

# **MICROWAVE ASSISTED SYNTHESIS METALLIC NANOSTRUCTURES**

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# A GREEN CHEMISTRY APPROACH

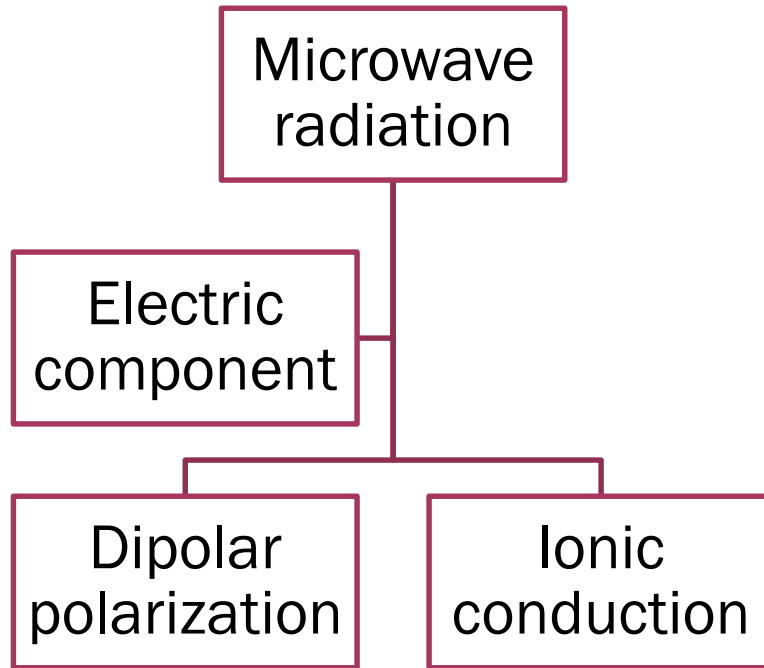
Green chemistry is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products.

A variety of metallic nanostructures, including spherical particles, sheets, plates, rods, wires, tubes, and dendrites can be achieved by microwave irradiation.

Out of the 12 principles of green chemistry, the following are taken care through MW synthesis

- ❖ Prevention of waste
- ❖ Less hazardous chemical synthesis
- ❖ Design for energy efficiency
- ❖ Inherently safer chemistry for accident prevention

# MICROWAVE IRRADIATION(0.3-300 GHZ)



# POSSIBLE EFFECTS OF MW HEATING

There are two kinds of effects of MW dielectric heating: thermal and non-thermal

## Thermal effects

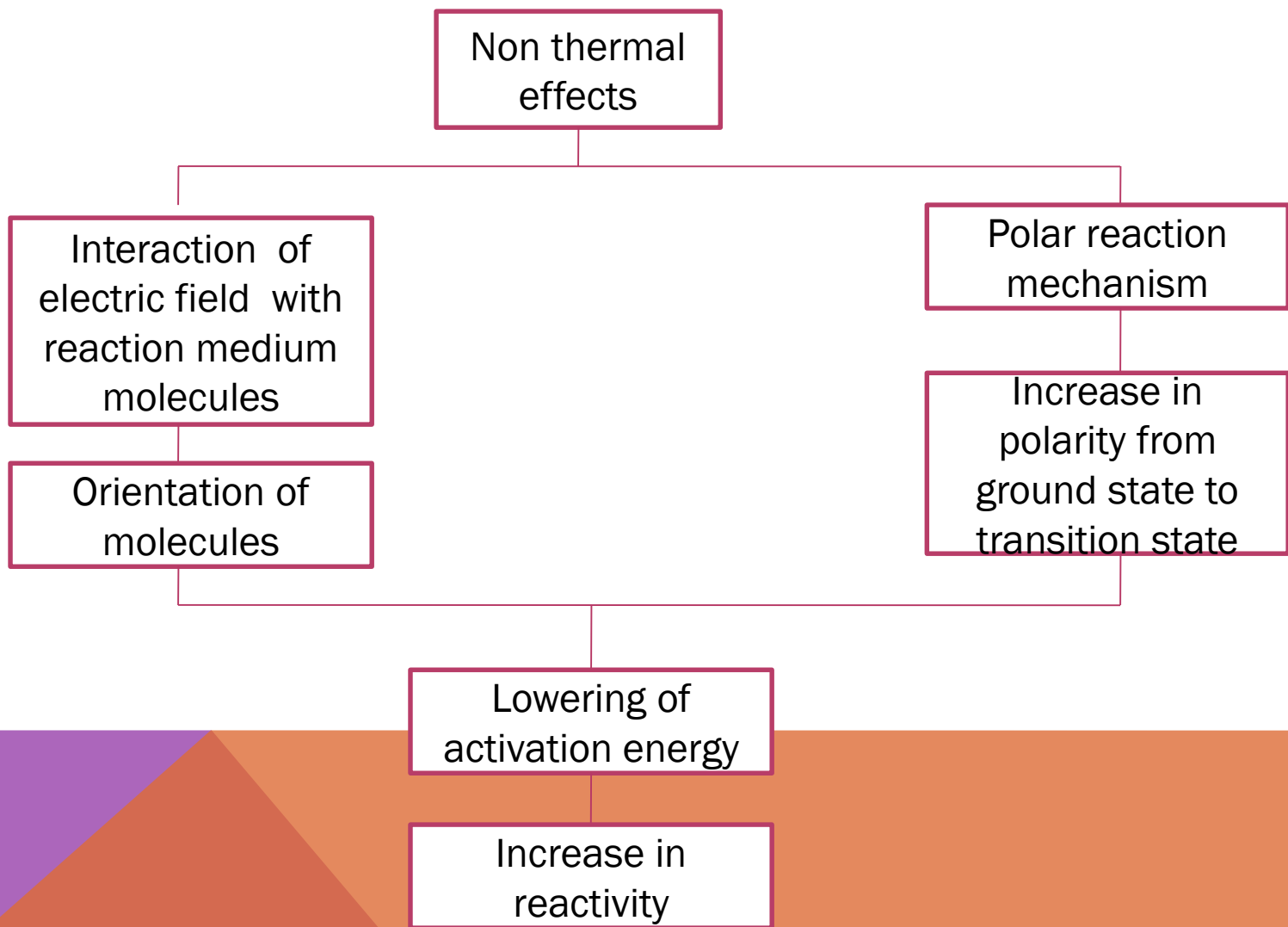
$$k = A \cdot e$$

Loss tangent factor

Superheating effects of solvents at atmospheric pressure

Selective heating of microwave absorbing reagents and catalysts

Elimination of wall effects



## PREPARATION OF AU SPHERICAL NANOPARTICLES:

- ❖ Au nanoparticles have been synthesized by reduction of Au salts in various solvents under oil-bath heating for many hours. When  $\text{HAuCl}_4$  was reduced in methanol or ethanol, [for 0.5-5 min in the presence of PVP under MW heating (480- 1100 W), mono dispersed, small spherical nanoparticles, with diameters below 11 nm, were synthesized within a few minutes.
- ❖ Spherical Au particles by using a closed chamber of an MW system with precise temperature control function.
- ❖ When  $\text{HAuCl}_4$  was reduced in an aqueous solution containing citrate as a stabilizer for 15- 30 min, Au particles sizes could be reduced from 85 to 13 nm with increasing reaction temperature, heating time, and rate of temperature increase.

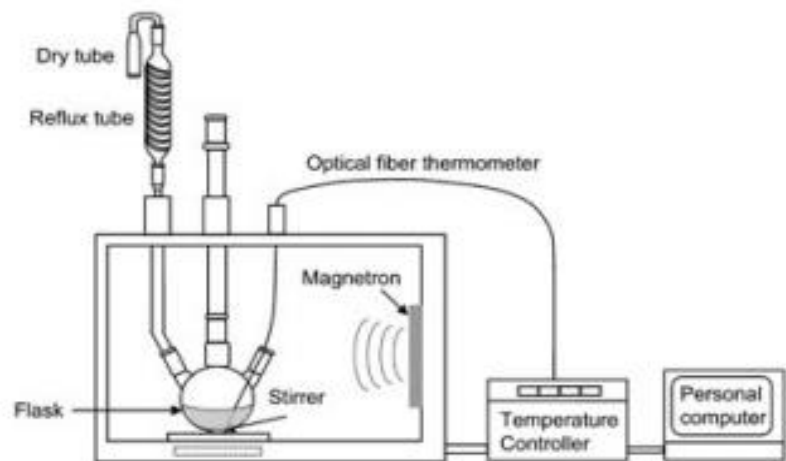
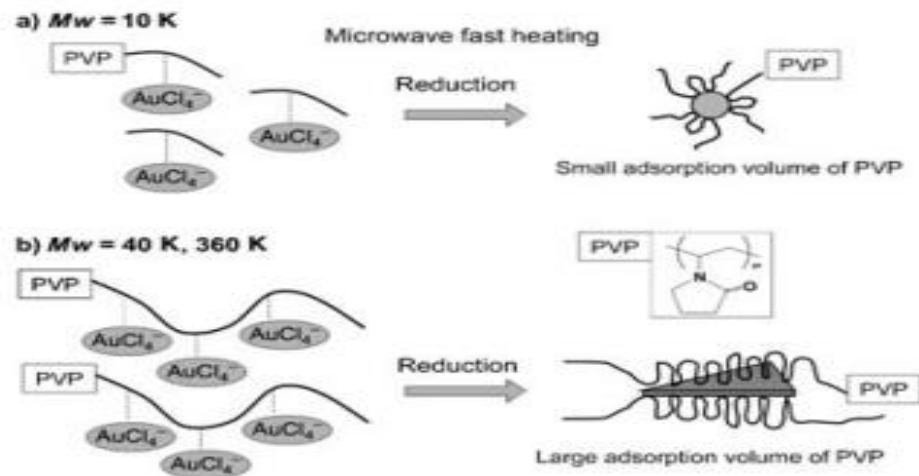
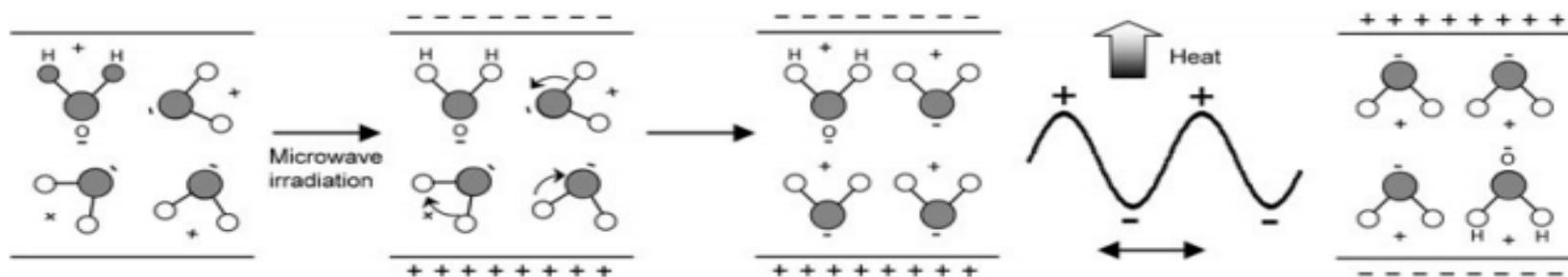


Figure 1. Apparatus used for the microwave-assisted synthesis of metallic nanostructures.



Scheme 2. Formation scheme of Au nanostructures by using PVP with different chain lengths.

- ❖ A commercial MW oven is modified by installing a condenser and thermocouple through holes in the top and a magnetic stirrer plate coated with Teflon in the bottom of the oven.
- ❖ A thermocouple made of an optical fiber, which is not damaged under MW irradiation, is used.
- ❖ A glass flask is placed in the MW oven with a power of 300– 1100 W and connected to a condenser, into which a mixture of metallic salt, surfactant, and, if necessary, a small amount of nucleation reagent is added.
- ❖ A surfactant such as polyvinyl pyrrolidone (PVP) acts as a stabilizer for the product nanostructures. The reagent solution is irradiated by MW in a continuous wave (CW) mode or a pulse mode.
- ❖ The pulse mode is more useful for the temperature control of the heating media. Products particles are generally characterized by using transmission electron microscopy (TEM), scanning electron microscopy (SEM), selected area electron diffraction (SAED) pattern, X-ray diffraction (XRD), and UV visible absorption spectroscopy.
- ❖ Before measuring the TEM photographs, surfactants were often separated from nanostructures by centrifugation.



Scheme 1. Heating mechanism of H<sub>2</sub>O by microwave irradiation.

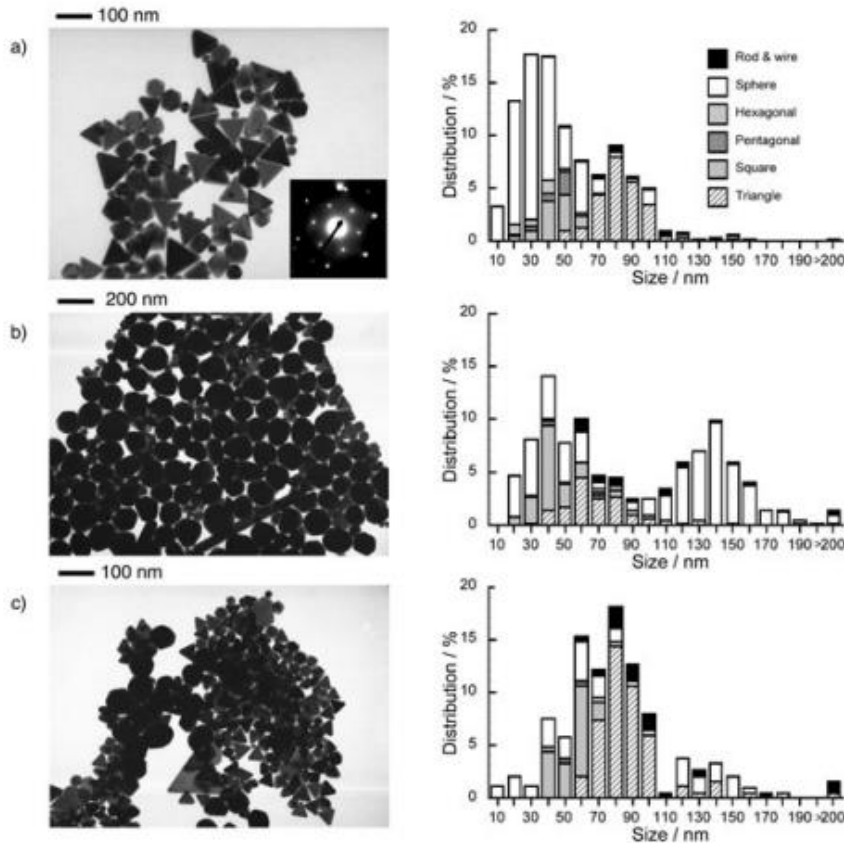


Figure 3. TEM photographs of Au nanostructures obtained by a) CW MW heating for 2 min, b) oil-bath heating for 19 min, and c) pulse MW heating for 19 min, and histograms of product distributions for experiment. Concentrations of  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$  and PVP (40K) were 2.4 mM and 0.25 M, respectively.

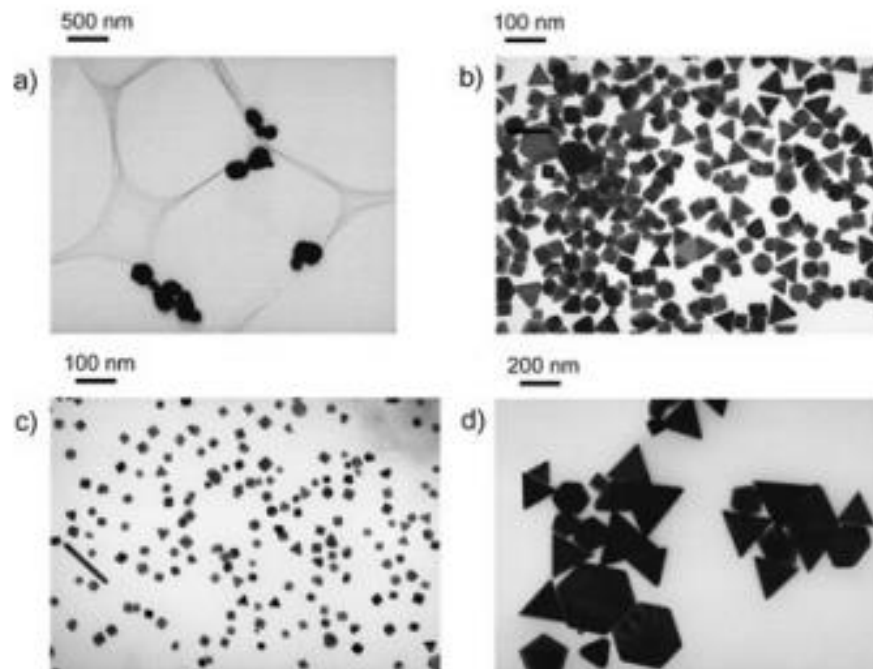


Figure 4. TEM photographs of Au nanostructures obtained by CW MW heating a) for 2 min from  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}/\text{EG}$ , b)–d) for 2 min from  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}/\text{PVP}(40\text{K})/\text{EG}$ . Concentrations of  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$  and PVP were a) 2.4 mM and 0 M, b) 1.2 mM and 0.5 M, c) 2.4 mM and 3 M, and d) 19.2 mM and 2 M, respectively.



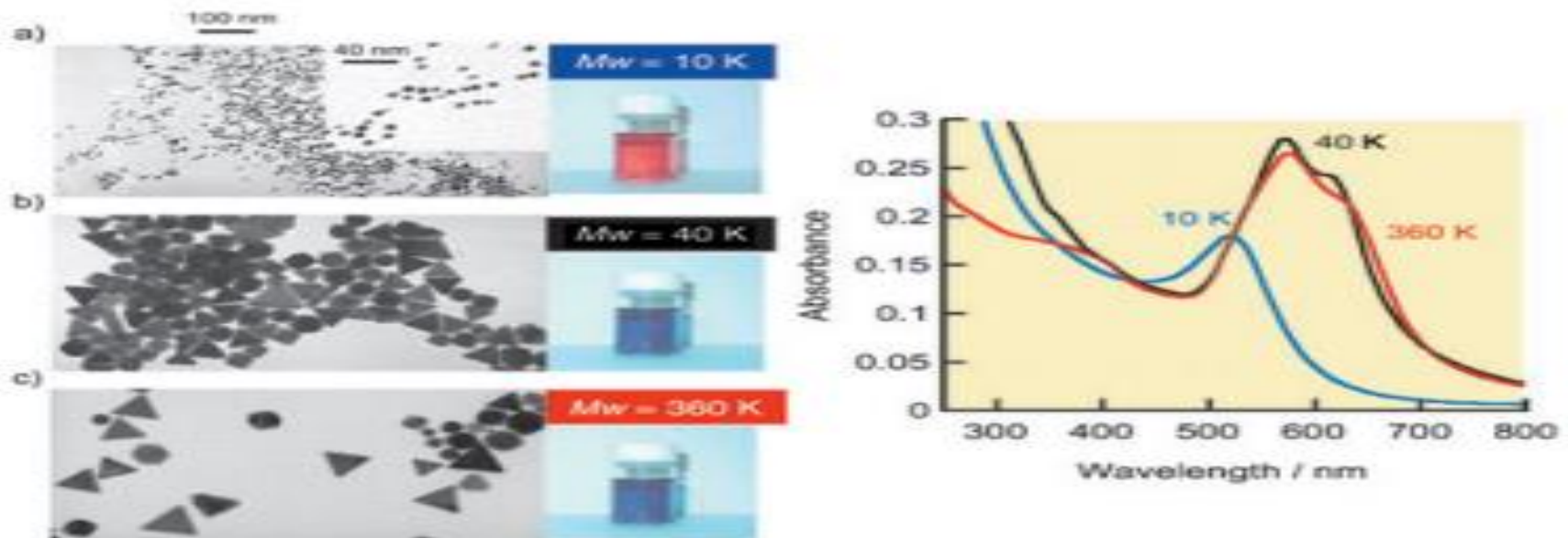


Figure 5. TEM photographs of Au nanostructures, color, and UV-visible spectra obtained from  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ /PVP/EG by CW MW heating for 2 min with PVP molecular weights of a) 10K, b) 40K, and c) 360K. Concentrations of  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$  and PVP were the same as those in Figure 3.

# ADVANTAGES

- ❖ faster reactions
- ❖ less byproducts
- ❖ pure compounds
- ❖ absolute control over reaction parameters
- ❖ selective heating / activation of catalysts
- ❖ low energy input (max=300w, typical reaction ~20w)
- ❖ green solvents (H<sub>2</sub>O, EtOH, acetone) used
- ❖ less solvent usage ( 0.5-5mL per reaction)
- ❖ software-supported experiment documentation

# APPLICATIONS

- ❖ Heck reaction
- ❖ Suzuki reaction
- ❖ Negishi and Kumada reaction
- ❖ Multicomponent reactions
- ❖ Solid phase synthesis
- ❖ Reactions in the absence of solvents

# CONCLUSION

- ❖ Uniform heating of the solution
- ❖ Homogeneous nucleation
- ❖ Shorter crystallization time
- ❖ Short thermal induction period, which can lead to energy savings
- ❖ Selective formation of specific morphology
- ❖ Absence of convection processes, easy control, and low cost.

## DISADVANTAGE:

- ❖ MW heating is a promising heating method, a further wide application to preparation and control of various kinds of metallic nanostructures, which are key materials in nanotechnology, is expected.
- ❖ Unfortunately, detailed mechanism for the preparation of metallic nanostructures under MW irradiation has not been clarified.

# REFERENCE:

❖ **Microwave-Assisted Synthesis of Metallic Nanostructures in Solution**

Masaharu Tsuji,\*[a] Masayuki Hashimoto,[b] Yuki Nishizawa,[b]  
Masatoshi Kubokawa,[b] and Takeshi Tsuji

❖ **Solid State Ionics**

F. Fievet, J. P. Lagier, B. Blin, B. Beaudoin, M. Fiflarz