

Microwave-Assisted Chemistry: Synthetic Applications for Rapid Assembly of Nanomaterials and Organics

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CONSPECTUS: The magic of microwave (MW) heating technique, termed the Bunsen burner of the 21st century, has emerged as a valuable alternative in the synthesis of organic compounds, polymers, inorganic materials, and nanomaterials. Important innovations in MW-assisted chemistry now enable chemists to prepare catalytic materials or nanomaterials and desired organic molecules, selectively, in almost quantitative yields and with greater precision than using conventional heating. By controlling the specific MW parameters (temperature, pressure, and ramping of temperature) and choice of solvents, researchers can now move into the next generation of advanced nanomaterial design and development.

Microwave-assisted chemical reactions are now well-established practices in the laboratory setting although some controversy lingers as to how MW irradiation is able to enhance or influence the outcome of chemical reactions.

Much of the discussion has focused on whether the observed effects can, in all instances, be rationalized by purely thermal Arrhenius-based phenomena (thermal microwave effects), that is, the importance of the rapid heating and high bulk reaction temperatures that are achievable using MW dielectric heating in sealed reaction vessels, or whether these observations can be explained by so-called “nonthermal” or “specific microwave” effects.

In recent years, innovative and significant advances have occurred in MW hardware development to help delineate MW effects, especially the use of silicon carbide (SiC) reaction vessels and the accurate measurement of temperature using fiber optic (FO) temperature probes. SiC reactors appear to be good alternatives to MW transparent borosilicate glass, because of their high microwave absorptivity, and as such they serve as valuable tools to demystify the claimed magical MW effects. This enables one to evaluate the influence of the electromagnetic field on the specific chemical reactions, under truly identical conventional heating conditions, wherein temperature is measured accurately by fiber optic (FO) probe.

This Account 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 ensuing 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.

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.



1. INTRODUCTION

The microwave heating technique, well-known for cooking foods, has been successfully making inroads in various chemistries in the laboratory such as nanomaterial synthesis,^{1–4} solid-state chemistry, nanotechnology,⁵ and organic synthesis.⁶ Under MW irradiation conditions, organic reactions can be accelerated and selectivities of the ensuing products can be

obtained by choosing appropriate MW parameters, thus offering several advantages over conventional heating, such as instantaneous and rapid heating (deep inside heating), high temperature homogeneity, and selective heating.^{6–8}

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MW-assisted synthesis fulfills the promise of being a fast synthesis practice. Since the first reports in 1986,^{9,10} the use of the MW heating technique has become an essential tool in all areas of synthetic organic chemistry, including solvent-free and water-mediated reactions (Figure 1).^{11–15} Lately, it has been

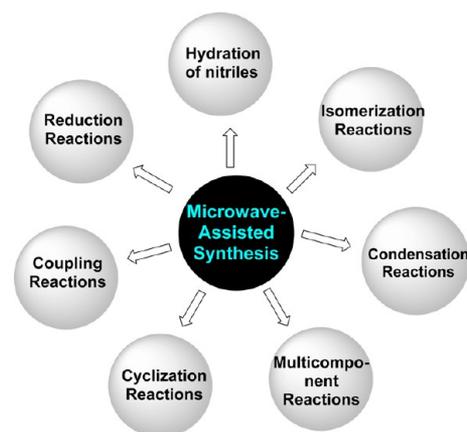


Figure 1. Applications of microwave-assisted synthesis.

postulated that the synthesis of nanomaterials, metal nanoparticles, and nanostructures, whose growth is highly sensitive to the reaction conditions, could benefit a great deal from the efficient and controlled heating provided by MW irradiation. The use of nanomaterials and magnetically recyclable catalysts in organic synthesis under benign aqueous reaction conditions is becoming increasingly popular.^{16,17}

The poor solubility of organic reactants in aqueous media is a major limitation for organic synthesis in water, which generally results in immiscible or biphasic reaction mixtures. This problem has been tackled by using surfactants, mixing with cosolvents, heating of the reaction mixture, or grinding of reactants. However, some of these issues have been addressed and solved by designing protocols based on the use of microwaves, ultrasound, or pressure reactors and other benign (co)solvents. Reactions in aqueous media are termed as “in-water” and “on-water” reactions, on the basis of the nature of reactants (solubility) during chemical reactions.¹¹ Higher pressure and temperature attained rapidly in MW-assisted processes may help increase the rate of reactions via enhanced homogeneous mixing of the reactants (in-water) and decreasing the hydrophobic effects (on-water). Despite these perceived limitations of reactions in water, it has great promise in MW-assisted organic synthesis (MAOS) and in MW-assisted nanomaterial synthesis (MANS).¹⁸

There is an ongoing debate^{19–22} between “specific MW effects” that cannot be (easily) emulated through conventional heating methods and “nonthermal MW effects”, which are proposed to explain unusual observations in MW-assisted chemistry.¹⁹ Kappe has asserted that the MW effect does not exist¹⁹ by repeating Dudley’s work on Friedel–Crafts benzylation of $[D_{10}]_p$ -xylene using the 2-benzyloxy-1-methylpyridinium salt.²¹ Dudley and Stiegman²⁰ agree that nonthermal MW effects do not exist but believe that “specific MW effects” are unequivocally observed in their system. An elegant summary²² is provided by Ritter on these traded dialogues between researchers and on more recent experimental work by Yamada et al. on enantioselective Claisen rearrangement (ECR) in the presence of chiral catalysts;²³ ECR was effectively

enhanced without any loss of enantioselectivity by MW irradiation and was accelerated by a factor of 10 under MW irradiation, compared with conventional heating.²³ Although these MW effects have not been comprehensively explained in the past and the reaction acceleration by MW irradiation still remains controversial, some results appear to show that the MW strategy does help to save time and attain selectivity in organic reactions. MW-assisted chemical reactions depend on the ability of the reaction mixture to efficiently absorb MW energy, which often depends on choice of solvents for the reaction. The ability of a specific solvent or material to convert MW energy into heat is determined by the so-called loss tangent (δ); the higher the $\tan \delta$ value, the better the solvent is for MW absorption and efficient heating (Table 1). The solvents employed for MW-assisted

Table 1. Loss Tangents of Frequently Used Solvents in Microwave-Assisted Reactions (2.45 GHz, 20 °C)²⁵

solvent	$\tan \delta$	solvent	$\tan \delta$
ethylene glycol (EG)	1.350	1,2-dichloroethane	0.127
ethanol	0.941	water	0.123
dimethyl sulfoxide (DMSO)	0.825	chloroform	0.091
methanol	0.659	acetonitrile	0.062
1,2-dichlorobenzene	0.280	tetrahydrofuran	0.047
<i>N</i> -methyl-2-pyrrolidone (NMP)	0.275	dichloromethane	0.042
acetic acid	0.174	toluene	0.040
dimethylformamide (DMF)	0.161	hexane	0.020

chemistry are classified as high ($\tan \delta > 0.5$), medium ($0.1 < \tan \delta < 0.5$), and low microwave absorbing ($\tan \delta < 0.1$).²⁴

2. MICROWAVE-ASSISTED CHEMISTRY: BASIC FACTS AND NEWER DEVELOPMENTS

During the past few years, innovative and important developments have occurred in MW-assisted synthesis to delineate MW effects, especially use of silicon carbide (SiC) reaction vessels and the accurate measurement of temperature using fiber optic (FO) temperature probes. The use of single mode MW reactors, especially in continuous flow reactions, are gaining popularity.²⁶

2.1. Silicon Carbide Reactors

One of the most striking benefits of the SiC reactors in MW-assisted chemistry is derived from the corrosion resistance of this ceramic material;²⁷ sintered “SiC” is more corrosion resistant and superior to glass even for concentrated acids or bases, chlorine, or HF gas.²⁸ Another salient feature of SiC reaction vessels is high MW absorptivity because it shields the contents of the reaction vessel from the electromagnetic field. SiC is a good MW susceptor, absorbing MW energy readily and strongly. The material can be heated quickly thus providing a more uniform temperature gradient within the heated material. Susceptor materials for hybrid MW heating need to be selected in such a manner as to provide constant heating at all temperature conditions; SiC and ionic liquids have been employed as susceptors because they enhance the overall capacity to absorb MWs and considerably minimize the required MW energy.^{29,30}

The common reaction vessels used in MW processing are generally made from MW-transparent materials, such as quartz, borosilicate glass, and Teflon. Consequently, MW-assisted reactions show an inverted thermal gradient compared with conventional thermal heating.³¹

2.2. Accurate Temperature Measurements

Most chemical reactions are sensitive to reaction parameters, particularly temperature, which needs to be measured accurately in MW-assisted reactions. External infrared (IR) and internal fiber optic (FO) temperature monitoring devices are now routinely incorporated into MW reactors³² to control the magnetron and the ramping of temperature. Notably, the stirring efficiency of the reactions can be supervised by a built-in integrated camera (Figure 2) in more sophisticated systems.

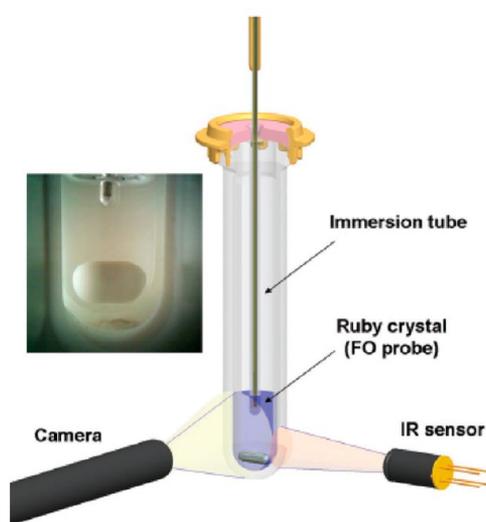


Figure 2. Schematic view of the utilized microwave cavity highlighting dual external (IR) and internal (FO) temperature control and the location of the built-in camera. The inset shows an image taken by the camera (2 mL liquid volume, magnetic stir bar).³³ Reprinted with permission from ref 33. Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA.

2.3. Single-Mode Microwave Reactors: Flow Chemistry

Recently, a single-mode MW reactor was used for continuous flow reactions under an elevated pressure,^{26,34} wherein the MW power was controlled by a temperature feedback module and resonance frequency autotracking function. This afforded precise temperature control of the fluids for rapid heating of liquid flow at pressures up to 10 MPa (Figure 3).

This type of continuous flow reactor is capable of operating in a genuine high-temperature/high pressure process window (310 °C/60 bar) under MW irradiation conditions. The system can be operated in an extremely energy efficient manner, utilizing 0.6–6 kW microwave power (2.45 GHz).³⁵ These continuous flow processes provide a universal tool to allow the quick transition from laboratory research platforms to industrial research development, thus eliminating the time- and material-consuming optimization from small-scale reactions to full-scale production. While the merits of flow synthesis, such as the ability to monitor the reaction in real time and make instantaneous changes to reaction conditions, have long been recognized, the impact of this technology in the chemical sector is still small, primarily because of poor reaction kinetics during the brief time that reagents are flowing together in a flow reactor.

The faster heating rate, small reactor volumes, and rapid change in reaction temperature in real time are some of the salient features of this continuous flow MW-assisted organic

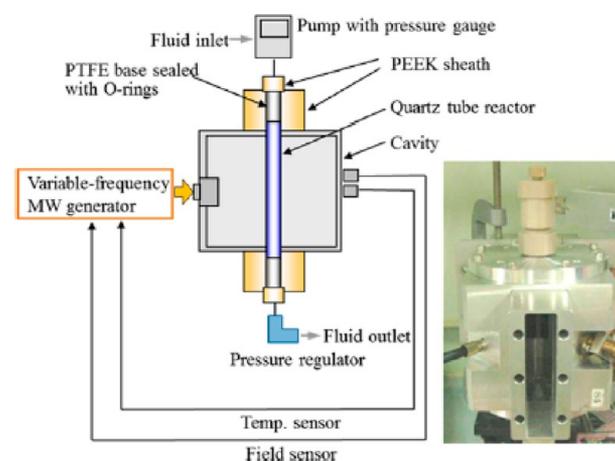


Figure 3. Experimental setup of the present MW-assisted flow reactor system and a photograph of the MW cavity part. The quartz reactor tube is connected with the PEEK sheath, which is designed to resist up to 10 MPa. Reprinted with permission from ref 26. Copyright 2013 American Chemical Society.

synthesis (CF-MAOS) system, which aims to be a unique laboratory tool for safe and fast optimization of reaction conditions and scale-out synthesis.

In this flow reactor, the reaction rate is increased by the rapid elevation of temperature and pressure, which can improve the productivity; low productivity is a common drawback of microflow reactors. Thus, the fusion of MW and a flow system does offer unique features that can be adapted to organic and inorganic materials syntheses.

3. MICROWAVE-ASSISTED ORGANIC SYNTHESIS (MAOS)

Many research and pharmaceutical laboratories today employ nonclassical forms of heating in a routine manner, which undoubtedly, is aided by the growing availability of carefully designed scientific MW reactors dedicated for chemical applications.

3.1. Synthesis of *N*-Heterocycles

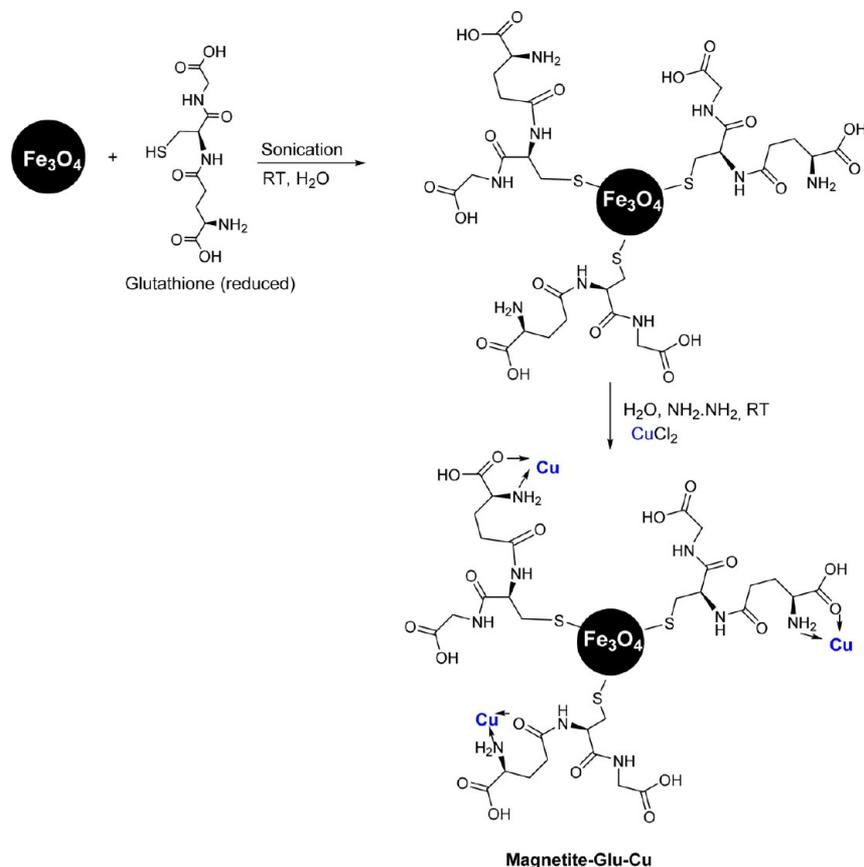
Synthesis of heterocyclic compounds via multicomponent coupling reactions (MCRs) offers various advantages, namely, cost effectiveness, efficiency, and lower waste generation than traditional synthetic protocols.^{36–38} Building *N*-heterocycles³⁹ by construction of multiple bonds in one-pot MCR syntheses paves the way for a sustainable approach to new molecule discovery in a benign fashion.⁴⁰

The synthesis of a variety of heterocycles (Paal–Knorr reactions, aza-Michael reactions, and pyrazole synthesis) has been achieved by magnetite decorated glutathione organo-catalysts (magnetite-Glu), which can be prepared by simple sonication of magnetite at room temperature with glutathione^{41,42} (Schemes 1 and 2).

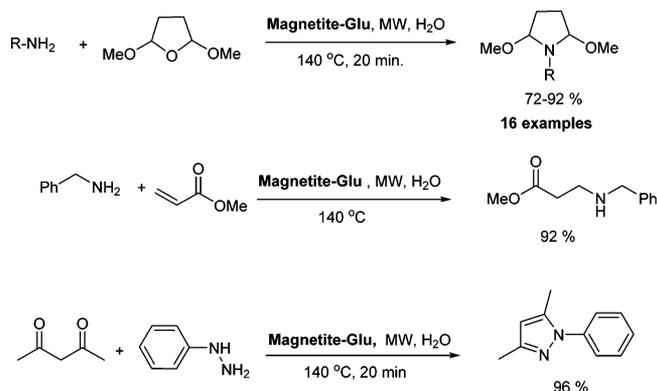
Thiazolo[3,2- α]pyridines and related fused heterocyclic compounds have displayed significant biological activities⁴³ and their chemoselective synthesis has been achieved via MW-assisted three-component reactions of malononitrile, aromatic aldehydes, and 2-mercaptoacetic acid in water (Scheme 3).⁴⁴

p-Dodecylbenzenesulfonic acid (DBSA) is a Brønsted acid catalyst endowed with surfactant properties that facilitate the dissolution of organic materials. Sriram et al. has reported the MW-assisted synthesis of novel isoniazid (INH) analogues⁴⁵

Scheme 1. Syntheses of Magnetite-Glu and Magnetite-Glu-Cu



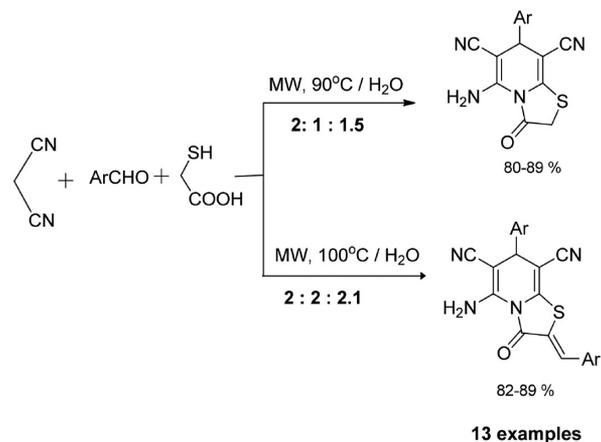
Scheme 2. Catalytic Activity of Magnetite-Glu Nanocatalyst



using benzaldehydes and dimedone in water with a catalytic amount of DBSA (Scheme 4).

The domino reactions of 2-(3-oxo-1,3-diarylpropyl)-1-cyclohexanones with phenylhydrazine hydrochloride in water results in the generation of pyrido[3,2,1-*jk*]carbazoles (Scheme 5).⁴⁶ The cascade process delivers a highly atom-efficient green pathway for the preparation of a library of corresponding pyridocarbazoles in aqueous media with minimum purification involved.

Pyrazoles and diazepines have been obtained under solvent-free and catalyst-free conditions using MW;⁴⁷ a complete conversion occurs at 120 °C in 5–15 min (Scheme 6), and the chemistry could be used for other fused pyrazoles and diazepines.

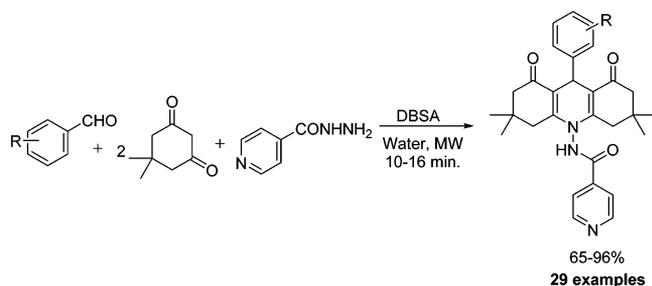
Scheme 3. Synthesis of Thiazolo[3,2- α]pyridines

3.2. Cross-Coupling Reactions

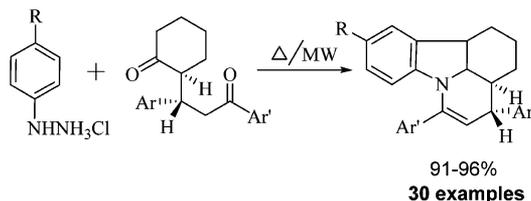
MW heating in aqueous medium is found to be advantageous for C–C coupling reactions such as the Sonogashira cross-coupling reaction.^{48–50}

Ley et al. have reported a rapid MW-assisted Sonogashira cross-coupling of aryl iodides and bromides with terminal alkynes using reusable Pd-EnCat™ TPP30 (encapsulated Pd with PPh₃) catalysts (Scheme 7).⁵¹ Various aryl bromides and iodides as well as heteroaryl species underwent coupling reactions with substituted terminal alkynes to afford the corresponding coupled products, in moderate to excellent yields.

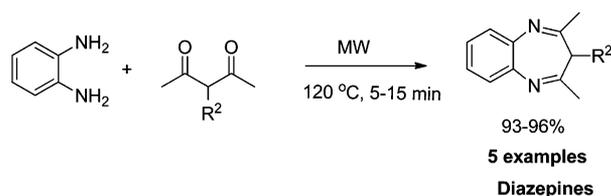
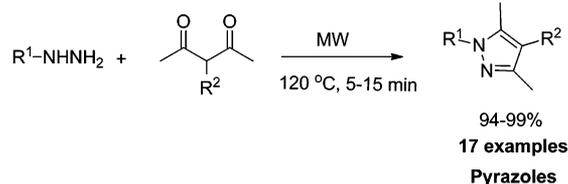
Scheme 4. Synthesis of Isoniazid (INH) Analogues



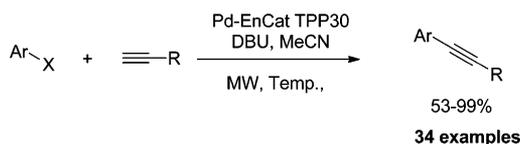
Scheme 5. Synthesis of Pyridocarbazoles



Scheme 6. Synthesis of Pyrazoles and Diazepines

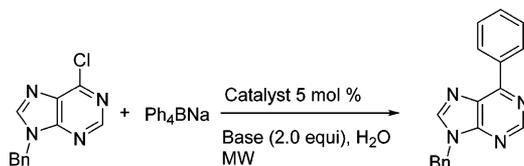


Scheme 7. Sonogashira Coupling Reaction



Qu et al. reported Suzuki–Miyaura reaction of nucleosides, 6-chloropurines, with arylation reagent, sodium tetraarylborate, in neat water (Scheme 8).⁵² Unprotected 6-chloropurine nucleo-

Scheme 8. Synthesis of 6-Arylpurines

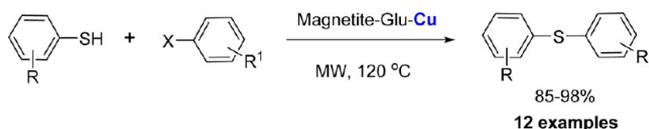


side, however, gave the C–N glycosidic bond cleaved product both in water and in ethanol.

The coupling to form a C–S bond has an integral value in several drug intermediates and pharmaceutical ingredients

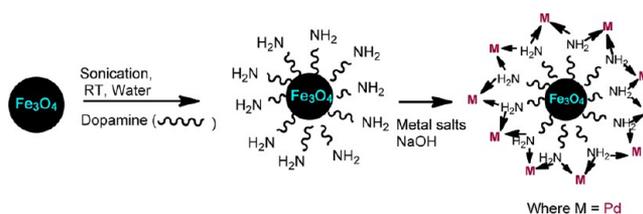
(Scheme 9).⁵³ The aforementioned magnetite-Glu-Cu catalyst (Scheme 1) proved useful for the coupling of aryl halides with thiophenols under MW-irradiation conditions.⁴⁹

Scheme 9. Coupling of Thiophenols with Aryl Halides

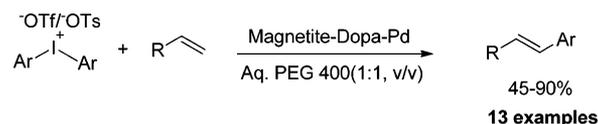


Along similar lines, a benign protocol for Heck-type arylation of alkenes and diaryliodonium salts on magnetically retrievable Pd nanocatalysts has been developed⁵⁴ via functionalization of magnetite with dopamine (magnetite-dopa-Pd; Schemes 10 and 11).

Scheme 10. Synthesis of Magnetite-dopa-Pd Nanocatalyst



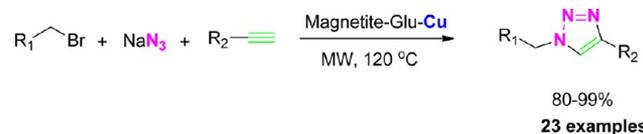
Scheme 11. Heck-type Arylation of Arenes



3.3. Huisgen 1,3-Dipolar Cycloadditions: Click Chemistry

Huisgen 1,3-dipolar cycloaddition reactions via click chemistry are instrumental in the synthesis of biologically active molecules and pharmaceutical intermediates.^{55–58} The synthesis of 1,2,3-triazoles has been accomplished in aqueous media, using magnetite-Glu-Cu (Cu on glutathione modified ferrites, Scheme 1) via multicomponent reactions under MW irradiation (Scheme 12).

Scheme 12. Magnetite-Glu-Cu Catalyzed Synthesis of 1,2,3-Triazoles

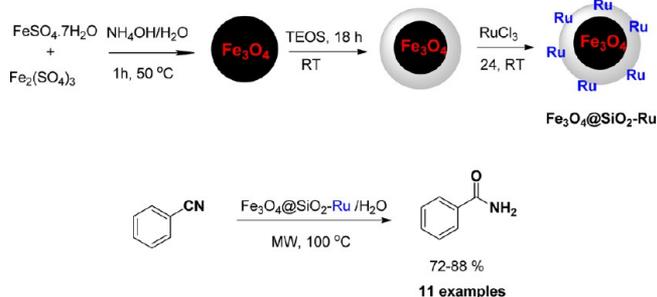


In the presence of bare magnetite or magnetite supported copper (magnetite-Cu), two products, the 1,4 adduct and 1,5 adduct, are formed in very low yield. However, excellent selectivity for 1,4-adduct formation in high yield is possible using the magnetite-Glu-Cu nanocatalyst.

3.4. Hydration of Nitrile and Hydrogenation Reactions

In recent years, several “greener” efforts have been introduced for the hydration of nitrile to amide in aqueous medium.^{58,59}

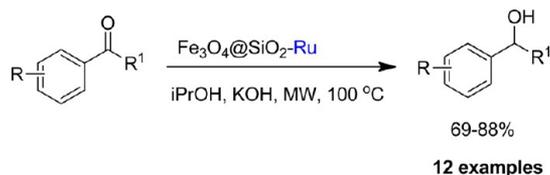
Scheme 13. Synthesis and Applications of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-Ru}(\text{OH})_x$



For example, magnetite-silica decorated ruthenium hydroxide ($\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-Ru}(\text{OH})_x$) nanoparticles, obtainable by a simple one-pot procedure (Scheme 13), were deployed for the hydrolysis of a variety of activated, inactivated, aliphatic, and heterocyclic nitriles to corresponding amides in aqueous medium under MW irradiation.⁶⁰

The transfer hydrogenation reactions find applications in the synthesis of dyes, biologically active compounds, and pharmaceuticals.⁶¹ $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-Ru}(\text{OH})_x$ has been employed for the transfer hydrogenation of carbonyl compounds using isopropyl alcohol as hydrogen source under MW irradiation conditions;⁶² the corresponding alcohols were obtained in good to excellent yield (Scheme 14).

Scheme 14. Transfer Hydrogenation Reduction of Carbonyl Compounds



The transfer hydrogenation of ketones is also accomplished on magnetite-supported Ni nanocatalysts under MW irradiation and isopropyl alcohol as hydrogen donor.⁶³

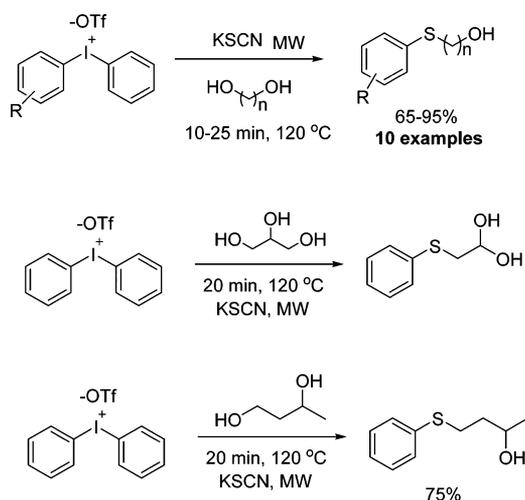
3.5. Synthesis of β - and γ -Hydroxy Sulfides

β - and γ -Hydroxy sulfides are well-known intermediates in organic synthesis and biologically active compounds that show anti-HIV, anticancer, and 5-hydroxytryptamine (5-HT) binding properties. Their preparation has been described⁶⁴ using readily available potassium thiocyanate (KSCN) and ethylene glycol/propylene glycol with diaryliodonium salts (Scheme 15) bearing counterions such as hexafluorophosphate, triflate, tosylate, and bromide. Furthermore, the reaction of diphenyliodonium triflate with glycerol delivered the corresponding product with excellent regioselectivity, along with diphenyl disulfide (Scheme 15).

4. MICROWAVE-ASSISTED NANOMATERIALS SYNTHESIS (MANS)

MW-assisted synthesis of inorganic nanomaterials and the use of nanocatalysts are growing rapidly. Inorganic nanomaterials include diverse classes of functional materials, namely, metals, metal oxides, sulfides, phosphates, and halides. Selected examples of nanoparticles are documented here to

Scheme 15. Synthesis of Hydroxyl Sulfides from Diaryliodonium Salts



underline the versatility of the MW-assisted approach for accessing a variety of nanomaterials. Additionally, a few selected examples of their application under MW irradiation are also detailed.

4.1. Synthesis of Pd Nanoparticles Using Vitamin B₁

A simple and facile approach for the synthesis of palladium (Pd) nanobelts, nanoplates, and nanotrees has been developed using vitamin B₁.⁶⁵ Notably, no capping agents are required and water is used as solvent for the synthesis of Pd nanoparticles with various morphologies (Figure 4). These highly structured Pd

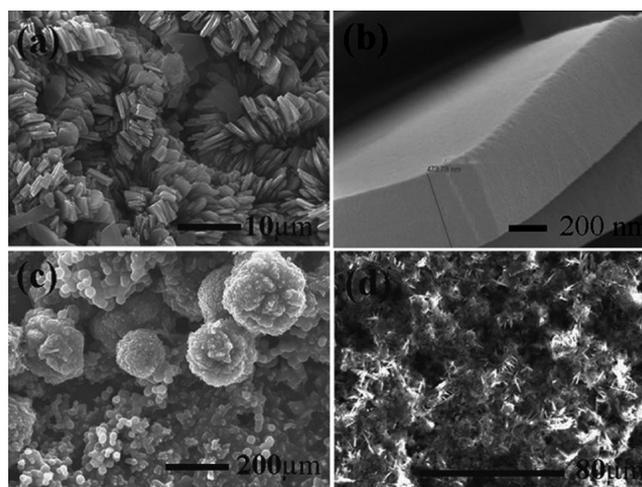


Figure 4. SEM images of Pd nanoparticles. Reprinted with permission from ref 65. Copyright 2009 the Royal Society of Chemistry.

materials with different morphologies were deployed for various C–C coupling reaction, such as Heck, Suzuki, and Sonogashira under MW irradiation (Scheme 16).

4.2. Synthesis of Nanocrystalline 3D Metal Oxides in Aqueous Media

Self-assembly of metal oxides into three-dimensional (3D) nanostructures occurs under MW irradiation conditions in aqueous medium without any capping or reducing agent.⁶⁶ Interestingly, metal oxides assembled into various 3D nanostructures

Scheme 16. Pd NP Catalyzed C–C Coupling Reactions

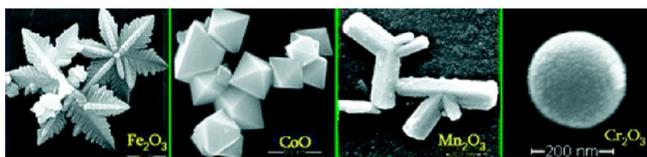
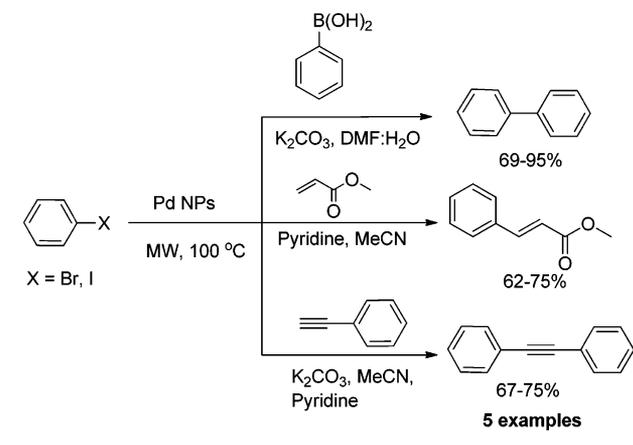


Figure 5. SEM images of various metal oxide nanostructures. Reprinted with permission from ref 66. Copyright 2009 American Chemical Society.

(octahedra, pine, triangular rods, spheres, and hexagonal snowflake-like morphologies) dictated by the specific metals used (Figure 5).

As-synthesized pine-like (Fe_2O_3) nanostructures could be easily decorated with dopa-Pd metal and were used for carbon–carbon coupling and hydrogenation reactions.⁶⁶

4.3. Nanoparticle Synthesis Using Glycerol

Glycerol, an abundant and safe byproduct from biodiesel production, has garnered attention as an alternative sustainable solvent for catalytic reactions⁶⁷ and nanomaterials synthesis⁶⁸ because of its unique physical and chemical properties, such as high polarity, low toxicity, high boiling point, and biodegradability.

Diameter-controlled Ag nanowires were fabricated using inexpensive and biodegradable solvent glycerol, which serves as both reductant and solvent under nonstirred MW irradiation conditions.⁶⁹ When the amount of sodium dodecyl sulfate

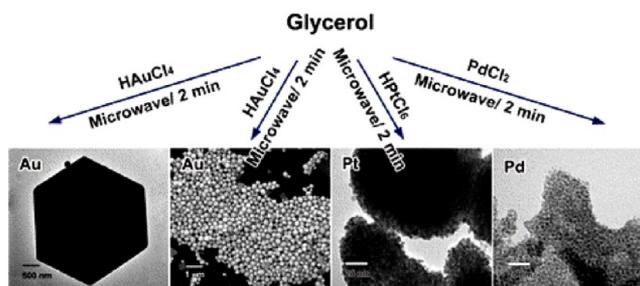


Figure 7. TEM and SEM images of Au, Pt, and Pd nanoparticles. Reprinted with permission from ref 70. Copyright 2013 American Chemical Society.

(SDS) used was low, bundles of Ag nanowires were obtained, while unbundled Ag nanowires were formed with a higher SDS amounts. The thickness of obtained Ag nanowires can be controlled by adjusting the relative amounts of glycerol and AgNO_3 (Figure 6).

The viability of this greener approach using glycerol has been established for the fabrication of Au, Pt, and Pd nanomaterials under MW irradiation conditions.⁷⁰ Surfactants, such as cetyltriethylammonium bromide (CTAB) and SDS, are employed for the syntheses of noble metal nanoparticles with different morphologies (Figure 7). In the presence of CTAB, Au nanosheets were formed within 2 min, and the size of the nanosheet can be controlled by glycerol content and MW irradiation time. The shapes of ensuing particles can be altered by the addition of various surfactants.

4.4. Synthesis of Nanoparticles Using Beet Juice

A facile and benign protocol has been established for the fabrication of hybrid AgCl/Ag plasmonic nanoparticles under MW irradiation conditions;⁷¹ beet juice, an abundant sugar-rich biorenewable agricultural vegetable byproduct, served as a reducing reagent. This method does not require additional reducing agent or surfactant, and the prepared plasmonic photocatalyst, AgCl/Ag , is efficient for application under visible light. This general protocol may be extended to other hybrid Ag halide/Ag photocatalysts, such as AgI/Ag and AgBr/Ag (Figure 8).

The same protocol has been employed for the green synthesis of noble metal (Ag, Au, Pt, and Pd) nanoparticles in aqueous solution under MW heating using beet juice.⁷² Ag, Au, Pt, and Pd nanoparticles <100 nm supported on carbon microspheres are obtained (Figures 9 and 10); Ag nanoparticles being supported

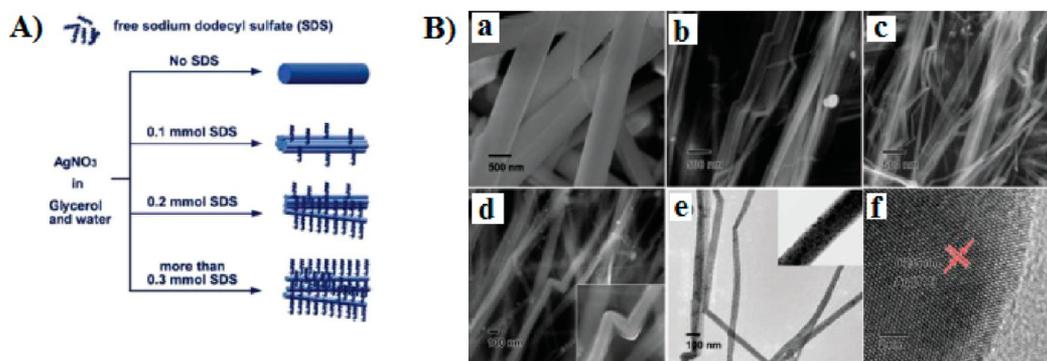


Figure 6. (A) Illustration of the formation process of Ag nanowires in the presence of SDS. (B) (a–d) SEM images of the Ag samples with different SDS amount (other chemicals, 0.3 mmol AgNO_3 , 4 mL of glycerol, and 4 mL of water): (a) no SDS; (b) 0.1 mmol SDS; (c) 0.2 mmol SDS; (d) 0.3 mmol SDS. (e) TEM and (f) HRTEM images of typical Ag nanowires. Reprinted with permission from ref 69. Copyright 2013 the Royal Society of Chemistry.

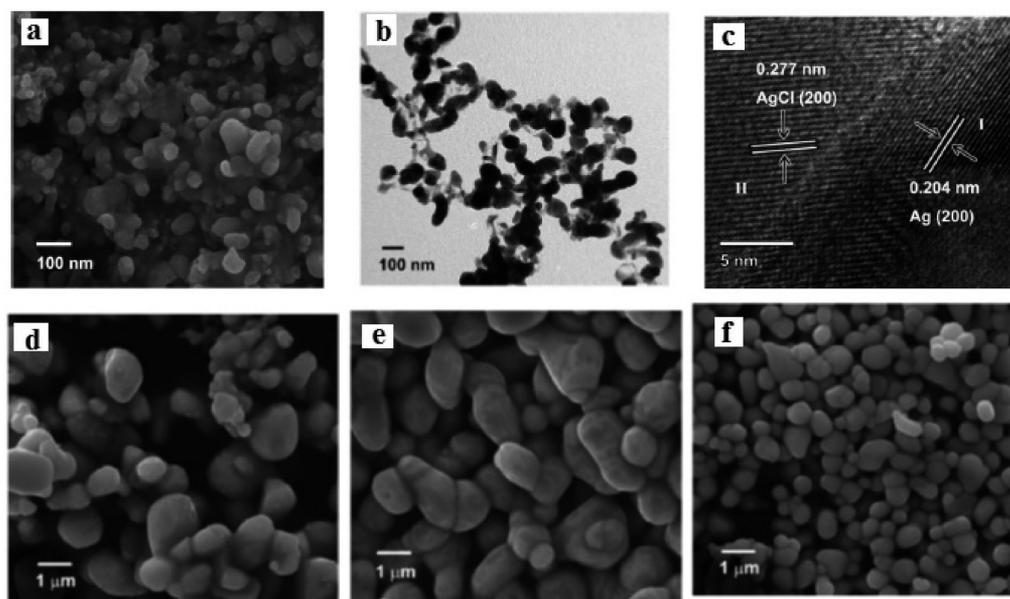


Figure 8. Images of AgCl/Ag NPs prepared with beet juice: (a) SEM image, (b) TEM image, and (c) HRTEM image. SEM images of (d) sample obtained after MW irradiation with glucose, (e) sample obtained after MW irradiation without any reducing reagent, and (e) AgCl obtained before MW irradiation. Reprinted with permission from ref 71. Copyright 2012 WILEY-VCH Verlag GmbH & Co. KGaA.

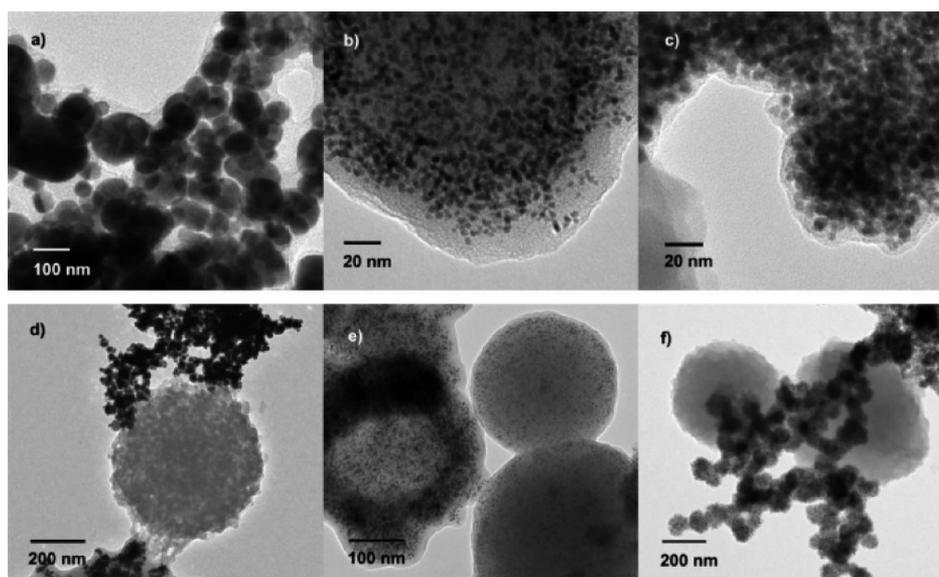


Figure 9. TEM images of typical Au, Pt, and Pd samples: (a) Au with capping; (b) Pt with capping; (c) Pd with capping; (d) Au with organic microspheres; (e) Pt with organic microspheres; (f) Pd with organic microspheres. Reprinted with permission from ref 72. Copyright 2012 the Royal Society of Chemistry.

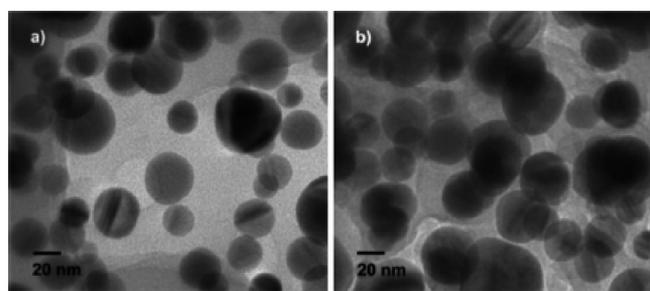


Figure 10. TEM images of Ag nanoparticles at different times: (a) 10 min; (b) 60 min. Reprinted with permission from ref 72. Copyright 2012 the Royal Society of Chemistry.

on carbon microspheres exhibited higher catalytic activity and durability than those prepared with NaBH_4 for the reduction of 4-nitrophenol to 4-aminophenol.

4.5. Synthesis of Noble Nanoparticles in Aqueous Medium

The size of the NPs has often been controlled by adjusting the molar ratio of the reactants. A very effective MW heating technique is established to synthesize shape controlled gold nanoparticles in the presence of 2,7-dihydroxy naphthalene (2,7-DHN) as a reducing agent.⁷³ The growth of the nanoparticles with different shapes, such as spheres, polygons, rods, and triangular/prisms, is achieved by varying the surfactant to metal ion molar ratios and the concentration of 2,7-DHN (Figure 11).

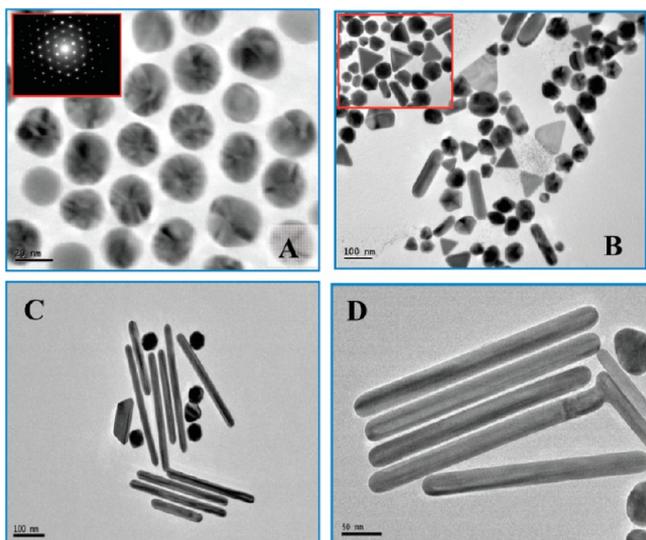


Figure 11. TEM image of different shaped Au NPs after 90 s of MW exposure: (A) image of spherical Au NPs; (B) low magnification images of mixed shaped gold NPs; (C, D) images of Au nanorods at different magnification. The insets of panels A and B show the corresponding electron diffraction of the particles and a higher magnified image. Reprinted with permission from ref 73. Copyright 2008 American Chemical Society.

5. CONCLUSION AND FUTURE ASPECTS

MW heating methods applicable under a variety of formats can address the problems of heating inhomogeneity found in conventional thermal techniques. 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.

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.

It appears that the capability to superheat the reaction raw materials above boiling points, in an operationally friendly and

safe manner with superb online and quick control over reaction temperature and pressure, is indicative of the fact that MW reactors are not to be easily replaced by other technologies in the coming years. This fascinating technique could be equally useful for the synthesis of unique core/shell, yolk/shell, single atom, or integrated-type nanomaterials.

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.

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Notes

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Prof. Rajender S. Varma was born in India (Ph.D., Delhi University 1976). After postdoctoral research at Robert Robinson Laboratories, Liverpool, U.K., he was faculty member at Baylor College of Medicine and Sam Houston State University prior to joining the Sustainable Technology Division at the US Environmental Protection Agency in 1999. He has over 40 years of research experience in management of multidisciplinary technical programs ranging from natural products chemistry to development of more environmentally friendly synthetic methods using microwaves, ultrasound, etc. Lately, he is focused on greener approaches to assembly of nanomaterials and sustainable applications of magnetically retrievable nanocatalysts in benign media. He is a member of the editorial advisory board of several international journals, has published over 380 scientific papers, and has been awarded 12 US Patents.

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