplishments in the growth of metal nanoparticles as catalysts by covering a selection of key aspects in this challenging domain and underlying new trends. Thus, each chapter illustrates one emerging domain of nanocatalysis with concrete applications and understanding of metal nanoparticle behavior through the presentation of the most relevant examples from the recent literature including those of the invited groups. As it can be seen in most of the chapters of this book, a cleaner chemistry and sustainable developments are at the center of current research efforts. The use of green solvents (for instance, water, polyols, glycerol, and in a certain extent ionic liquids) as synthesis or/and reaction media has already shown to be efficient to provide highly performant nanocatalysts for diverse organic transformations. Also, the

Study of catalyst lifetimes (in terms of recovering, recycling, durability, and repeatability) is among the objectives of many present works. Concerning the catalytic performances, if highest possible activities are always targeted, high selectivity (both chemo- and stereoselectivity) have become a key point in order to limit as possible product separation steps, which are often costly regarding solvent and energy consumption. Also, the development of nanocatalysts based on earth-abundant and cheap metals is more pertinent nowadays. This allows to face the decrease of noble metal reserves on the Earth and to reduce the catalyst costs. This is particularly relevant with regard to the scale up of catalysts for industrial processes. This allows not only to take advantage of natural chemicals but also to valorize certain wastes issued from biomass (for instance, woody cellulose, chitin from shellfish shells, etc.). Another important development is the use of raw chemicals issued from chemical industry (like CO2) or resulting from the increasing human activities. Concerning the improvement of catalytic transformations, which are at the basis of the production of energy vectors such as hydrogen production (either directly from water through the water-splitting process or from dehydrogenation of formic acid that can derive from CO2), among other present challenges in this domain, nanochemistry already proved to bring powerful solutions.

Kim-Hung Huynh et al. (2020) Metallic alloy nanoparticles are made by fusing two or more metals together. Because of their synergistic properties, bimetallic or trimetallic NPs are known to be better than monometallic NPs. Based on their plasmonic, catalytic, and magnetic capabilities, we explain the structure, production process, properties, & biological uses of metallic alloy NPs in this study.

Jaison Jeevanandam 2018) NMs have risen to power in scientific innovations as a result of their tunable physical, chemical, & biological properties, as well as their superior performance over bulk material. The size, content, shape, & origin of NMs are used to classify them. The ability to forecast the distinctive features of NMs makes each classification more valuable. Because of the rising manufacturing of NMs & their commercial uses, toxicity issues are unavoidable. The goal of the study is to compare synthetic (manufactured) with naturally occurring NPs) & NSMs to identify their nanoscale features and to identify specific knowledge gaps related to NPs & NSMs in the environment risk assessment. The paper discusses the history and classifications of NMs, as well as the many sources of NPs & NSMs, both natural and synthetic, & their hazardous effects on mammalian cells or tissues. The forms of hazardous reactions linked to NPs & NSMs, as well as the policies in place in various nations to mitigate the dangers, are also highlighted.

Marcos Fernández-Garca and colleagues (2017) The fundamental science, synthesis, characterization, physicochemical properties, & applications of oxide NPs are all covered in this chapter. Describes the fundamental aspects that evaluate the growth & behavior of these systems, momentarily explores synthetic procedures utilizing bottom-up & top-down fabrication technologies, describes advanced experimental techniques & state-of-the-art theory results being used characterize the physico-chemical properties of oxide solids, & summarizes current knowledge about key oxide materials with great technical applications.

L. Shang et al (2014) With rapid growth of nanotechnologies, a thorough understanding of the interactions between manufactured NMs with cells, tissues, & organisms has become increasingly relevant, particularly in terms of potential health risks. This study offers an overview of current nano-bio dynamics research, with an emphasis on the impact of NP size on their interactions with live cells. We review basic methods for determining NP size & discuss new research on the effects of NP size on passive and active cellular internalisation & intracellular localization. The effects of cytotoxicity are also highlighted.

We revealed that stepwise seed-mediated growth could be expanded in non-aqueous solution (solvothermal synthesis) & enhanced as a method for controlling the homogeneous structure of palladium nanoparticles (Pd NPs) over a wide range in Lei Zhang et al. (2012). Pd(acac)2 was reduced with formaldehyde in various organic amine solvents to produce monodisperse Pd NPs with a size of about 5 nm. The size of monodisperse Pd NPs may be carefully adjusted from 5 to 10 nm via an enhanced stepwise seed-mediated synthesis. Without any size selection, the Pd NPs could self-assemble into a well-shaped superlattice crystal.

CONCLUSION

This study concluded the definitions, latest studies, and challenges involved the synthesis of noble metal nanoparticles. Noble metals were once mostly valued for their attractive & bright colours in their bulk form, but their applications have recently grown considerably more sophisticated. This has happened as a result of recent advancements in fundamental chemistry and physics, and also advances in materials science for manipulating matter at the nanoscale. Properties and synthesis of different kinds of nanomaterials are also reviewed with special emphasis on the semiconductor-noble metal and noble metal–noble metal hybrid nanomaterials. Due to their exceptional electrical, optical, magnetic, & thermal capabilities, metallic nanomaterials, a novel form of nanomaterial, have intriguing promises in the realms of microelectronics, optoelectronics, & sensors, particularly in catalytic regions.

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