

Nanoscience and nanotechnology – A review

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ABSTRACT

Nanoparticles have special physical and chemical properties which are not seen in the bulk material. They are becoming widely used in the various branches of science and technology. Nanoparticles can be prepared from many materials. In this review article, different types of synthesis, characterization and development of new and novel strategies of generation of nanoparticles are discussed.

Key words: Nanomaterials, SERS, quantum dots, nanotubes, nanocapsules.

INTRODUCTION

Nanoscience is an emerging area in which the size and the structure of materials as well as devices are controlled at the nanometer scale. Nanoparticles act as a bridge between bulk materials and molecular structures. Bulk materials have constant physical properties, regardless of their size. But in the nanoscale level, size dependent properties such as quantum confinement in semiconductors, surface plasmon resonance in metal particles and superparamagnetism in magnetic materials are observed. The properties of the nanocrystalline materials change due to their small grain size, the large percentage of atoms in their grain boundaries and the interaction between grains. Nanomaterials have special physical and chemical properties such as small size effect, surface effect, the quantum size effect and macro-quantum tunneling effect¹. Nanomaterials are becoming widely used in electronics, magnetics, optics, biomedicine, pharmaceuticals, cosmetics, energy sensors, catalyzers and other fields². With the development and application of nano-science and technology, more nanomaterials are entering

into the environment and becoming pollutants via a variety of routes³, which greatly increases the risk of human exposure. Previous research has shown that nanomaterials can penetrate the blood-brain barrier, the placenta barrier, and other natural protective barriers, revealing their potential as serious biohazards^{4,5}. Nanomaterials have toxic effects on the target at the whole organism level, the cell level, the subcellular level, or the functional macro-biomolecular level, e.g. genes and proteins⁶⁻¹². The environmental genotoxic behaviour of silver nanoparticles combined with the detergent cetylpyridine bromide was reported by Chi *et al.*¹³. The optical properties of nanoscale materials differ greatly from their bulk counterparts^{14,15}. Because of their special optical, magnetic and catalytic properties, some metal nanoparticles suspended in solutions are expected to be used as functional materials¹⁶⁻¹⁸. Nanosize metals have been shown to exhibit novel size-dependent optical properties which cannot be explained classically¹⁹. For example, gold nanoparticles show photoluminescence only when their size become less than 50 nm in diameter²⁰. For the study of the size-dependent properties, it is necessary to

prepare Ag nanoparticles of different size. The most commonly employed method in the preparation of metal nanoparticle is chemical reduction. However, the size of particles cannot be changed easily. Recently, a novel approach to prepare "chemical pure" Ag colloids is laser ablation of pure Ag in aqueous in a size-selected and size-controlled manner²⁰⁻²⁵. It is well known that nano size has great influence on the performance of several material systems. Moreover, the role of dimensionality in shaping the spin-polarized electronic structure of nanocrystalline diluted magnetic semiconductors is important in understanding their ferromagnetic behaviour²⁶⁻³².

Zhao *et al.*³³ reported SERS active three silver nano particles of different size characterized by the UV-vis absorbance spectra and TEM images with different photoluminescence spectra indicating that the photoluminescence property of silver nanoparticles is dependent on the size. Nano-structured Ni(II)-curcumin modified glass carbon electrode for electrocatalytic oxidation fructose is reported by Elahi *et al.*³⁴. A highly sensitive assay for spectrofluorimetric determination of reduced glutathione using organic nano-probes was reported by Wang *et al.*³⁵ and in this study, the new nanometer-sized fluorescent particles have the potential to overcome problems encountered by organic small molecules by combining the advantages of high photobleaching threshold, high quantum yield, long fluorescence lifetime, good chemical stability and wide excitation spectral properties. The development of organic nanoparticles for biological labeling or fluorescent probes will open up new possibilities for many multicolor experiments and diagnostics. It is expected that this kind of nano particles as effective biological labels will have more and more applications in biochemistry and life science research. Fine metal particles have applications in the area of catalysis, opto-electronics due to their size-dependent optical, electrical and electronic properties³⁶⁻³⁹. Palladium is a versatile catalyst for many organic transformations⁴⁰ such as Mizoraki-Heck^{41,42}, Suzuki-cross-coupling^{43,44}, Stille⁴⁵⁻⁴⁷ and Sonogashira⁴⁷ coupling reactions. Formation, stabilization and the size of the palladium nanoparticles has a critical role in all these reactions. Preparation of palladium nanoparticles has been

reported using hydrazine⁴⁰, hydrogen⁴⁸ and sodium borohydride⁴⁹. Evidence for monoalkoxide species on the surface of palladium nanoparticles synthesized in ethylene glycol is reported by Arora *et al.*⁵⁰. Nanoparticles can be fashioned from many materials and have a wide functional diversity very different from bulk materials, with their electronic, optical and catalytic properties originating from their quantum scale dimensions. These confinement effects often yield nanomaterials with greatly improved and potentially controllable properties. Metals exhibit a particularly wide range of material behavior along the atom to bulk transition. At sizes comparable to the Fermi-wavelength of an electron, optical properties are significantly modified, and discrete nanocluster energy levels become accessible. Metal nanoclusters exhibit molecule-like transitions as the density of states is insufficient to merge the valence and conduction bands. Such studies have yielded fluorescent Au nanoclusters with emission in the near IR, red and blue with increasingly higher energy emission with decreasing nanocluster size⁵¹⁻⁵⁴. The optical properties of metallic colloids have led to many applications exploiting their plasmon absorbance or their ability to enhance the Raman effect⁵⁵⁻⁵⁹. Research has also focused on their use as the components of diffraction gratings. In order to tailor the new generation of nanodevices and "smart" materials, way to organize the nanoparticles into controlled architectures must be found. All nanoparticle syntheses involve the use of a stabilizing agent, which associates with the surface of the particle, provides charge or solubility properties to keep the nanoparticles suspended, and thereby prevent their aggregation⁶⁰. Controlling the size, shape and structure of metal nanoparticles is technologically important because of the strong correlation between these parameters and optical, electrical and catalytic properties⁶¹. Cu nanoparticles have been synthesized through different methods such as thermal decomposition⁶²⁻⁶⁵, metal salt reduction⁶⁶, microwave heating⁶⁷, radiation methods⁶⁸, micro emulsion techniques⁶⁹, laser ablation⁷⁰, polyol method⁷¹, solvothermal method⁷², thermal and sonochemical reduction⁷³. Among various techniques developed for the synthesis of copper and copper oxide nanoparticles, thermal decomposition is a novel method to produce stable monodispersed⁷⁴ and it is a rapidly developing research area. The control of the morphology of

metal nano-particles has attracted much attention in recent years, with applications in catalysis^{75,76}, nano-structured machinery^{76,77}, and smart sensors⁷⁸⁻⁸³. For decades, gold nano-crystals have been extensively studied, mostly in the form of spherical particles. A range of gold nano-structures, such as plates^{75,76,78,81,83-92}, rods^{93,94}, hyper branched shapes⁹⁵, and other forms⁹⁶⁻⁹⁹ have been synthesized by different methods. Pure Fe nanoparticles have been successfully studied for a wide range of applications such as magnetic recording media¹⁰⁰, environmental remediation¹⁰¹, rocket solid fuels¹⁰² and biomedical fields¹⁰³. Several synthesis approaches, including inert gas evaporation¹⁰⁴, chemical vapor condensation¹⁰⁵, sol-gel¹⁰⁶, sonochemical¹⁰⁷, wet chemical¹⁰⁸, and laser-driven thermal methods¹⁰⁹ are applied for the fabrication of Fe nanoparticles.

In the past decades, quantum dots (QDs) have been one of the fastest moving and exciting interfaces of nanotechnology¹¹⁰. Colloidal QDs made of ZnS, CdS, ZnSe, CdTe and PbSe, emitting from the UV to the infrared have been prepared¹¹¹⁻¹¹⁵. Compared with traditional organic dyes and fluorescence proteins, QDs offers advantages in many aspects such as a narrow, tunable, symmetric emission from visible to infrared wavelengths, high quantum yields and photochemical stability^{110,116}. Since 1998, QDs with variable surface capping ligands have extensively been used as fluorescent species for cell labeling, tumor imaging and clinical diagnosis¹¹⁷⁻¹²³. Recently, QDs have attracted considerable attention as novel luminescence indicators of chemical and biological ionic species. It was found that Cu^{2+} , Hg^{2+} , Ag^+ and CN^- affected the fluorescence intensity of QDs dramatically and methods for determination of these ions by water-soluble QDs had been proposed¹²⁴⁻¹²⁶. QDs have also been applied in quantitative determination of biological macromolecules and drugs based on fluorescence quenching or enhancement. The analytes affects the fluorescence of CdSe QDs via electrostatic interactions, hydrogen bonds, van der Waals interactions, hydrophobic, and steric contacts within the binding site and so on. For example, Chen *et al.*¹²⁷ used functionalized CdS nanocrystals as the fluorescence probes in the ultrasensitive detection of peptides. Li *et al.*¹²⁸ proposed a new assay of ciprofloxacin based on the measurement

of enhanced fluorescence intensity signal resulting from the interaction of functionalized nano-CdS with ciprofloxacin. Recent interest in the development of new and novel strategies for the generation of gold nanoparticles stems from their potential applications in the fields of physics, chemistry, biology, medicine and materials science^{129,130}. Nanosize metals such as gold and silver have also been shown to exhibit size dependent optical properties^{16, 33}. It is also reported¹³¹ that nanoparticles with anisotropic shapes provide enhanced optical properties, which lend the candidates for spectroscopic technique such as SERS. It is reported that only particles whose photoluminescence blinks are SERS enhancing¹³² and that intensity of both Raman and photoluminescence signals are controlled by the same mechanism of enhancement. Most recently, Wang and Wang¹³⁰ have prepared hexagon shaped gold nanoplates by microwave assistant method which would prove to be much suitable for SERS experiments. Gold nanoparticles based fluorescent probes have been used in the identification of pathogenic bacterial in DNA-micro array technology¹³³. The advantage of using gold nanoparticles in biological labeling is that visible light can be used to observe a colour shift from red to blue when it forms aggregates¹³⁴⁻¹³⁶. Very small nanoparticles are essential for biological labeling while for SERS studies using gold, large particle sizes are preferred. Zhu *et al.*¹³⁷ reported the synthesis of gold nano particles via mixing the aqueous solution of HAuCl_4 and Triton X-100 at room temperature and found that gold nanoparticles can also be synthesized in absence of photo-irradiation. The synthesis of a new nano-blue ceramic pigment using the combination between co-precipitation and combustion synthesis method is reported by Ahmed *et al.*¹³⁸ and the structure of pigments is assigned based on the thermogravimetric and differential thermogravimetric analysis, X-ray diffractions, and UV-vis spectroscopy. Recently, nanoparticles used as probes for protein determination have attracted great interests because of their excellently optical properties and chemical stability. Microdetermination of proteins by resonance light scattering technique based on aggregation of ferric nanoparticles is reported recently¹³⁹. Preparation of nano alumina via resin synthesis is reported by Ibrahim and Abu-Ayana¹⁴⁰

and synthesis of copper and copper(I) oxide nanoparticles by thermal decomposition of a new precursor is reported by Salavati-Niasari and Davar¹⁴¹. A novel approach for preparing Ag nanoparticles using Ag microparticles as precursors in supercritical water was reported by Li and Zhang¹⁴² and according to them, the highly destructive ability of super critical water could cause Ag microparticles to break down into Ag nanoparticles with regular shape and small size by optimizing the parameters such as the reaction time, temperature and pressure. Viswanathan *et al.*¹⁴³ obtained zinc oxide nanoparticles by oxidation of zinc acetate in super critical water and the effects of flow rate and feed concentration were also studied. Magnetic nanostructures are of much interest because of their applications in a variety of areas such as magnetic inks, magnetic recording media, biomedical purpose, etc.¹⁴⁴⁻¹⁴⁷. With the advancement of materials technology, especially in the area of nanoparticles, efforts have been made to alter the magnetic properties by controlling the preparation conditions¹⁴⁸⁻¹⁵². Various approaches have recently been reported for fabricating Fe₃O₄ nanocrystals with varied morphologies, such as hollow spheres^{153, 154}, nanorods¹⁵⁵⁻¹⁶², nanowires¹⁶³⁻¹⁶⁶, nanochains¹⁶⁷, nanotubes^{168,169}, nanoflowers¹⁷⁰ and nanopyramids¹⁷¹. Micro-scale magnetite with a well defined structure has also been reported in the literatures. Li and co-workers¹⁷² developed a simple solvothermal method to prepare single-crystal magnetite micro-spheres for potential applications in biological fields. Liu and Kim¹⁷³ reported the synthesis of nanostructured magnetite plates by a simple solvothermal route where ethylenediamine was used as the solvent and reducing agent. Nowadays nanodiamond thin films are getting particular attention because of their peculiarities such as smooth surfaces and outstanding field emission properties. Having the outstanding properties of chemical vapor deposition diamond, ultra smooth surface, nanocrystalline diamond is expected to be ideal material for applications in a variety of fields such as optics, electronics, and also biomedicine and biosensors¹⁷⁴. The synthesis of thin diamond films from faceted nano-sized crystallites is reported recently¹⁷⁵. Carbon nanoparticles have gained increasing interest because of their various promising applications including electrodes of fuel cell, battery storage, filler of polymer, nanocomposite

of solar cell and air filter¹⁷⁶⁻¹⁸³. While there are many methods, such as laser ablation¹⁷⁸, pyrolysis of carbon-metallic compounds¹⁷⁹ and catalytic vapor deposition^{180,181}, 'arc in liquid' has been recognized as one of effective techniques to synthesize carbon nanoparticles with various advantages over others¹⁸²⁻¹⁸⁵. Synthesis of various carbon nanostructures by electrical arc discharge in liquid media (deionization and liquid nitrogen)¹⁸⁶ is also reported. The modification of the system components, such as the liquid media, the material of electrodes could provide some novel products with relatively low cost. Charinpanitkul *et al.*¹⁸⁷ reported the carbon nanostructures synthesis by arc discharge between carbon and iron electrodes in liquid nitrogen. Since the discovery of fullerene in 1985¹⁸⁸, a considerable amount of research effort has been devoted to carbon nanomaterials, such as carbon nanotubes, nanocapsules, nanohorns, onions and so on¹⁸⁹⁻¹⁹³. Because these carbon nanomaterials show unique electronic, mechanical and optical properties that are not present in bulk carbon, they have attracted much attention not only from academic researchers, but also from the industrial world as next generation industrial materials. As a result, carbon nanomaterials have been the subject of widespread research and development activities from basic research to applied technologies. Applications of carbon nanomaterials in such products as resin fillers¹⁹⁴, supercapacitors¹⁹⁵, hydrogen storage materials¹⁹⁶, field emission electron sources¹⁹⁷, nanometer sized field effect transistor¹⁹⁸, sensors and probes¹⁹⁹ have been proposed. Jha *et al.*²⁰⁰ reported a green low-cost and reproducible yeast mediated biosynthesis of Sb₂O₃ nanoparticles. Thermal plasma systems have been employed in synthesizing nanomaterials of variety of oxides and nitrides²⁰¹⁻²⁰⁴. Large quantities of nano-particles are required in several industrial applications²⁰⁵, and thermal plasma technique is suitable for such productions. All these applications require particles of wires ranging in diameters between 10 and 100 nm, wherein the surface effects of nanomaterials play an important role. These surface effects are also governed to a certain extent by the crystalline phases of nanomaterials. For example, nanocrystalline anatase phase of titanium oxide is a much efficient photo catalyst as compared to its rutile phase²⁰⁶.

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