



A REVIEW ON MICROWAVE ASSISTED SYNTHESIS OF SOME NANOPARTICLES

M. Gnana Ruba Priya*¹, Bincy Raj² and Rashmi T.³¹Department of Pharmaceutical Chemistry, Dayananda Sagar University, Bangalore-560078.²Department of Pharmacognosy, Dayananda Sagar University, Bangalore-560078.³Department of Pharmaceutical Chemistry, Bharathi College of Pharmacy, Mandya-571422.***Corresponding Author: M. Gnana Ruba Priya**

Department of Pharmaceutical Chemistry, Dayananda Sagar University, Bangalore-560078.

Article Received on 22/05/2020

Article Revised on 12/06/2020

Article Accepted on 03/07/2020

ABSTRACT

Microwave-assisted synthesis is popular in areas ranging from biochemical processes to nanotechnology. Chemical reactions are often faster than traditional reflux condenser heating methods, and have higher yields and fewer side products. Current microwave reactors provide excellent control over reaction mixing, withstand high temperatures and pressures, and demonstrate exceptional reproducibility from reaction-to-reaction. Speed and efficiency are aided by the direct heating of the reaction mixture, heating solvents beyond their boiling points at high pressure, and uniform heating profiles. In this review paper, the colloid of silver (Ag), gold (Au), platinum (Pt), and gold–palladium (Au–Pd) nanoparticles has been prepared by a low cost microwave technique where microwave radiation was used as a heating source. Compared to a thermal heating method, microwave radiation gave a much faster reaction. MW-assisted methods have been employed for the convenient and reproducible synthesis of well-defined noble and transition core–shell metallic nanoparticles with tunable shell thicknesses. Some of the distinctive attributes of MW-selective heating in the synthesis and applications of magnetic nanocatalysts in organic synthesis under benign reaction conditions are highlighted. Sustainable nanomaterials and their applications in benign media are an ideal blend for the development of greener methodologies in organic synthesis; MW heating provides superb value to the overall sustainable process development via process intensification including the flow systems.

KEYWORDS: Microwave Assisted, Nanoparticle, Colloidal Nanoparticles, Organic Synthesis.**INTRODUCTION**

Microwave-assisted organic synthesis has revolutionized organic synthesis.^[1-3] Small molecules can be built in a fraction of the time required by classical thermal methods. As a result, this technique has rapidly gained acceptance as a valuable tool for accelerating drug discovery and development processes. This article outlines the basic principles behind microwave technology and summarizes recent trends and areas in drug discovery where this technology has made an impact. Microwave chemistry is based on two main principles, the dipolar mechanism and the electrical conductor mechanism. The dipolar mechanism occurs when, under a very high frequency electric field, a polar molecule attempts to follow the field in the same alignment. When this happens, the molecules release enough heat to drive the reaction forward. In the second mechanism, the irradiated sample is an electrical conductor and the charge carriers, ions and electrons, move through the material under the influence of the electric field and lead to polarization within the sample. These induced currents and any electrical resistance will heat the sample. This Account summarizes a microwave

(MW)-assisted synthetic approach for producing silver nanostructures. MW heating has received considerable attention as a promising new method for the one-pot synthesis of metallic nanostructures in solutions. Researchers have successfully demonstrated the application of this method in the preparation of silver (Ag), gold (Au), platinum (Pt), and gold–palladium (Au–Pd) nanostructures. MW heating conditions allow not only for the preparation of spherical nanoparticles within a few minutes but also for the formation of single crystalline polygonal plates, sheets, rods, wires, tubes, and dendrites. The morphologies and sizes of the nanostructures can be controlled by changing various experimental parameters, such as the concentration of metallic salt precursors, the surfactant polymers, the chain length of the surfactant polymers, the solvents, and the operation reaction temperature. In general, nanostructures with smaller sizes, narrower size distributions, and a higher degree of crystallization have been obtained more consistently via MW heating than by heating with a conventional oil-bath. The use of microwaves to heat samples is a viable avenue for the greener synthesis of nanomaterials and provides several

desirable features such as shorter reaction times, reduced energy consumption, and better product yields. MW heating methods applicable under a variety of formats can address the problems of heating in homogeneity found in conventional thermal techniques.^[4,5] MW use provides increased reaction kinetics, rapid initial heating, and, hence, enhanced reaction rates culminating in clean reaction products with rapid consumption of starting materials and higher yields. There is no doubt that MW-assisted chemistry has helped to radically reduce the reaction time and increase product yields by diminishing the formation of unwanted byproducts during the reactions. The applications of this fascinating technology have been adopted in drug discovery explorations and pharmaceutical industry including peptide and protein synthesis. MW-assisted synthesis has made seminal contributions in the synthesis of 3D materials and well-defined nanomaterials under benign aqueous conditions and without employing capping or reducing agents. The use of MW-assisted synthesis opens the window to unique opportunities in the generation of nanomaterials of uniformly small size, which is not easily achievable via other synthesis techniques. Prompted by developments in flow chemistry, a novel single-mode MW reactor has been introduced for continuous flow reactions under elevated pressure (up to 10 MPa), where MW power is controlled by a temperature feedback module and resonance frequency autotracking function. These newer additions to MW technology should help in the synthesis of well-defined and advanced nanomaterials in conjunction with continuous flow technology. Additionally, the use of SiC reaction vessels could introduce new salient features (high temperature and pressure resistant up to 200 bar) compared with traditional borosilicate vessels. Microwave heating with the high efficiency in energy transfer leads to rapid volumetric heating, simple, capable of improving the reaction rates and uniformity of products as a solution for these problems. Besides, some advantages for microwave synthesis include the increase of collision possibility between molecules and the decrease in the activation energy. The result is that the reactants could enhance reactions. Therefore, it is showed that the synthesis of gold nanoparticles by microwave heating has the advantage over conventional methods.

In this review paper, the colloid of silver (Ag), gold (Au), platinum (Pt), and gold–palladium (Au–Pd) nanoparticles has been prepared by a low cost microwave technique where microwave radiation was used as a heating source. Compared to a thermal heating method, microwave radiation gave a much faster reaction and provided a higher concentration and a narrow size distribution of gold nanoparticles with the same concentration of chloro auric acid and sodium citrate solution. Other conditions, such as concentration of sodium citrate have the effects on the size and distribution of gold nanoparticles. The prepared gold nanoparticles were characterized by UV–vis spectroscopy, XRD and TEM. It can be found that the

size of the particles decreases with increasing the concentration of sodium citrate. Besides, the morphology of gold nanoparticles has a spherical shape with face centered-cubic crystalline structure This paper describes the current status of MW-assisted synthesis highlighting the introduction of various prototypes of equipment, classes of organic reactions pursued using nanomaterials, and the synthesis of unique and multifunctional nanomaterials; the resulting nanomaterials possess zero-dimensional to three-dimensional shapes, such as spherical, hexagonal, nanoprisms, star shapes, and nanorods. The synthesis of well-defined nanomaterials and nanocatalysts is an integral part of nanotechnology and catalysis science, because it is imperative to control their size, shape, and compositional engineering for unique deployment in the field of nanocatalysis and organic synthesis.

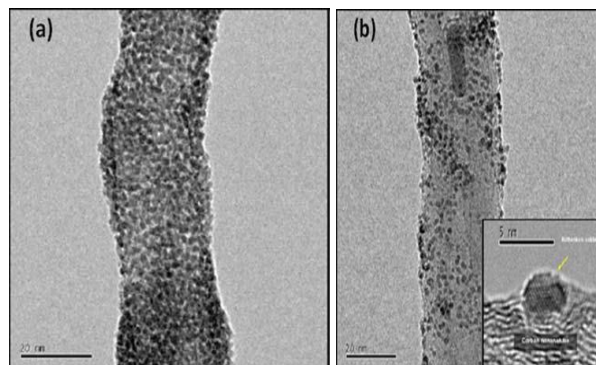
Synthesis^[6-10] of metal and metal oxide nanoparticles supported on CNT by microwave method

TiO₂ derivatives with distinct morphologies have been successfully obtained by microwave assisted hydrothermal synthesis in acidic and alkaline medium using mild conditions. Titanium tetra isopropoxide (TTIP) was used as precursor in different environmental conditions under low temperatures, inferior to 150 °C, and short synthesis times, from 2 to 60 min. X ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and N₂ adsorption at 77 K (BET) were used to characterize the micro structural properties of the oxides. In the acidic synthesis the reaction time and temperature are not accompanied by significant changes in the structure of the material. However, in the basic conditions, the concentration of Na⁺ ions strongly influences the particle morphology and growth. The morphology of the nanoparticles shows irregular spheres in acidic conditions, while in alkaline medium, needle like structures are formed as well as aggregated nanotube-like structures synthesized in only 30 min. Besides the difference in the morphology and structure, in both systems, high surface area was obtained. TiO₂ derivatives with distinct morphologies have been successfully obtained by microwave assisted hydrothermal synthesis in acidic and alkaline medium using mild conditions. Titanium tetraisopropoxide (TTIP) was used as precursor in different environmental conditions under low temperatures, inferior to 150 °C, and short synthesis times, from 2 to 60 min. X ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and N₂ adsorption at 77 K (BET) were used to characterize the microstructural properties of the oxides. In the acidic synthesis the reaction time and temperature are not accompanied by significant changes in the structure of the material. However, in the basic conditions, the concentration of Na⁺ ions strongly influences the particle morphology and growth. The morphology of the nanoparticles shows irregular spheres in acidic conditions, while in alkaline medium, needle like

structures are formed as well as aggregated nanotube-like structures synthesized in only 30 min. Besides the difference in the morphology and structure, in both systems, high surface area was obtained. It treated ultrasonically with glycol solution and showed agglomerations. But looking at the TEM image (Figure 6(a)) some agglomerations exist in some parts of the composites but not as much as is reported on the image (image not shown here) where glycol was not used. It is evident that glycol reduces agglomerations; therefore, the agglomerations heremay have been caused by the operating conditions of the microwave such as the high power, residence time, or temperature, though the temperature was not mentioned. The XRD pattern (refer to Figure 6(b)) further confirmed the presence of ZnS-coated MWCNTs composites with the mean size diameter calculated by the Debye-Scherrer equation to be 1 nm. The diffraction peaks identified the sample as a mixture of sphalerite crystal ZnS and MWCNTs. The TEM image and XRD spectra confirmed the formation of NPs on the CNTs, and it can be concluded that the synthesis of the CNTs coated with NPs does not merely depend on the precursor salt, but also has a strong correlation with the synthesis conditions and the method used.

Ghosh et al. reported the coating of platinum NPs on carbon-nitride nanotubes prepared by a microwave assisted method compared to the NaBH₄ chemical reduction method. In this study, N-doped MWCNTs were dispersed in 2-(2-methoxyethoxy)-ethanol solvent under mild sonication for the ease of Pt coating. H₂PtCl₆·H₂O was added to the above solution and stirred for 10 min. The resultant solution was divided into six parts; one part underwent the NaBH₄ route and the other five parts were subjected to microwave irradiation for 30, 50, 70, 90, and 110 s. Finally, the solid was washed and dried. These samples were labelled depending on the MW-irradiation times, for example, MW50, MW110, and so forth. According to the TEM characterization performed on the samples, the platinum NPs were nicely distributed on the CNTs in both methods as presented (parts (a), (b), and (c) of Figure 7). The Pt NPs grown by NaBH₄ treatment (Figure 7(a)) were observed to be small (average diameter 3 nm) and have a low density. However, those grown by microwave irradiation (refer to Figures 7(b) and 7(c)) were found to be larger and the population gradually increased with irradiation time. Microwave irradiation for 50 and 110 s resulted in 10.2 and 19.8 nm Pt particles, respectively. In this paper, the NaBH₄-mediated chemical reduction process resulted in small size Pt NPs coated on the carbon nitride nanotubes with low density while the microwave assisted method gave larger NPs with high population density. In the XPS spectrum (not shown here), the peak intensities showed that NaBH₄ treatment led to the incomplete reduction of Pt ions; meanwhile, the microwave irradiation not only offered complete Pt reduction, but also enabled control of the particle size and density as a function of the irradiation time. The

complete reduction of the Pt ions shows the uniform heating of the material to completion when using the microwave method and how comparative the method can be in synthesizing CNT composites in fewer steps. It is also useful that the authors have included the reaction mechanisms of both methods in the paper.



Microwave-assisted synthesis of PbS nanostructures Herein, a quick, convenient and simple route to the preparation of PbS nanostructures by microwave irradiation in ethylene glycol is presented. The ethylene glycol played a dual role as solvent and as passivating molecule which controlled the particle size and morphology of PbS nanoparticles. The products were characterized using absorption spectroscopy, X-ray powder diffraction (XRD), and transmission electron microscopy (TEM).

The synthesis of PbS nanostructures by microwave irradiation of single source precursor compounds in ethyleneglycol medium is reported. Pb(II) bis(N-ethyl-N-phenyldithiocarbamate) and Pb(II) bis(N-butyl-N-phenyldithiocarbamate) represented as complexes respectively were utilised. The prepared PbS nanostructures were characterized using X-ray diffraction (XRD), Transmission electron microscopy (TEM), and absorption spectroscopy. The results showed that complex (1) can project the formation of nanorod with basal plane, while project the formation of nanocube with (001) basal plane. The formation of different morphologies in ethylene glycol may also be due to the selective binding to specific crystallite facets of the PbS through the hydroxyl groups of ethylene glycol. In the nanorod, the selective stabilization of the face of PbS, resulted in anisotropic growth along the face. The high resolution TEM images showed distinct lattice fringes which confirmed the crystallinity of the nanostructures. The band gap energies were obtained as 1.10 and 1.12 eV for the nanorods and nanocubes respectively, a significant blue shift from the bulk value (0.4 eV) which could be ascribed to quantum confinement effect. The result established the significant effect of the precursor type on the morphologies of the PbS. Novel Pb(II) dithiocarbamate complexes have been utilised as single source precursors to synthesize PbS nanostructures by microwave irradiation technique. The results show that the precursor type has significant effect on the morphology, size and optical properties of the PbS

nanostructures. The prepared nanostructures ranged from rods to cubic shapes. It is suggested that this facile microwave irradiation route to PbS nanorods and nanocubes could also be used for the synthesis of nanostructures of other technologically important chalcogenide semiconductors. Novel Pb(II) dithiocarbamate complexes have been utilised as single source precursors to synthesize PbS nanostructures by microwave irradiation technique. The results show that the precursor type has significant effect on the morphology, size and optical properties of the PbS nanostructures. The prepared nanostructures ranged from rods to cubic shapes. It is suggested that this facile microwave irradiation route to PbS nanorods and nanocubes could also be used for the synthesis of nanostructures of other technologically important chalcogenide semiconductors.

Effect of Microwave Radiation Power on the Size of Aggregates of ZnO NPs Prepared Using Microwave Solvo thermal Synthesis^[11,12]

This paper reports the possibility of changing the size of zinc oxide nanoparticles (ZnO NPs) aggregates through a change of synthesis parameters. The effect of the changed power of microwave heating on the properties of ZnO NPs obtained by the microwave solvothermal synthesis from zinc acetate dissolved in ethylene glycol was tested for the first time. It was found that the size of ZnO aggregates ranged from 60 to 120 nm depending on the power of microwave radiation used in the synthesis of ZnO NPs. The increase in the microwave radiation power resulted in the reduction of the total synthesis time with simultaneous preservation of the constant size and shape of single ZnO NPs, which were synthesized at a pressure of 4 bar. All the obtained ZnO NPs samples were composed of homogeneous spherical particles that were single crystals with an average size of 27 nm with a developed specific surface area of 40 m²/g and the skeleton density of 5.18 (0.03) g/cm³. A model of a mechanism explaining the correlation between the size of aggregates and the power of microwaves was proposed. This method of controlling the average size of ZnO NPs aggregates is presented for the first time and similar investigations are not found in the literature. This method of controlling the average size of ZnO NPs aggregates is presented for the first time and similar investigations are not found in the literature. A method of controlling the average size of ZnO NPs aggregates obtained in the microwave solvothermal synthesis was achieved, which consists of changing the precursor heating speed by changing the microwave radiation power. The phenomenon of ZnO NPs aggregation is related to a certain temperature range, in which the intermediate (LHZA) decomposes to ZnO NPs and only thanks to that can the change of the heating speed enable controlling the size of the obtained ZnO NPs aggregates with the following average sizes: 60, 90 and 120 nm. The increase in the microwave power caused a significant change in the heating speed and at the same time a decrease of the time of reaching the pressure of 4 bar in the MSS2

reactor. The change in the microwave power and the change in the total synthesis duration does not affect the average size of ZnO crystallites obtained from the precursor with a constant composition (EG, (Ac)₂Zn_2H₂O, H₂O) in the case of microwave solvothermal synthesis. Our paper shows the unique potential of application of stop-flow microwave reactors for controlling the size of ZnO NPs aggregates, which are composed of homogeneous ZnO NPs with a constant size. Without accurate characterization, which deliberately does not take into account the measurements of size of NPs ZnO aggregates, it is possible to unwittingly obtain different sizes of NPs aggregates with the constant average size of single ZnO NPs preserved, which cannot be repeated. This may contribute to obtaining batches of ZnO NPs characterized by completely different properties, e.g., toxicity.

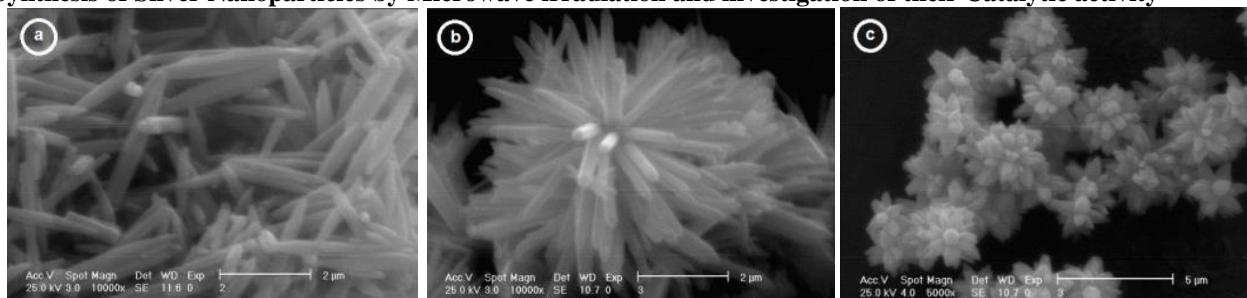
Synthesis of Colloidal PbSe Nanoparticles Using a Microwave-Assisted Segmented Flow Reactor^[13-15]

Colloidal lead selenide nanoparticles (PbSe NPs) were synthesized using a microwave-assisted continuous flow reactor. Rapid heating of precursors was performed in the microwave reaction zone to initiate nucleation and was followed by an oil bath growth zone. In this study we have evaluated the effect of the nucleation temperature on the PbSe NP size distributions, crystallographic structure, particle shape, and particle composition. The PbSe NP size could be varied from 11.2 to 13.9 nm by adjusting the microwave nucleation temperature between 124 to 159 °C. It was found that nucleation of Pb rich species occurred in the microwave reaction zone, while PbSe NPs form in the growth zone. summary, a microwave-assisted segmented flow reactor was used to synthesize high quality PbSe NPs with low coefficients of variation (~15%). No additional crystalline impurities were observed in XRD. PbSe NP diameters were found to increase from 11.2 to 13.9 nm with decreasing T_μW. As the PbSe NP size increased the shapes of the particles were observed to evolve from semi-spherical and octahedral to multi-faceted structures. Observation of crystalline planes indicates that particles have a truncated octahedral morphology for a T_μW of 159 °C, but have both facets for a T_μW of 124 °C. Pb rich nucleates were observed directly after the microwave indicating that reduction of Pb occurs during the nucleation zone, and that PbSe NPs form in the growth zone. These results demonstrate the use of a microwaveassisted segmented flow reactor as an effective method for the synthesis of high quality colloidal NPs Microwave-assisted synthesis^[16,17] of zinc oxide nanoparticles Synthesis of nanoparticles and ultrafine particles of zinc oxide with controlled morphology using microwave irradiation is carried out by various methods. The effect of type of precursor as well as the time and the microwave irradiation power on the structure and size of ZnO nanoparticles have been studied. Particles Studied by SEM, TEM images and XRD analyze. By increasing the time of synthesis from 10 to 15 minutes needle-shaped particles with a diameter

of 50-150 nm can be achieved. While increasing the microwave power from 540 to 680 watts, flower-shaped particles are obtained. By replacing zinc nitrate with zinc acetate, at different power and time of irradiation,

needle-shaped particles are obtained and diameter of needles is decreased.

Synthesis of Silver Nanoparticles by Microwave irradiation and investigation of their Catalytic activity^[18-20]



In summary, zinc oxide nanoparticles with various morphology and particle size successfully synthesis with microwave-assisted hydrothermal procedure. Flower-type, needle-type and spherical type nanoparticles have successfully synthesized with this hydrothermal procedure. XRD analyses and SEM images let us to conclude that formation of zinc oxide nanoparticle, following dissolution-precipitation of $Zn(OH)_4$

Synthesis of Silver Nanoparticles by Microwave irradiation and investigation of their Catalytic activity^[20-25]

In this study, silver nanoparticles (AgNPs) have been synthesized in aqueous medium by a simple, efficient and economic microwave assisted synthetic route using hexamine as the reducing agent and the biopolymer pectin as stabilizer. The synthesized AgNPs were characterized by UV-vis. spectroscopy, Energy dispersive X-ray (EDX), X-ray diffraction (XRD) and Transmission electron microscopy (TEM) techniques. TEM images suggest that the nanoparticles are of spherical shape with an average diameter of 18.84 nm. The reduction of 4-nitrophenol to 4-aminophenol by $NaBH_4$ in aqueous medium was selected as a model reaction to investigate the catalytic activity of AgNPs. The pectin stabilized silver nanoparticles (AgNPpectin) were found to exhibit very good catalytic activity and the reaction followed pseudo-first order kinetics. The rate of reaction was found to increase with increasing temperature and the activation energy was found to be 47.3 kJ mol⁻¹. In this work, we have reported a rapid facile microwave based method for the synthesis of silver nanoparticles in aqueous medium using the non-toxic hexamine as reducing agent and the easily available biopolymer pectin as the capping agent. The various characteristics of the synthesized silver colloids are analyzed by UV-vis., XRD, EDX and TEM analyses. The catalytic activity is investigated by studying the reduction of 4-nitrophenol to 4-aminophenol by $NaBH_4$. The reaction follows pseudo-first kinetics and the rate constant is found to increase as the concentration of the catalyst is increased. The temperature dependence of reaction rate is studied by conducting the reaction at four different temperatures.

The rate of reaction is found to increase with increasing temperature and the activation energy is found to be 47.3 kJ mol⁻¹. Since this method is relatively simple, fast and environment friendly, this can be scaled up for the bulk production of silver nanoparticles.

Recent Trends in the Microwave-Assisted Synthesis of Metal Oxide Nanoparticle Supported on Carbon Nanotubes and Their Applications^[25-30]

The study of coating carbon nanotubes with metal/oxides nanoparticles is now becoming a promising and challenging area of research. To optimize the use of carbon nanotubes in various applications, it is necessary to attach functional groups or other nanostructures to their surface. The combination of the distinctive properties of carbon nanotubes and metal/oxides is expected to be applied in field emission displays, nanoelectronic devices, novel catalysts, and polymer or ceramic reinforcement. The synthesis of these composites is still largely based on conventional techniques, such as wet impregnation followed by chemical reduction of the metal nanoparticle precursors. These techniques based on thermal heating can be time consuming and often lack control of particle size and morphology. Hence, there is interest in microwave technology recently, where using microwaves represents an alternative way of power input into chemical reactions through dielectric heating. This paper covers the synthesis and applications of carbon-nanotube-coated metal/oxides nanoparticles prepared by a microwave-assisted method. The reviewed studies show that the microwave-assisted synthesis of the composites allows processes to be completed within a shorter reaction time with uniform and well-dispersed nanoparticle formation.

Microwave Synthesis of Silver Nanoparticles Using Different Pentose Carbohydrates as Reducing Agents^[30-35]

A fast, green and readily reproducible microwave-based method for the production of high quality silver nanoparticles (AgNPs) in high yield is presented. Starch is used as a stabilizing agent with few pentose different reducing carbohydrates as D-ribose, D-arabinose and L-arabinose. From the UV-vis peak profile spectra of the

solutions of the silver nanoparticles, the authors have investigated the size of the NPs together with the average diameter, shape, and aggregation state of the colloidal AgNPs. TEM measurements and EDX analysis have confirmed the morphology of our AgNPs. AgNPs were synthesized under microwave irradiation using ribose and arabinose as the reducing agents and starch as the stabilizing reagent. Microwave radiation can achieve a complete conversion after only 1 minute when L-arabinose is used, between 2 and 8 minutes with D-arabinose and between 2-5 minutes using D-ribose. Silver colloidal solution was characterized by UV-visible spectroscopy, SEM and EDX. The UV-visible spectra showed that the synthesized samples have an absorbance peak at 410 nm. Increasing reaction time is leading to a shift of the absorbance peak towards 420-430 nm. TEM images confirm a uniform particle size around 20-30 nm. Microwave assisted synthesis of copper oxide and its application in electrochemical sensing Copper oxide nanopowders were prepared using copper acetate as the precursor and polyethylene glycol (PEG) as stabilizer in ethanol medium. The mixture containing copper acetate, sodium hydroxide and PEG was irradiated with microwave and nanometric copper oxide particles were formed within 8 min. The prepared nanoparticles were characterized using x-ray diffraction, UV-vis spectroscopy and scanning electron microscopy. The average particle size was found to be 4 nm. This was used to modify glassy carbon electrode with PVDF & DMF as binder and used for sensing of carbohydrates (glucose and sucrose) and H_2O_2 . The copper oxide nanoparticles showed excellent sensitivity in the range of 0.1 mM to 1 mM when chronoamperometry was carried out at 0.6 V Vs. Ag/AgCl. The observed sensitivity is much higher when compared with conventional micron sized copper oxide particles.

CuO nanoparticles were successfully synthesized by microwave irradiation with phase purity and high crystallinity as seen by XRD; its optical properties and morphological studies were analyzed by UV-Vis spectroscopy and SEM analysis respectively. Using these nanoparticles, a sensitive amperometric electrochemical sensor for detecting glucose, sucrose and hydrogen peroxide is demonstrated.

Microwave-Assisted Synthesis of Alumina Nanoparticles Using Some Plants Extracts^[36,37]

In present study we used five green plants for microwave assisted synthesis of Alumina nanoparticles from Aluminum nitrate. Structural characterization was studied using x-ray diffraction that showed semi-crystalline and possibly, amorphous structure. Fourier infrared spectroscopy was used to determine Al-O bond and functional groups responsible for synthesis of nanoparticles. FTIR confirmed existence of Al-O band and bio-functional groups, originated from plant extract. Morphology and size of nanoparticles were investigated using scanning electron microscopy, transmission electron microscopy and atomic force microscopy

techniques. It was observed that nanoparticles have near-spherical shape. Average size of clusters of nanoparticles varied with different routes from of 60 nm to 300 nm. AFM images showed that Individual nanoparticles were less than 10 nm. *Syzygium aromaticum*, *Origanum vulgare*, *Origanum majorana*, *Theobroma cacao* and *Cichorium intybus* were used as green routes for microwave assisted synthesis of alumina nanoparticles.

XRD pattern of particles synthesized with *Syzygium aromaticum* showed semi-crystalline structure while others showed no significant peak that might be assigned to nano dimension of particles or their amorphous structure. FTIR studies of nanoparticles showed peaks in range of 450-1000 cm^{-1} , assigned to AlO_4 and AlO_6 bonds, and some peaks in range of 1000-1750 cm^{-1} : assigned to bio-functional groups responsible for particles synthesis. SEM analysis of nanoparticles showed clusters of nanoparticles in 60-300 nm range. TEM and AFM analysis revealed that individual nanoparticles have less than 10 nm size.

Synthesis of Pt Nanoparticles and Nanorods by Microwave-assisted Solvothermal Technique^[38-40]

Platinum nanoparticles and nanorods were synthesized by microwave-assisted solvothermal techniques. Changing the reaction conditions controlled particle size and morphology. The effects of the reaction conditions, such as the molar ratio of the polyvinylpyrrolidone (PVP) repeating unit to the metal sources, the concentration of metal sources, the reaction temperature, and the presence of distilled water were investigated. Nanoparticles of Pt were approximately 3nm in size. Produced nanoparticles and nanorods were characterized by transmission electron microscopy. Image JTM software was used to calculate the particle size and size distribution.

Well-dispersed Pt nanoparticles were obtained using methanol as a reducing agent. The morphology of the Pt nanoparticles is dependent on the temperature, the concentrations of PVP and Pt^{4+} , and the presence or absence of distilled water. Without distilled water in the reaction system, Pt nanospheres were obtained. The particle size was approximately 2 to 3 nm at 120 °C for 60 min. With distilled water in the system, Pt nanorods could be obtained. A higher temperature, a lower concentration of PVP, and a proper concentration of Pt^{4+} favored the formation of Pt nanorods. In addition, Pt nanoparticles were also synthesized using ethanol as a reducing agent at 120 °C. However, the Pt nanoparticles obtained were not dispersed. At 90°C for 1 hr, Pt nanoparticles did not form. Both microwave-assisted and conventional methods produced Pt nanoparticles with similar morphology and particle size. However, it takes more time to produce particles with similar size by the conventional method with its slower kinetics compared to the microwave-assisted solvothermal method.

Easy and Fast Preparation of TiO₂ - based Nanostructures Using Microwave Assisted Hydrothermal Synthesis^[41-45]

TiO₂ derivatives with distinct morphologies have been successfully obtained by microwave assisted hydrothermal synthesis in acidic and alkaline medium using mild conditions. Titanium tetraisopropoxide (TTIP) was used as precursor in different environmental conditions under low temperatures, inferior to 150 °C, and short synthesis times, from 2 to 60 min. X ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and N₂ adsorption at 77 K (BET) were used to characterize the microstructural properties of the oxides. In the acidic synthesis the reaction time and temperature are not accompanied by significant changes in the structure of the material. However, in the basic conditions, the concentration of Na⁺ ions strongly influences the particle morphology and growth. The morphology of the nanoparticles shows irregular spheres in acidic conditions, while in alkaline medium, needle like structures are formed as well as aggregated nanotube-like structures synthesized in only 30 min. Besides the difference in the morphology and structure, in both systems, high surface area was obtained.

Synthesis of Silver Nanoparticles by Microwave irradiation and investigation of their Catalytic activity^[46-50]

In this study, silver nanoparticles (AgNPs) have been synthesized in aqueous medium by a simple, efficient and economic microwave assisted synthetic route using hexamine as the reducing agent and the biopolymer pectin as stabilizer. The synthesized AgNPs were characterized by UV-vis. spectroscopy, Energy dispersive X-ray (EDX), X-ray diffraction (XRD) and Transmission electron microscopy (TEM) techniques. TEM images suggest that the nanoparticles are of spherical shape with an average diameter of 18.84 nm. The reduction of 4-nitrophenol to 4-aminophenol by NaBH₄ in aqueous medium was selected as a model reaction to investigate the catalytic activity of AgNPs. The pectin stabilized silver nanoparticles (AgNP/pectin) were found to exhibit very good catalytic activity and the reaction followed pseudo-first order kinetics. The rate of reaction was found to increase with increasing temperature and the activation energy was found to be 47.3 kJ mol⁻¹. In this work, we have reported a rapid facile microwave based method for the synthesis of silver nanoparticles in aqueous medium using the non-toxic hexamine as reducing agent and the easily available biopolymer pectin as the capping agent. The various characteristics of the synthesized silver colloids are analyzed by UV-vis., XRD, EDX and TEM analyses. The catalytic activity is investigated by studying the reduction of 4-nitrophenol to 4-aminophenol by NaBH₄. The reaction follows pseudo-first kinetics and the rate constant is found to increase as the concentration of the catalyst is increased. The temperature dependence of reaction rate is studied by conducting the reaction at four

different temperatures. The rate of reaction is found to increase with increasing temperature and the activation energy is found to be 47.3 kJ mol⁻¹. Since this method is relatively simple, fast and environment friendly, this can be scaled up for the bulk production of silver nanoparticles.

Microwave-assisted green synthesis of Gold nanoparticles and its catalytic activity^[51,52]

The present work demonstrated a green approach of synthesis of gold nanoparticles using *Eupatorium odoratum* leaf extract as reducing and stabilizing agent assisted with microwave irradiation. Effects of various concentrations of leaf extract on the preparation of gold nanoparticles have been investigated and it was monitored by undertaking UV-vis spectroscopic studies. The experimental results showed that the surface Plasmon resonance (SPR) peak blue shifted with increase in the concentration of leaf extract indicating the decrease of nanoparticles size, which was further confirmed by the Dynamic light scattering (DLS) data. Synthesized particles were further characterized by Fourier Transform Infra-Red spectroscopy (FTIR) and Transmission Electron Microscopy (TEM). All the characterization results confirmed the formation of stable spherical mono-dispersed gold nanoparticles with size ranging from 10-20 nm. The catalytic activity of prepared gold nanoparticles was checked by reducing Nitrophenol to Aminophenol in presence of an excess amount of sodium borohydride. The progress of the reaction was examined by observing the absorbance peak of UV-vis spectroscopy. The study showed positive results and it was found that gold nanoparticles synthesized with 600 µL leaf extract have greater catalytic activity. It was also found that gold nanoparticles remained stable for long duration of time. In summary, we reported a low cost one pot and controlled green synthesis of GNPs using *Eupatorium odoratum* leaf extract assisted with microwave irradiation. The characterization of the prepared nanoparticles by Uv-Vis spectroscopy, DLS, TEM, FTIR confirmed the formation of well small size spherical stable gold nanoparticles and presence of bio-molecules responsible for the formation of the nanoparticles. Moreover, the gold nanoparticles remained stable for long days. The size of the gold nanoparticles can be tuned by varying the concentration of leaf extract solution. The method is very rapid, it takes only a minute for the synthesis of nanoparticles and a very small amount of leaf extract is sufficient for the synthesis. The prepared GNPs were tested to check the catalytic behaviour on 2, 4, 6-tri Nitrophenol and it showed positive results in catalyzing the reaction of reduction of Nitrophenol to Aminophenol in presence of sodium borohydride

Microwave-assisted green synthesis of Gold nanoparticles and its catalytic activity

The present work demonstrated a green approach of synthesis of gold nanoparticles^[53,54] using *Eupatorium*

odoratum leaf extract as reducing and stabilizing agent assisted with microwave irradiation. Effects of various concentrations of leaf extract on the preparation of gold nanoparticles have been investigated and it was monitored by undertaking UV-vis spectroscopic studies. The experimental results showed that the surface Plasmon resonance (SPR) peak blue shifted with increase in the concentration of leaf extract indicating the decrease of nanoparticles size, which was further confirmed by the Dynamic light scattering (DLS) data. Synthesized particles were further characterized by Fourier Transform Infra-Red spectroscopy (FTIR) and Transmission Electron Microscopy (TEM). All the characterization results confirmed the formation of stable spherical mono-dispersed gold nanoparticles^[54-58] with size ranging from 10-20 nm. The catalytic activity of prepared gold nanoparticles was checked by reducing Nitrophenol to Aminophenol in presence of an excess amount of sodium borohydride. The progress of the reaction was examined by observing the absorbance peak of UV-vis spectroscopy. The study showed positive results and it was found that gold nanoparticles synthesized with 600 µL leaf extract have greater catalytic activity. It was also found that gold nanoparticles remained stable for long duration of time. In summary, we reported a low cost one pot and controlled green synthesis of GNPs using *Eupatorium odoratum* leaf extract assisted with microwave irradiation. The characterization of the prepared nanoparticles by UV-Vis spectroscopy, DLS, TEM, FTIR confirmed the formation of well small size spherical stable gold nanoparticles and presence of bio-molecules responsible for the formation of the nanoparticles. Moreover, the gold nanoparticles remained stable for long days. The size of the gold nanoparticles can be tuned by varying the concentration of leaf extract solution. The method is very rapid, it takes only a minute for the synthesis of nanoparticles and a very small amount of leaf extract is sufficient for the synthesis. The prepared GNPs were tested to check the catalytic behaviour on 2, 4, 6-tri Nitrophenol and it showed positive results in catalyzing the reaction of reduction of Nitrophenol to Aminophenol in presence of sodium borohydride.

CONCLUSION

Innovative MW-assisted synthesis could be performed in liquid-gas phase reactions through gas addition accessories designed for reactions with gaseous reagents; this approach could be used for hydrogenation, carbonylation, and other reactions. In light of these developments, it is apparent that the synergy between MW reaction conditions and benign reaction medium will continue to offer several advantages in the design of future synthetic protocols for organics and nanomaterials.

REFERENCES

1. Nadagouda, M. N.; Speth, T. F.; Varma, R. S. Microwave-assisted green synthesis of silver

- nanostructures. *Acc. Chem. Res.*, 2011; 44: 469-478.
- Recent Trends in the Microwave-Assisted Synthesis of Metal Oxide Nanoparticles Supported on Carbon Nanotubes and Their Applications *Journal of Nanomaterials*, 2011; 20: 15-25.
 - S. Iijima, "Helical microtubules of graphitic carbon," *Nature*, 1991; 354(6348): 56-58.
 - P. Kim, L. Shi, A. Majumdar, and P. L. McEuen, "Thermal transport measurements of individual multiwalled nanotubes," *Physical Review Letters*, 2001; 87(21): 2155021-2155024.
 - S. Berber, Y. K. Kwon, and D. Tománek, "Unusually high thermal conductivity of carbon nanotubes," *Physical Review Letters*, 2000; 84(20): 4613-4616.
 - E. W. Wong, P. E. Sheehan, and C. M. Lieber, "Nanobeam mechanics: elasticity, strength, and toughness of nanorods and nanotubes," *Science*, 1997; 277(5334): 1971-1975.
 - Klingshirn, C.F.; Waag, A.; Hoffmann, A.; Geurts, J. *Zinc Oxide*, 1st ed.; Springer: Berlin, Germany, 2010; ISBN 978-3-642-10576-0.
 - Ozgur, U.; Hofstetter, D.; Morkoc, H. *ZnO devices and applications: A review of current status and future prospects*. *Proc. IEEE*, 2010; 98: 1255-1268.
 - Zhang, Y.; Nayak, T.R.; Hong, H.; Cai, W. *Biomedical Applications of Zinc Oxide Nanomaterials*. *Curr. Mol. Med.*, 2013; 13: 1633-1645.
 - Martínez-Carmona, M.; Gun'ko, Y.; Vallet-Regí, M. *ZnO Nanostructures for Drug Delivery and Theranostic Applications*. *Nanomaterials*, 2018; 8: 268.
 - Wise FW. Lead salt quantum dots: the limit of strong quantum confinement. *Accounts of Chemical Research*, 2000; 33: 773-80.
 - Allan G, Delerue C. Confinement effects in PbSe quantum wells and nanocrystals. *Physical Review B.*, 2004; 70: 245321.
 - Hillhouse HW, Beard MC. Solar cells from colloidal nanocrystals: Fundamentals, materials.
 - Devices, and economics. *Current opinion in colloid & interface science*, 2009; 14: 245-59.
 - Nozik AJ. Multiple exciton generation in semiconductor quantum dots. *Chemical Physics Letters*, 2008; 457: 3-11.
 - Cui D, Xu J, Xu S-Y, Paradee G, Lewis BA, Gerhold MD. Infrared photodiode based on colloidal PbSe nanocrystal quantum dots. *Nanotechnology*, *IEEE Transactions on.*, 2006; 5: 362-7.
 - Agocs, E., Fodor, B., Pollakowski, B., Beckhoff, B., Nutsch, A., Jank, M., Petrik, P., Approaches to calculate the dielectric function of ZnO around the band gap. *Thin Solid Films*, 2014; 571(3): 684-688.
 - Al-Gaashani, R., Radiman, S. Tabet, N., Daud, A.R., Effect of microwave power on the morphology and optical property of zinc oxide nano-structures prepared via a microwave-assisted aqueous solution

- method. *Materials Chemistry and Physics*, 2011; 125(3): 846-852.
19. Belomestnykh, I. P., Voikina, N. V., Phase Composition of Products of The Reaction Of Zinc and Chromium Nitrates with Ammonia and its Effect on the Catalytic Properties of Zinc-Chromium Oxide Systems. *Kinetics and Catalysis*, 1987; 28(3 Pt 2): 602-608.
 20. Caglar, Y.Y., Gorgun, K. Aksoy, S., Effect of deposition parameters on the structural properties of ZnO nanopowders prepared by microwave-assisted hydrothermal synthesis. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2015; 138: 617-622.
 21. Cao, J., Wang, J., Microwave-assisted synthesis of flower-like ZnO nanosheet aggregates in a room-temperature ionic liquid. *Chemistry Letters*, 2004; 33(10): 1332-1333.
 22. Cao, Y., Liu, B., Huang, R., Xia, Z., Ge, S., Flash synthesis of flower-like ZnO nanostructures by microwave-induced combustion process. *Materials Letters*, 2011; 65(2): 160-163.
 23. Fragalà, M. E., Aleeva, Y. Malandrino, G., Effects of Metal-Organic Chemical Vapour Deposition grown seed layer on the fabrication of well aligned ZnO nanorods by Chemical Bath Deposition. *Thin Solid Films*, 2011; 519(22): 7694-7701.
 24. Murray R.W., *Nanoelectrochemistry: metal nanoparticles, nanoelectrodes and nanopores*, Chem Rev., 2008; 108: 2688-2720.
 25. Kundu S, Mandal M, Ghosh S.K. and Pal T., Photochemical deposition of SERS active silver nanoparticles on silica gel and their application as catalysts for the reduction of aromatic nitro compounds, *J. Colloid Interface Sci.*, 2004; 272: 134-144.
 26. Eychmuller A., Structure and photophysics of semiconductor nanocrystals, *J. Phys. Chem. B*, 2000; 104.
 27. Salata O.V., Applications of nanoparticles in biology and medicine, *J. Nanobiotechnol*, 2004; 2: 3-9.
 28. Ren X., Meng X., Chen D., Tang F. and Jiao J., Using silver nanoparticle to enhance current response of biosensor, *Biosens. Bioelectron.*, 2005; 21: 433-437.
 29. Kruis FE, Fissan H, Peled A. Synthesis of nanoparticles in the gas phase for electronic, optical and magnetic applications—a review. *J Aerosol Sci.*, 1998; 29(5): 511-35.
 30. Da Costa Cunha G, Romão LPC, Macedo ZS. Production of alpha-alumina nanoparticles using aquatic humic substances. *Powder Technol*, 2014; 254(0): 344-51.
 31. Itoh T, Uchida T, Matsubara I, Izu N, Shin W, Miyazaki H, et al. Preparation of γ -alumina large grain particles with large specific surface area via polyol synthesis. *Ceram Int.*, 2015; 41(3, Part A): 3631-8.
 32. Tahmasebpour M, Babaluo AA, Shafiei S, Pipelzadeh E. Studies on the synthesis of α -Al₂O₃ nanopowders by the polyacrylamide gel method. *Powder Technol*, 2009; 191(1–2): 91-7.
 33. Zaki T, Kabel KI, Hassan H. Preparation of high pure α -Al₂O₃ nanoparticles at low temperatures using Pechini method. *Ceram Int.*, 2012; 38(3): 2021-6.
 34. Z. Liu, X.Y. Ling, X. Su, J.Y. Lee, *J. Phys. Chem. B.*, 2004; 108: 8234.
 35. Y. Shen, J. Liu, A. Wu, J. Jiang, L. Bi, B. Liu, Z. Li, S. Dong, *Langmuir*, 2003; 19: 5397.
 36. T. S. Ahmadi, Z. L. Wang, T. C. Green, A. Henglein, M. A. ElSayed, *Science*, 1996; 272: 1924.
 37. S. Komarneni, D. Li, B. Newalkar, H. Katsuki, A. S. Bhalla, *Langmuir*, 2002; 18: 5959.
 38. Chen X, Mao SS. *Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications*. *Chemical Reviews*, 2007; 107(7): 2891-2959. DOI: 10.1021/cr0500535.
 39. Chen D, Huang F, Cheng YB, Caruso RA. Mesoporous Anatase TiO₂ Beads with High Surface Areas and Controllable Pore Sizes: A Superior Candidate for High-Performance Dye-Sensitized Solar Cells. *Advanced Materials*, 2009; 21(21): 2206-2210. DOI: 10.1002/adma.200802603.
 41. Ismail AA, Bahnemann DW. Mesoporous titania photocatalysts: preparation, characterization and reaction mechanisms. *Journal of Materials Chemistry*, 2011; 21(32): 11686-11707. DOI:10.1039/C1JM10407A.
 42. Murray R.W., *Nanoelectrochemistry: metal nanoparticles, nanoelectrodes and nanopores*, Chem Rev., 2008; 108: 2688-2720.
 43. Kundu S, Mandal M, Ghosh S.K. and Pal T., Photochemical deposition of SERS active silver nanoparticles on silica gel and their application as catalysts for the reduction of aromatic nitro compounds, *J. Colloid Interface Sci.*, 2004; 272: 134-144.
 44. Eychmuller A., Structure and photophysics of semiconductor nanocrystals, *J. Phys.*, 2000, Chem. B, 104.
 45. Salata O.V., Applications of nanoparticles in biology and medicine, *J. Nanobiotechnol*, 2004; 2: 3-9.
 46. Ren X., Meng X., Chen D., Tang F. and Jiao J., Using silver nanoparticle to enhance current response of biosensor, *Biosens. Bioelectron.*, 2005; 21: 433-437.
 47. Liz-Marzán L. M., Tailoring surface plasmons through the morphology and assembly of metal nanoparticles. *Langmuir*, 2006; 22: 32–41.
 48. Dreaden E. C., Alkilany A. M., Huang X., Murphy C. J., El-Sayed M. A., The golden age: Gold nanoparticles for biomedicine. *Chem. Soc., Rev.*, 2012; 41: 2740-2779.
 49. Voliani V., Ricci F., Signore G., Nifosì R., Luin S., Beltram F., Multiphoton molecular photorelease in

- clickchemistry- functionalized gold nanoparticles. *Small.*, 7: 3271-3275.
50. Gutierrez-Wing C., Esparza R., Vargas-Hernandez C., Fernandez García M. E., Jose-Yacaman M., Microwave-assisted synthesis of gold nanoparticles selfassembled into self-supported superstructures. *Nanoscale*, 2012; 4: 2281-2286.
 51. Daniel M., Astruc D., Gold nanoparticles: Assembly, supra molecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, an nanotechnology. *Chem. Rev.*, 2004; 104: 293-346.
 52. Liz-Marzán L. M., Tailoring surface plasmons through the morphology and assembly of metal nanoparticles. *Langmuir*, 2006; 22: 32-41.
 53. Dreaden E. C., Alkilany A. M., Huang X., Murphy C. J., El- Sayed M. A., The golden age: Gold nanoparticles for biomedicine. *Chem. Soc. Rev.*, 2012; 41: 2740-2779.
 54. Voliani V., Ricci F., Signore G., Nifosì R., Luin S., Beltram F., , Multiphoton molecular photorelease in clickchemistry- functionalized gold nanoparticles, 2011; *Small.* 7: 3271-3275.
 55. Gutierrez-Wing C., Esparza R., Vargas-Hernandez C., Fernandez García M. E., Jose-Yacaman M., Microwave-assisted synthesis of gold nanoparticles selfassembled into self-supported superstructures. *Nanoscale*, 2012; 4: 2281-2286.
 56. Daniel M., Astruc D., Gold nanoparticles: Assembly, supra molecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology. *Chem. Rev.*, 2004; 104: 293-346.
 57. Haruta M., Catalysis of gold nanoparticles deposited on metal oxides. *Cattech*, 2002; 6: 102-115.
 58. Kisailus D., Najarian M., Weaver J. C., Morse D. E., Functionalized gold nanoparticles mimic catalytic activity of a polysiloxane-synthesizing enzyme. *Adv. Mater.*, 2005; 17: 1234-1239.