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Microwave-Assisted Green Synthesis of Silver Nanostructures

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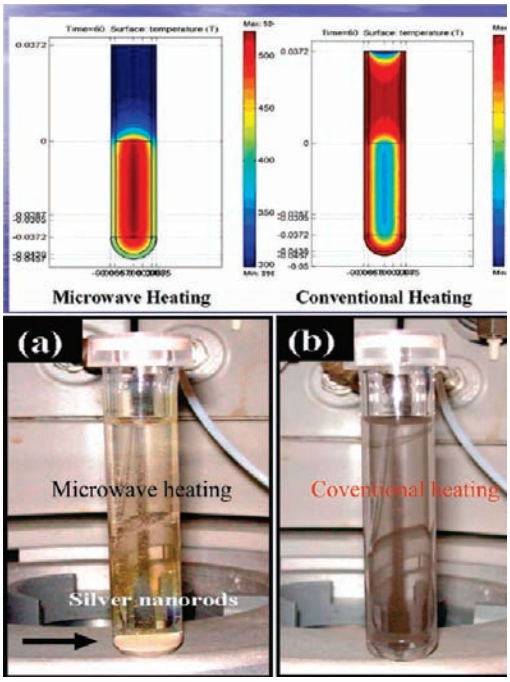
CONSPECTUS

Over the past 25 years, microwave (MW) chemistry has moved from a laboratory curiosity to a well-established synthetic technique used in many academic and industrial laboratories around the world. Although the overwhelming number of MW-assisted applications today are still performed on a laboratory (mL) scale, we expect that this enabling technology may be used on a larger, perhaps even production, scale in conjunction with radio frequency or conventional heating.

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.

I. Introduction

Microwave (MW) chemistry has an advantage over conventional heating methods for conducting chemical reactions and has the potential to emerge as the preferred technology for performing chemical synthesis over the next decade.[1−6] Microwave heating is a dipolar phenomenon

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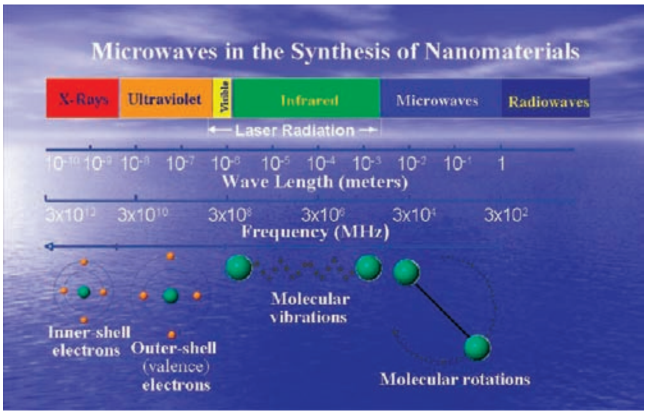

FIGURE 1. Electromagnetic spectrum. Reprinted with permission from ref 67.

with frequencies that range from 0.3 to 300 GHz. Domestic MW ovens and reactors for chemical reactions all operate at 2.45 GHz, a frequency region assigned for heating applications.[7] Microwaves fall in between infrared and radio frequency waves in the electromagnetic spectrum (shown in Figure 1).

There are two main principles involved in microwave chemistry, the dipolar mechanism and the electrical conductor mechanism. The dipolar mechanism occurs when, under a very high frequency electric field, the 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 (electrons, ions, etc.) are moved through the material under the influence of the electric field, E, resulting in a polarization, P. These induced currents will cause heating in the sample due to any electrical resistance (Figure 2). With a good conductor, complete polarization may be achieved in approximately 10−18 s, indicating that, under the influence of a 2.45 GHz microwave, the conducting electrons would move precisely in phase with the field.

This Account gives an overview of microwave-assisted synthesis of silver nanostructures. MW heating as a technique has been well explored in materials and organic synthesis, while its application in nanomaterials synthesis is still in its infancy. During the past 25 years, microwave chemistry has steadily moved from a laboratory curiosity to a well-established synthetic technique that is used in many academic and industrial laboratories around the world. Although the overwhelming number of MW-assisted applications today are still performed on a laboratory (mL) scale, there is an expectation that this enabling technology may be used on a larger, perhaps even production, scale in conjunction with radio frequency or conventional heating. At this point, it is important to evaluate the genuine benefits of microwave technology as applied to synthetic nanochemistry. This Account covers some of our own recent work along with others in the production of silver nanostructures using microwave irradiation.

II. Synthesis of Silver Nanoparticles using MW and Polyol Method

Silver (Ag) nanoparticles display several interesting properties that could be improved through the nanoscale control of morphology.[8] The application of Ag includes catalytic reactions such as Ag-catalyzed heterocyclizations; the addition of nucleophiles to alkynes, allenes, and olefins; cycloaddition reactions (with special focus on enantioselective [3 + 2]-cycloaddition of azomethine and nitrilimines); and [4 + 2]-cycloaddition of imines.[9] Additionally, acetylenic Csp-H and Csp-Si bond transformations can be achieved through Ag-catalyzed processes.[10]Another quality of Ag is that it is the most accepted catalyst for the oxidation of ethylene to ethylene oxide and methanol to formaldehyde.[8] Ag also has the highest electrical and thermal conductivity among metals, making it a popular material for electrical contacts and an additive for conducting adhesives.[8] Finally, Ag is perhaps most widely recognized for its unique optical properties and nonlinear optical (NLO) properties.[11]

Microwave heating was discovered in the early 1940s and has been used successfully in the food industry with numerous applications in chemistry since 1986.[12−17] However, applications are now beginning to surge for the use of MW heating in the generation of nanomaterials.[4] The rapid consumption of starting materials in kinetically driven reactions reduces the formation of agglomerates in MW-assisted methods for nanomaterials with narrow-size distribution. In the general synthesis of nanoparticles via a bottom-up approach, the reduction of inorganic salts and their subsequent capping is the common procedure. Among these, a reduction method based on ethylene glycol (EG), also known as the polyol method, has been used for the preparation of nanoparticles of pure metals.[8] In addition to their reducing power, polyol solvents such as EG are very suitable for microwave-assisted reactions because of their relatively high dipole moment.

Zaleski et al. have developed MW-assisted aerobic synthesis of Ag nanowires using NaCl and $AgNO_3$ (ratio 1:6 to 1:3) in EG in the presence of polyvinyl pyrrolidone (PVP).[18] The desirable outcome is highly dependent upon the MW

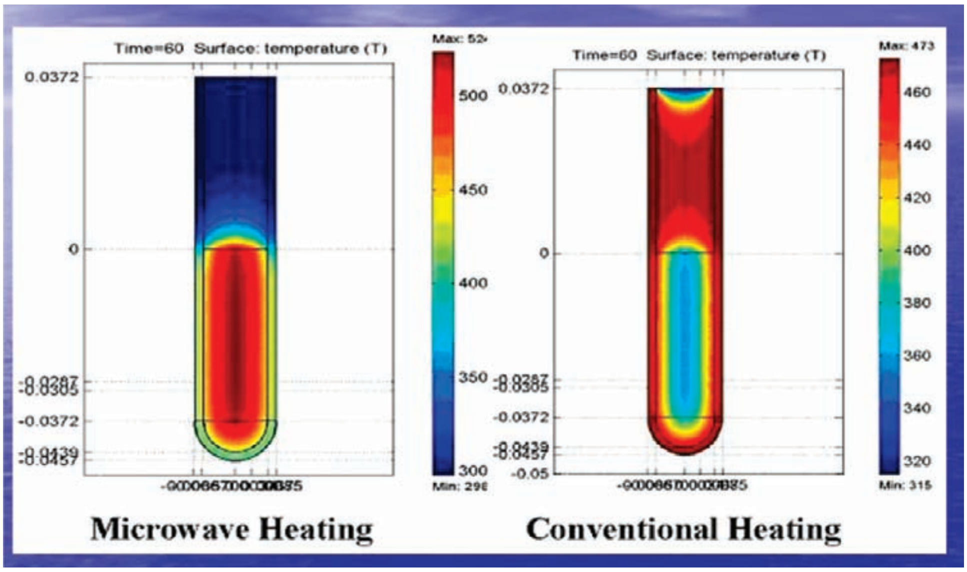

FIGURE 2. Temperature profile after 60 s as affected by MW irradiation (left) compared to treatment in an oil-bath (right). MW irradiation raises the temperature of the whole reaction volume simultaneously, whereas in the oil heated tube the reaction mixture in contact with the vessel wall is heated first. Reproduced with kind permission from Springer Science+Business Media B.V., ref 68.

heating power, time, NaCl:$AgNO_3$ ratio, and the presence of O_2 as an etching coreagent. They also observed that extended MW heating resulted in the fusing of proximite wires or the degradation of shorter wires (presumably via the etching reaction). Bhalla et al. extended a similar strategy to produce Ag and Pt nanostructures using EG and PVP in the presence of NaOH.[19] In the latter method, use of NaOH produced spherical particles in contrast to wire formation. By using dodecylthiol with EG, Komarneni et al.[20] were able to produce self-assembled hexagonal Ag nanoparticles with a one-step interface reaction under MW-assisted solvothermal conditions. This step was completed without the requirement of the presynthesis of uniform Ag nanoparticles or special precursors using a size-selective precipitation technique. The ratio between EG and dodecylthiol shows its effect on the nucleation and growth of Ag nanostructures and, thus, the morphology and arrangement of the obtained nanoparticles. Using Pt seeds in the presence of PVP and EG, Zhang and co-workers[21,22] were able to produce Ag nanoparticles, mixtures of one-dimensional (1-D) Ag nanorods and nanowires, and three-dimensional (3-D) spherical, triangular-bipyramidal, and cubic nanoparticles within a few minutes. Pandian and Grace synthesized uniform and stable polymer-protected spherical Pt, Pd, Ag, and ruthenium (Ru) nanoparticles using glycerol both as a solvent as well as a reducing agent without use of any additional capping/dispersant.[23] The study compared mode of reflux (conventional heating) and MW-heating on the size and morphology of nanoparticles synthesized. On the other hand, Devi et al.[24] used ethanol as a reducing agent to generate Ag nanoparticles using MW and PVP as a stabilizing agent. The particles produced were spherical in nature with sizes ranging from 10 to 11 nm diameter. Depending upon the chain length of the polymer PVP used, it is possible to produce different shapes of Ag nanostructures. One such example is the production of spherical nanoparticles, nanosheets, polygonal nanoplates, nanorods, and nanowires.[25] When a short chain PVP (mol wt ~10000) was used, nanosheets and nanoplates were dominantly produced, while nanorods and nanowires were preferentially formed using longer chain PVPs (mol wt ~ 40 000–360 000). The effect of Cl^- (NaCl and KCl) along with Pt seeds was explored in the formation of Ag nanowires by Kamarudin et al.[26] The experimental results showed that Pt seeds are probably not responsible for nucleation and subsequent evolution of 1D Ag products, but that Cl^- ions indeed influence the formation of the 1D Ag nanostructures. Due to its simplicity, the polyol method was subsequently extended to prepare composite core–shells.[27] Au@Ag core–shell nanocrystals have been synthesized using a MW-polyol method by Nishio et al.[27] In the two-step process, $HAuCl_4 \cdot 4H_2O$ was initially reduced in EG in the presence of PVP as a polymer surfactant and a mixture of triangular twin platelike, octahedral, and multiple-twinned decahedral Au nanocrystals (having only 111 facets) were produced. These Au seeds were used to reduce

Ag to produce triangular-bipyramidal, cubic, and rod/wire Ag shells having 100 facets.

III. Use of Polymers as Stabilizing and Reducing Agents in the Presence of MW

A wide variety of polymers have been used as capping or dispersing agents, including PVP, poly(ethylene glycol) (PEG), polyacrylamide, starch, carboxymethyl cellulose sodium (CMC), β- cyclodextrin, poly(aryl ether)s (PAEs), and poly(propyleneimine). The polymers can act as nanoparticle stabilizers and complexing agents.

Recently, Liz-Marzan and Patoriza-Santos reported that PVP is capable of complexing and stabilizing Ag and Au nanoparticles formed through the reduction of Ag^+ or $AuCl^{4-}$ ions with *N*,*N*-dimethylformamide (DMF). The reduction can be accomplished under both reflux and MW irradiation conditions, but each of these methods leads to different nanoparticle morphology and particle stability.[28]

Gedanken and Groisman attempted to prepare particles of varying sizes through continuous MW synthesis[29] using different polymers and surfactants such as polyvinyl alcohol, poly(methyl methacrylate) (PMMA), polycarbonate, nylon-6, and linoleic acid. They were also able to synthesize biodiesel using the same strategy. Complete conversion of commercially available vegetable oils to fatty-acid esters and glycerol was accomplished in this newly designed system. The effects of $AgNO_3$ concentration, PVP concentration, reaction time, and reaction temperature were studied using variable frequency microwave (VFM).[30]

There are several reports available to synthesize core–shell and alloy nanoparticles. Devi et al. have prepared different alloy compositions such as Au–Ag along with Ag and Au synthesis in the presence of a polyacrylamide polymer.[31] The obtained particles were spherical in shape with sizes ranging from 5 to 50 nm.

A green process that uses starch and microwaves was described by Nair et al. wherein they were able to produce ∼12 nm size Ag nanoparticles.[32] Ag nanoparticles are prepared by a simple green method where sodium salt of carboxymethyl cellulose (CMC) is employed to work as both a reducing and a stabilizing reagent in the reaction.[33]

Using PVP and β-cyclodextrin, Liu et al. prepared Ag nanoparticles with the aid of MW heating. The particle size control was achieved by varying the concentration of methanolic NaOH, methanolic HCl, and $AgNO_3$ along with added polymer.[34] The MW-based thermal process was applied to the preparation of dendrimer-protected poly(propyleneimine) Ag nanoparticles. Here the dendrimer was used as capping and reducing agent without use of any added reducing agents.[35]

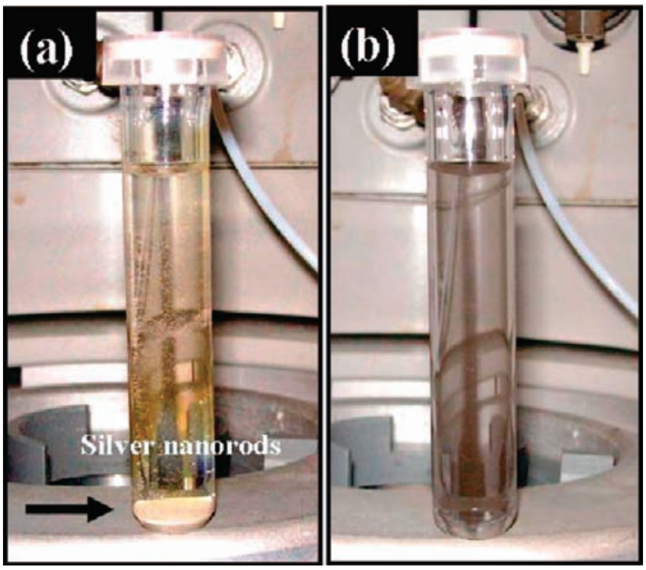

FIGURE 3. Photographic image of (a) precipitated Ag nanorods after MW irradiation for 2 min and (b) control reaction of the same reaction composition carried out using oil bath at 100 °C for 1 h.

Our group established several green methodologies to synthesize bulk quantities of Ag and other noble metal nanostructures. Synthesis of Ag nanorods was achieved through the use of benign PEG under MW irradiation conditions (Figures 3 and 4).[36] The nanorod formation depended upon the concentration of PEG (mol wt ∼ 300) used in the reaction with Ag salt; this process uses no surfactant or reducing agent (Figure 5). Another greener approach generates bulk quantities of nanomaterials using MW irradiation in the presence of CMC, by reacting respective metal salts with the sodium salt of CMC in aqueous media. The noble metals such as Au, Pt, and Pd do not reduce at room temperature with aqueous solutions of CMC, but do so rapidly under microwave irradiation conditions at 100 °C.[37]

The MW irradiation method accomplishes the cross-linking reaction of poly(vinyl alcohol) (PVA) with metallic and bimetallic systems.[38] Nanocomposites of PVA cross-linked metallic systems such as Pt, copper (Cu), and indium (In), and bimetallic systems such as Pt–In, Ag–Pt, Pt–iron (Fe), Cu–Pd, Pt–Pd, and Pd–Fe were prepared expeditiously by reacting the respective metal salts and 3 wt % PVA under MW irradiation. Throughout the process, the temperature was maintained at 100 °C; this was a radical improvement over the methods for preparing cross-linked PVA described in the literature. The general preparative procedure is versatile and provides a simple route to manufacturing useful metallic and bimetallic nanocomposites with

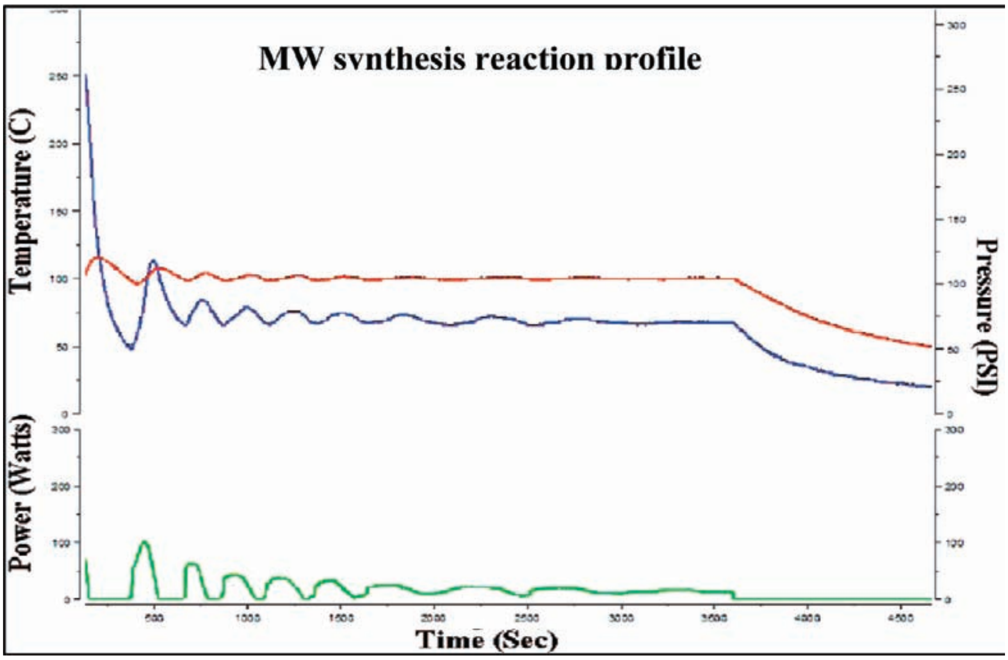

FIGURE 4. Reaction profile of 4 mL PEG + 4 mL $AgNO_3$ irradiated at 100 °C for 1 h using MW.

various shapes, such as nanospheres, nanodendrites, and nanocubes.

A facile MW method has accomplished alignment and decoration of noble metals such as Ag and Pd on carbon nanotubes (CNTs) wrapped with CMC.[39] CNTs, such as single wall nanotubes (SWNTs), multiwall nanotubes (MWNTs), and Buckminsterfullerenes (C-60), were well dispersed using the sodium salt of CMC under sonication. Addition of respective noble metal salts then generated noble-metal-decorated CNT composites at room temperature (Figure 6). However, aligned nanocomposites of CNTs could only be generated by exposing the above nanocomposites to MW irradiation. The general preparative procedure is versatile and provides a simple route to manufacturing useful metal-coated CNT nanocomposites.

The in situ formation of well-dispersed Ag nanoparticles in an insulating polymer matrix such as poly(aryl ether) has been achieved by Swager et al.[40] This method provides a generalized approach to the facile preparation of well-dispersed metal nanoparticle embedded thin films.

Polyacrylamide nanocomposites with Pt, Ag, and Cu that are homogeneously dispersed in the polymer matrix have been successfully prepared with the corresponding metal salt and acrylamide monomer in EG via MW heating.[41] The stabilization of nanoparticles was achieved through polymerization of an acrylamide monomer to a polyacrylamide; EG was used as reducing agent as well as a solvent.[41] Using polyamide and polyethylene naphthalate, Schubert and coworkers were able to use inkjet printing and MW sintering of conductive Ag.[42,43] Hybrid films containing Ag nanoparticles (and in the presence of MW irradiation) were produced using styrene and starch by Macquarrie et al.[44] The oxidation of styrene to polystyrene was accomplished through MW irradiation. The well-dispersed Ag nanoparticles were prepared in reactive methacrylate monomers under MW irradiation conditions, and then successive polymerization of the monomer containing the resulting nanoparticles successfully yielded a monohybrid of the Ag nanoparticles dispersed in the polymer matrix.[45]

IV. MW-Assisted Doping of Nanocomposites

The nanocomposite of mesoporous ZnO and Ag was synthesized by MW radiation in a 15 min reaction carried out under an argon atmosphere.[46] The self-assembly of microwire patterns of 52 nm aluminum and 19 nm Ag nanoparticles was demonstrated under MW heating using novel surfactant−solvent systems.[47] The MW method has been developed to prepare a wide variety of pure metallic and bimetallic alloy nanoparticles with controlled size and shape that include nanoalloys of Au, Ag, Pt, Pd, Ru, rhodium (Rh), Cu, and nickel (Ni).[48] Similarly, the core−shell approach for the production of patterned films of nanometer-sized Au/Ag bimetallic core/shell nanoparticles on silicon wafers was accomplished.[49] Ag-modified titanium oxide ($Ag{-}TiO_2$) nanoparticles with various Ag/Ti molar ratios were prepared by the MW-assisted method and compared with the

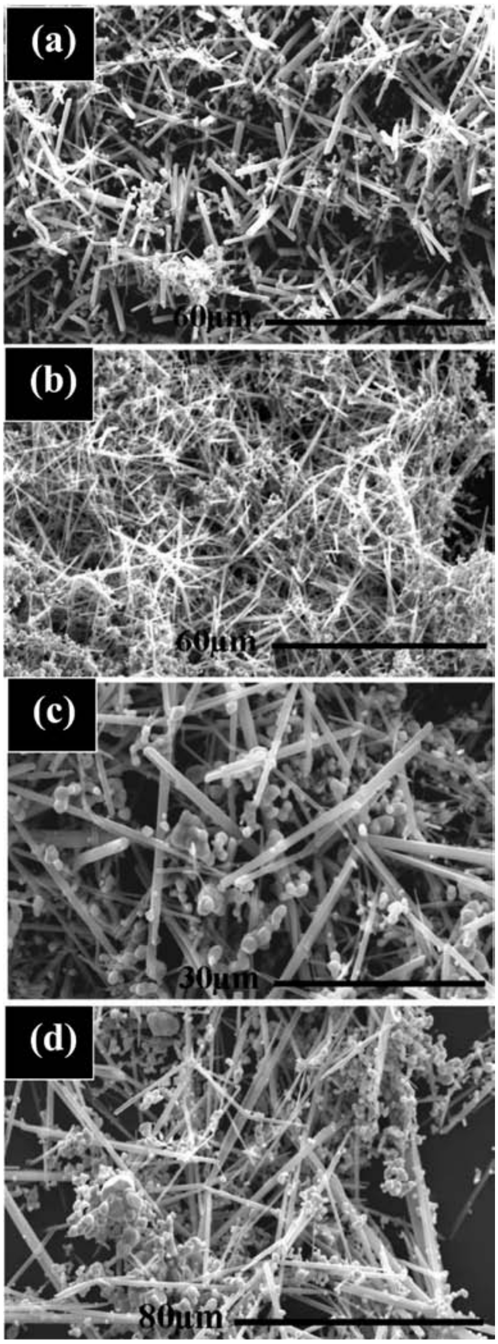

FIGURE 5. SEM images of Ag nanorods synthesized via MW irradiation for 1 h using (a) 4 mL PEG + 4 mL $AgNO_3$ (0.1 N), (b) 5 mL PEG + 3 mL $AgNO_3$, (c) 3 mL PEG + 5 mL $AgNO_3$, and (d) 2 mL PEG + 6 mL $AgNO_3$ compositions.

hydrothermal method.[50] Ag-doped CdS nanoparticles were synthesized by an ultrasound-assisted MW synthesis method.[51]

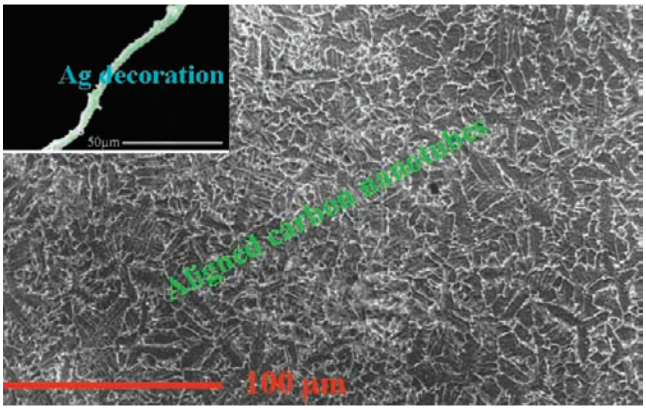

FIGURE 6. X-ray mapping image of Ag metal decorated CMC-SWNTs (inset) and aligned carbon nanotubes in CMC after MW irradiation.

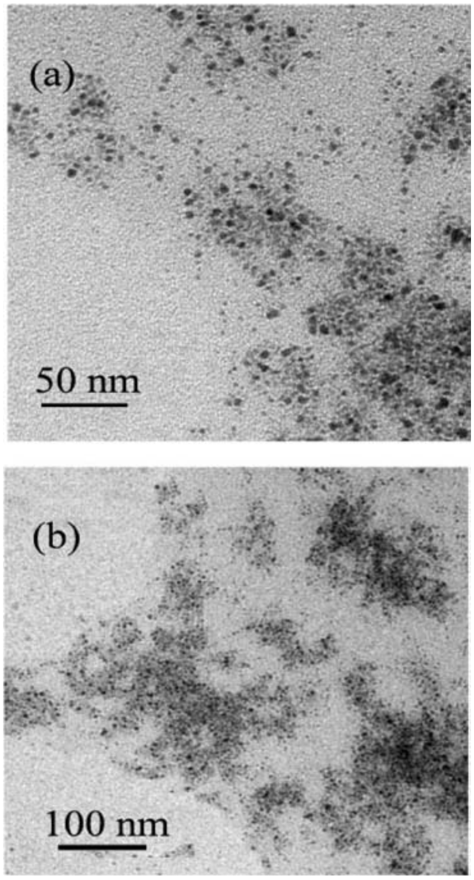

FIGURE 7. TEM micrographs of the as synthesized nanoparticles at (a) 75 W and (b) 100 W for 30 s with a $AgNO_3$ to glutathione mole ratio of 1.0:0.15.

V. Use of Different Reducing Agents under MW Irradiation

Alkaline 2,7-dihydroxy naphthalene (2,7-DHN) is being used as a reducing agent to prepare Ag nanoparticles under MW irradiation in just 60 s using a nonionic surfactant (TX-100) media.[52] The aqueous process uses L-lysine or L-arginine as a reducing agent and soluble starch as a protecting agent in the synthesis of nearly monodispersed Ag nanoparticles in large quantities via a MW-assisted "green" chemistry method.[53] Ko et al. reduced Ag ions to

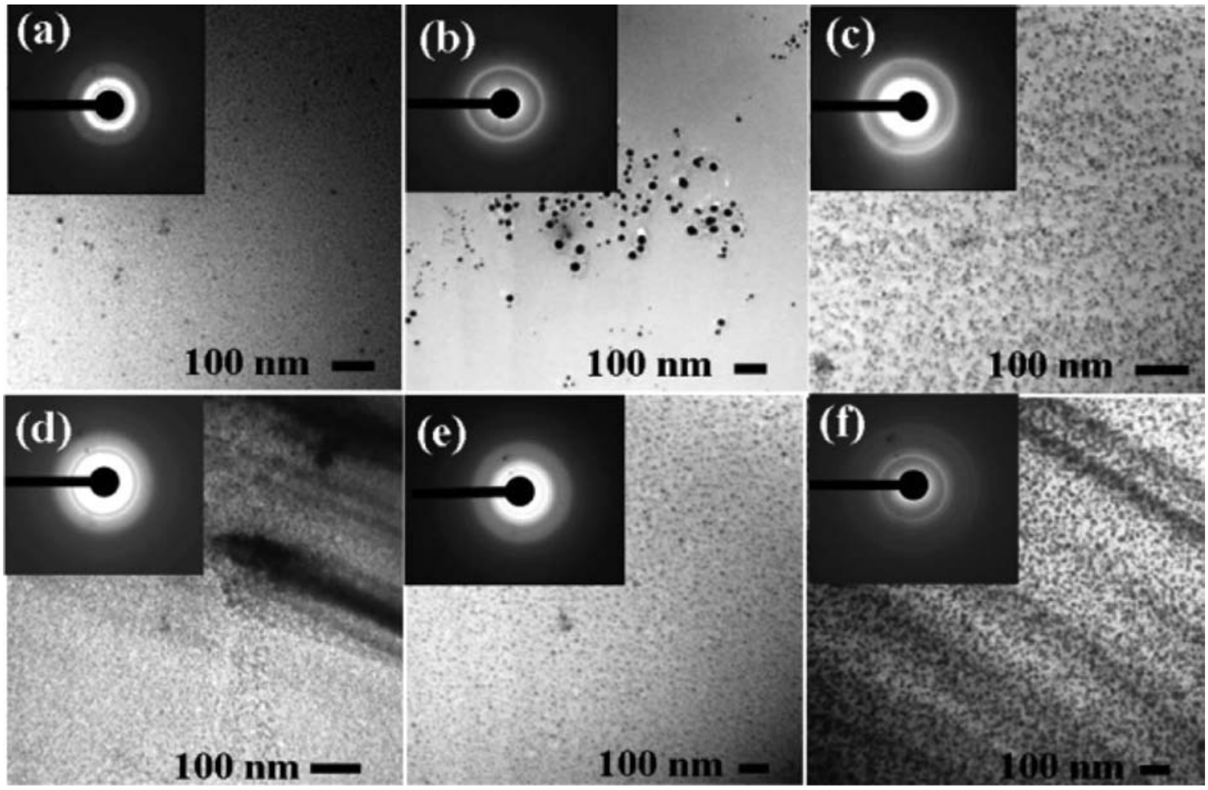

FIGURE 8. TEM images of Ag and Pd nanostructures synthesized using MW irradiation in the presence of PVP as capping agent: (a) Ag with α-D-glucose; (b) Ag with sucrose; (c) Ag with maltose; (d) Pd with α-D-glucose; (e) Pd with maltose; (f) Pd with sucrose. The insets show corresponding electron diffraction patterns.

Ag metal on the surface of Au seeds under rapid MW heating in the presence of sodium citrate.[54] A sensitive Ag substrate for surface-enhanced Raman scattering (SERS) spectroscopy was synthesized under multimode MW irradiation using formaldehyde which was employed as both the reductant and MW absorber in the reductive process.[55]

Large-scale and size-controlled generation of Ag nanoparticles has been rapidly accomplished under MW irradiation conditions from an aqueous solution of $AgNO_3$ and trisodium citrate in the presence of formaldehyde as a reductant.[56]

Ag nanoparticles ranging from 5 to 10 nm in size have been synthesized under MW irradiation conditions using glutathione, an absolutely benign antioxidant that serves as the reducing as well as capping agent in aqueous medium. This rapid protocol yields the nanoparticles within 30–60 s at a power level as low as 50 W (Figure 7). The effect of MW power on the morphology of ensuing Ag nanoparticles is investigated for this green and sustainable procedure, which is adaptable for the synthesis of Pd, Pt, and Au nanoparticles as well.[57]

VI. Use of Sugars as Reducing Agents with Microwaves

Sugars can be used as reducing agents for the MW-assisted synthesis of noble metals.[58] This method, however, needs a very long heating time (2 h). The former method has been accelerated for the shape-controlled synthesis of Au nanostructures with various shapes such as prisms, cubes, and hexagons and exploits MW-assisted spontaneous reduction of noble metal salts using an aqueous solution of α-D-glucose, sucrose, and maltose.[59] The expeditious reaction is completed under MW irradiation conditions in 30–60 s and can be applied to the generation of nanospheres of Ag, Pd, and Pt (Figure 8).

Ag nanoparticles with diameters in the range of 10–25 nm have been synthesized using a simple sucrose ester micellar-mediated method.[60] Ag nanoparticles were formed by adding $AgNO_3$ solution into the sucrose ester micellar solution containing NaOH at atmospheric condition after 24 h of aging time. A trace amount of DMF in the sucrose ester solution served as a reducing agent while NaOH acted as a catalyst. This is another simple method that uses sucrose to make Ag nanostructures without using any additional

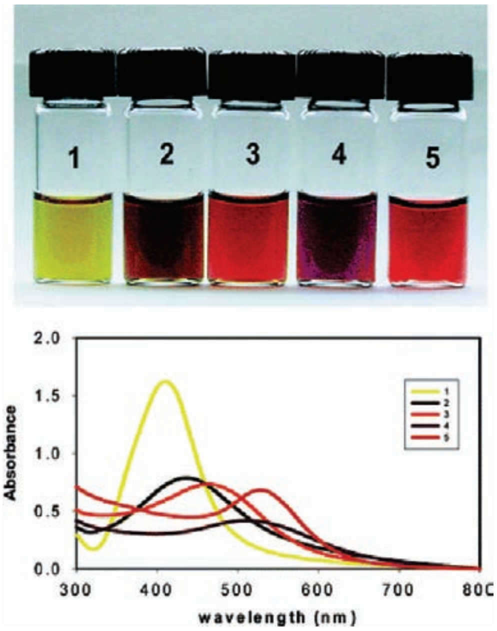

FIGURE 9. Photographic images of the aqueous dispersions of starch stabilized Au, Ag and the various Au−Ag alloy compositions. The Au/Ag mole ratios are (1) 0:1; (2) 0.25:0.75; (3) 0.5:0.5; (4) 0.75:0.25; (5) 1:0. The corresponding UV spectra (surface−plasmon absorption bands) are also shown. Reproduced with permission by the Royal Society of Chemistry.

reducing or capping agent under MW irradiation of a solution of $AgNO_3$.[61]

An environmentally benign MW method that uses starch and sugar for the preparation of Ag nanoparticles and a room temperature method for the preparation of Au and Au−Ag nanoparticles in water have been reported.[62] The alloy nanoparticles prepared in this process are homogeneous, and their sizes are well within the quantum size domain (<10 nm), where they are more applicable to size-dependent changes in electronic properties (Figure 9). Use of starch restricts the growth of the Ag and Au nanoparticles as compared to micrometer particles.[59]

VII. Formation of Ag Dendrites under MW Irradiation

Well-defined Ag dendrites were successfully prepared in DMF solution containing PVP as the stabilizer under MW irradiation by Rong et al.[63] It was found that MW power and the existence of PVP played important roles in the formation of well-defined Ag dendrites.

Normally, one reduces Ag^+ ions to metallic Ag using a variety of organic and/or inorganic reagents. Capping agents such polymers, surfactants, and so forth are commonly used to prevent agglomeration of the Ag particles. The fact that Ag dendrites can form spontaneously in the absence of capping agents,[64] and have, alternatively, been observed in the presence of capping agents in other studies,[63] raises the potential role of the TEM grid in orchestrating dendridic growth (Figure 10) in these studies.

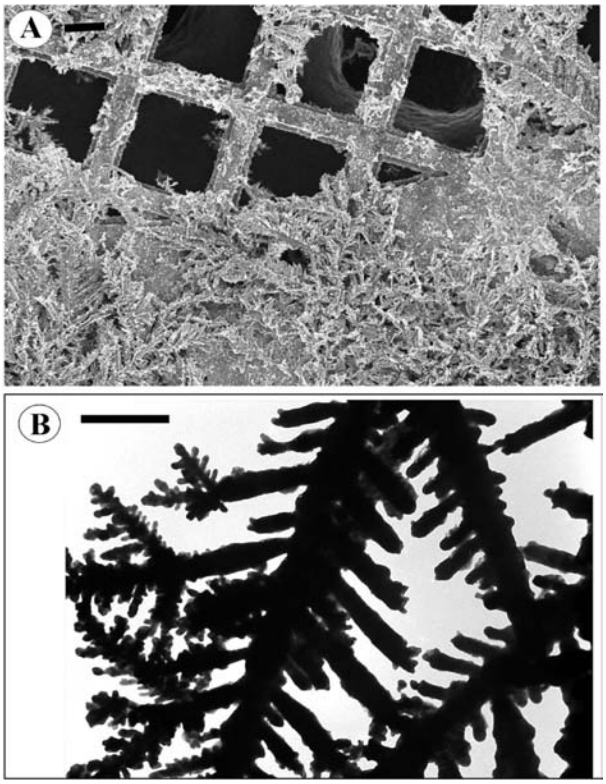

FIGURE 10. (A) SEM image of Ag dendrites formed on a TEM grid (scale 10 μm) and (B) TEM image of Ag dendrites formed on a TEM grid (scale 500 nm).

This study, triggered by a curious inconsistency between TEM and SEM images, provides a rapid and facile entry to a range of technologically important noble metal architectures, while at the same time underscoring the need for caution while interpreting TEM data in the absence of confirmatory SEM or other related imaging data. We believe these findings in nanoscience discipline will give insight into interpretation of results based only on a widely used analytical tool, TEM. Importantly, it provides a useful method to generate noble nanostructures without using any surfactant/capping agent.

VIII. Conclusion

Microwave technology is emerging as an alternative energy source powerful enough to accomplish chemical transformations in minutes, instead of hours or even days. Consequently, microwave irradiation is presently seeing an exponential increase in acceptance as a technique for enhancing chemical synthesis. In the context of nanomaterial synthesis, it is more relevant when the realization of the material properties is based solely on the size and shape; the control over the synthetic methodologies becomes an issue. This is because the growth of the materials in nanoscale is largely dependent on the thermodynamic and kinetic barriers in the reaction as defined by the reaction trajectory and is influenced by vacancies, defects, and surface reconstructions. Conventional thermal techniques are based on conduction of blackbody radiation to drive the reaction where the reaction vessel acts as an intermediary for energy transfer from the heating mantle to the solvent and finally to the reactant molecules. This can cause sharp thermal gradients throughout the bulk solution and inefficient, nonuniform reaction conditions. This has been a problematic issue in the synthesis of nanomaterials where uniform nucleation and growth rates are critical to material quality.

MW heating methods can address the problems of heating inhomogeneity in conventional thermal techniques, as its 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. The methodology is applicable under a variety of conditions[65] even for enzymatic and biological systems; the yield of Ag nanoparticles production using *Bacillus subilis* bacteria can be accelerated with MW irradiation.[66]

By judicious choice of the solvents, passivating ligands, and reactants, selective heating preferentially produces specific nanostructures. The use of MW irradiation as an efficient, environmentally friendly, and economically viable heating method for the production of nanomaterials has great potential.[69]

BIOGRAPHICAL INFORMATION

Dr. Mallikarjuna Nadagouda was born in India and received his Ph.D. (2003) from Gulbarga University. He worked with Prof. Alan G. MacDiarmid (2000 Nobel Laureate) at the University of Texas at Dallas and was a recipient of ORISE postdoctoral fellowship to work with Prof. Rajender S. Varma at NRMRL, USEPA prior to joining his current position at EPA, Cincinnati, OH. He has worked in the areas of analytical chemistry, green chemistry, polymer blends, solid coatings, nanomaterials, polymer nanocomposites, and solid state chemistry. He has published over 110 papers in reviewed journals and holds several patents.

Dr. Thomas Speth is a Professional Engineer who has conducted drinking-water-treatment research at the USEPA for 24 years. He has a Ph.D. in Environmental Engineering from the University of Cincinnati, a Masters degree in Civil/Environmental Engineering from Michigan Technological University, and a Bachelors degree in Chemical Engineering from Michigan Technological University. Dr. Speth is a member of the AWWA, ASCE, ACS, and IHSS. He has served as Division Trustee for AWWA's Water Quality & Technology Division, and as Associate Editor for ASCE's *Journal of Environmental Engineering*. He is currently serving on the Editorial Board for the AWWA Journal. He is Branch Chief of the Treatment Technology Evaluation Branch at the EPA and is currently serving as the Acting Division Director of the Water Supply and Water Resources Division.

Prof. Rajender S. Varma was born in India and obtained his Ph. D. from Delhi University in 1976. After postdoctoral positions at Robert Robinson Laboratories, University of Liverpool, U.K., and University of Tennessee, he was a faculty member at Baylor College of Medicine, Senior Scientist at Houston Advanced Research Center, and Research Professor at Sam Houston State University prior to joining as senior scientist in the Sustainable Technology Division at the U.S. Environmental Protection Agency in 1999. He has over 35 years of research experience in management of multidisciplinary technical programs ranging from natural products chemistry, pulp and paper technology, and therapeutics, to development of genosensor technology, specifically the applications and interface of chemical science with biology, solid state chemistry, bioelectronics, nanomaterials, and development of environmentally friendlier alternatives for synthetic methods using microwaves, ultrasound, and mechanochemical approaches. The primary focus is to evaluate novel and safer environmental protocols in industrial chemistry and its impact in human health and environmental sciences. He has published over 310 scientific peer-reviewed papers and has been awarded eight U.S. Patents.

FOOTNOTES

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