

# Influence of Microwave Radiation on the Growth of Gold Nanoparticles and Microporous Zincophosphates in a Reverse Micellar System

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The water core of reverse micelles has been extensively used as the site for synthesis of a variety of materials. However, water-in-oil reverse micelles have a limited range of temperatures over which they are stable as a single phase. Directing heat to the water cores, the usual site of synthesis without heating the bulk provides added opportunities for synthesis. Microwave radiation is a method for superheating the water cores. In this study, we use an H<sub>2</sub>O–sodium bis(2-ethylhexyl) sulfosuccinate (AOT)–heptane reverse micelle system for the synthesis of Au particles by hydrazine reduction of HAuCl<sub>4</sub> in the presence and absence of microwave radiation. The duration of the microwave radiation was limited to a 2-min duration at a power of 300 W, thereby ensuring that the reverse micelle phase is maintained during the synthesis. At all hydrazine concentrations studied (0.5–2 M), the presence of microwave radiation led to an increase in the particle size of Au. The second system examined was the growth of microporous zincophosphate-X (ZnPO-X, an analogue of the faujasite structure) synthesized from H<sub>2</sub>O–dioctyldimethylammonium chloride (DODMAC)–heptane reverse micelle system. Microwave radiation was applied for 1 min at 150 W at various stages of the nucleation and growth process, and did not disrupt the reverse micelle system. Product analysis after 48 h of reaction showed that the 1-min microwave pulse, if applied during the nucleation stage (the first 4 h), promoted the formation of NaZnPO<sub>4</sub>·H<sub>2</sub>O over ZnPO-X. The effect of the microwave pulse at the growth stage was to promote the formation of ZnPO-X. Absorption of the microwave radiation by the water core and surrounding polar surfactant molecules leads to a rapid rise in local temperature (predicted to be ~150 °C/min for the AOT system), increasing the rates of intramicellar reactions.

## Introduction

Reverse micelles provide a novel medium for the synthesis of a variety of particles, including metals, semiconductors, and ceramics.<sup>1–3</sup> By controlling the ratio of the amount of water to surfactant, the nature of surfactant, the cosurfactant, and the hydrocarbon, the size and shape of the micelle can be altered and can influence the morphology of the final product. Synthesis of gold nanoparticles using reverse micelles has been extensively studied. Chiang reported the influence of metal salt concentration, molar ratios of reductant to metal salt, sequence of addition, and size of micelle droplet on the size, shape, and dispersity of gold nanoparticles.<sup>4,5</sup> Arcoleo and Liveri reported that gold particle size was highly dependent on the water-loading levels of the microemulsions.<sup>6</sup> Agglomeration of gold particles was reported when sizes exceeded 8 nm.<sup>7</sup>

The thermal stability of the reverse micelles determines the temperature range over which reactions can be conducted. Growth of microporous materials in reverse micelles at high temperatures has been reported, but the integrity of the microemulsion was not maintained. Dutta and Robins grew zeolite A starting with their precursors entrapped in reverse micelles.<sup>8</sup> Microemulsions and pseudophase reverse micelles have been employed in the

growth of zeolite A,<sup>9</sup> silicalite-1,<sup>10</sup> silica,<sup>11</sup> and microporous aluminophosphates.<sup>12</sup> Ensuring the integrity of the reverse micelle system during the growth of microporous materials was possible with zincophosphates because the synthesis was accomplished under ambient conditions.<sup>13–16</sup> Using a dioctyldimethylammonium chloride (DODMAC)-based reverse micelle and a tetramethylammonium ion as a template, Castagnola and Dutta reported the synthesis of ZnPO-X.<sup>13,14</sup> An optimized system for the growth of ZnPO-X in DODMAC/isooctane reverse micelles employing 1,4-diazobicyclo[2.2.2]octane (DABCO) as a template was reported by Singh et al.<sup>15,16</sup>

Providing thermal energy to promote reactions within the reverse micelles without destroying the microemulsion should allow new opportunities for synthesis. Organic solvents such as hexane, heptane and octane (nonpolar) do not heat readily when exposed to microwave radiation. Therefore, for a water-in-oil reverse micelle exposed to microwave radiation, the polar parts will preferentially absorb the radiation and provide the opportunity for selective heating of the water cores.

There have been several recent reports on the use of microwave radiation for materials synthesis using microemulsion media.

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For synthesis of gold nanoparticles in water/oil microemulsions, the use of microwave radiation made it possible to use alcohol as a reductant.<sup>17</sup> The use of citrate as a reducing agent for  $\text{HAuCl}_4$  has also been reported.<sup>18</sup> In these studies, it is unclear if the integrity of the microemulsion upon microwave dielectric heating was maintained. The synthesis of  $\sim 5$  nm  $\text{TiO}_2$  particles in a polystyrene-*block*-poly(ethylene oxide) diblock copolymer-based reverse micelle system was made possible by microwave treatment for 5 min, without any reported increase in the overall temperature of the reaction medium.<sup>19</sup> Microwave radiation at five different frequencies (2.45–18 GHz) was used to examine the synthesis of CdS using water/sodium bis(2-ethylhexyl) sulfosuccinate (AOT)/*n*-heptane reverse micelles.<sup>20</sup> Temperatures were maintained at 30 °C by water cooling, and thus it is certain that the micelle structure was maintained. With 12 GHz radiation, the CdS particle sizes were  $\sim 20\%$  larger compared to a nonmicrowaved sample. Irradiation at other frequencies showed a decrease in size.

Microwave heating has been used in the synthesis of microporous materials in water-in-oil microemulsions. For  $\text{AlPO}_4\text{-5}$  synthesis, the temperature was 180 °C, so the emulsion integrity was not maintained, yet the morphology of the crystals was different compared to those of traditional hydrothermal synthesis.<sup>21</sup> Zeolite A nanocrystals of 40–80 nm have been synthesized from a cetyltrimethylammonium bromide, *n*-butanol-cyclohexane-based reverse micelle using microwave radiation.<sup>22</sup> The temperature of the reaction system was as high as 75 °C, and it is unclear whether the microemulsion was stable, although the results clearly demonstrate that the microwave irradiation of the mixed phases had a profound effect on the size and morphology of the zeolite. Microwave radiation has also been proposed as an effective method for deemulsification.<sup>23</sup>

In this study, we explore how the influence of microwave radiation alters the synthesis process in reverse micelles using gold growth in an AOT system and microporous zincophosphate (faujasite structure) in a DODMAC system as examples, the latter system being very susceptible to thermal effects. Caution was taken to maintain the bulk temperature of the entire system so that no phase separation was observed. On the basis of comparisons of microwaved versus nonmicrowaved synthesis, a model for the effect of microwave radiation on the water pools of the reverse micelle is proposed.

## Experimental Section

**Synthesis of Gold Nanoparticles.** AOT (98%, Aldrich), *n*-heptane (Mallinckrodt),  $\text{HAuCl}_4\cdot 3\text{H}_2\text{O}$  (hydrogen tetrachloroaurate (III), 99.99%, 49.5% Au, Alfa Aesar),  $\text{N}_2\text{H}_4\cdot \text{H}_2\text{O}$  (hydrazine hydrate, Aldrich), nanopure water (resistivity, 18.0 ohms), and *n*-hexadecanethiol (98%, Lancaster) were all utilized as received.

The surfactant solution of 0.1 M AOT in heptane was prepared by dissolving 11.113 g of AOT in 250 mL heptane. A 0.5 M solution of  $\text{HAuCl}_4$  was prepared. Solutions of hydrazine hydrate were prepared with the following concentrations: 2 M, 1 M, and 0.5 M. A 0.065 mL aliquot of each of the  $\text{HAuCl}_4\cdot 3\text{H}_2\text{O}$  and hydrazine hydrate solutions was added to separate 6-mL portions of the AOT/heptane solution. The solutions were then shaken and sonicated for

about 30 s. For nonmicrowaved experiments, the two reverse micelle solutions were mixed and allowed to react, typically for 4 min. After completion of the reaction, 10 drops of hexadecanethiol were added to cap the gold particles. An experiment in which growth continued for 15 min was also performed.

For microwave experiments, the  $\text{HAuCl}_4$  containing reverse micelle solution was put into a microwave vessel and sealed off, except for a small ventilation hole. The hydrazine hydrate micelle solution was injected into the vessel through the ventilation hole. The vessel was closed, and microwaving was started within 19 s of mixing. The microwave was operated at 300 W, typically for 2 min. After a total reaction time of 4 min, the sample was removed from the vessel, and 10 drops of hexadecanethiol was added. The microwave used was CEM Corporation's MARS 5 model. The resulting temperature was recorded to ensure that the heating was consistent from sample to sample. For 2 min of microwaving, the final temperatures were all in the range of 37–39 °C. The pressure did not increase enough (did not reach 1 psi) to register on the meter over the 2 min of microwaving. Experiments were also done with varying microwave times.

**Synthesis of Zincophosphate-X (ZnPO-X).** Bardac LF-80, a surfactant that is 80% DODMAC, was obtained from Lonza, Inc. (Fair Lawn, NJ). It was concentrated by evaporation at a reduced pressure and then dried under vacuum at an elevated temperature. Zinc nitrate hexahydrate (Aldrich, 98%), 1-decanol (Alfa Aesar, typically 99%), sodium hydroxide pellets (Baker Analyzed), phosphoric acid (Mallinckrodt, N.F. Food Grade, 85%) and isooctane (Fisher, HPLC grade) were used as received. The purification of DABCO (Aldrich, 98%) was carried out by recrystallization in hexane. A previously reported procedure for preparing the reverse micellar solutions was followed.<sup>15</sup> The surfactant solution was 0.33 M 1-decanol and 0.19 M DODMAC in isooctane. Two reverse micelle solutions were prepared and then mixed to initiate the reaction. One solution contained sodium hydroxide, the template DABCO, and phosphoric acid, while the second solution contained the zinc nitrate hexahydrate. The preparation of reverse micelle solutions was done by injecting 0.2 mL of the aqueous reactant species for every 10 mL of the surfactant solution and then shaking until the solution was clear. The  $[\text{H}_2\text{O}]/[\text{DODMAC}]$  ratio was approximately 6. A microwave power of 150 W and a microwave duration of 1 min was used at various times during the crystallization. This combination allowed for the perturbation of the system, but also kept the bulk solution temperature under 45 °C.

**Instrumental Methods.** A Philips Tecnai TF20 transmission electron microscope (TEM) at a power of 200 kV was used to acquire images. Scanning electron microscopy (SEM) data was recorded on a JSM-5500 scanning electron microscope. A Shimadzu UV-2501PC spectrometer was used for UV–vis measurements. Dynamic light scattering (DLS) was used to monitor the growth versus time of a nonmicrowaved sample grown over 22 h. A Brookhaven Instruments 9000 digital correlator with a detector positioned 90° from the incident laser was employed. The Coherent Innova 90c argon ion laser was operated at 200 mW at a wavelength of 514.5 nm. The cumulant analysis algorithm was used to calculate particle size.

Capillary X-ray diffraction was used to determine crystal structure and to determine the peak intensity ratios between  $\text{ZnPO-X}$  and  $\text{NaZnPO}_4\cdot \text{H}_2\text{O}$  (P6). Several peaks were compared, including the 6(2 $\theta$ ), 26.3(2 $\theta$ ), and 31.6(2 $\theta$ ) peaks associated with  $\text{ZnPO-X}$  and the 11.4(2 $\theta$ ), 26.7(2 $\theta$ ), and 31.9(2 $\theta$ ) peaks of P6. The X-ray diffractometer used was a Bruker D8 Advance equipped with a copper anode X-ray tube. A capillary unit was installed that allowed for the analysis of minute samples, and the tube output was filtered with a Ge monochromator to produce pure  $\text{K}\alpha_1$  radiation. A Braun position sensitive detector (PSD) was utilized. All capillary X-ray diffraction (XRD) work was baseline corrected using Galactic's Grams Spectral Notebook 7.0, employing a multipoint correction to correct for a drift in baseline starting at 4° 2 $\theta$  and extending to about 11° 2 $\theta$ . For this reason, the peaks located at 26.3 and 26.7° 2 $\theta$  were used for the quantitative comparisons.

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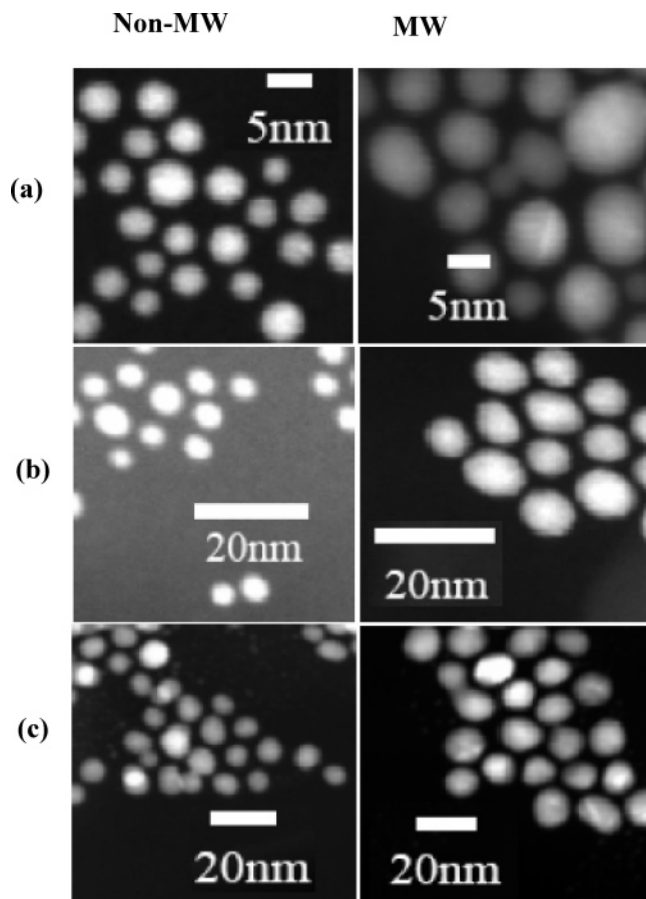
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**Figure 1.** TEM images of Au particles obtained with and without microwaving using different amounts of hydrazine in an AOT reverse micelle system. Hydrazine concentrations: (a) 2 M, (b) 1 M, (c) 0.5 M (MW = microwaved).

## Results

### Effect of Microwave Radiation on Gold Particle Synthesis.

After a solution of AOT/heptane was microwaved (without water) for 2 min at 300 W, the temperature rise of the solution was  $\sim 2$  °C. With water (water-to-solvent ratio of  $\sim 1:100$ ) in the micelle cores, the change in bulk solution temperature for comparable treatment was between 10 and 14 °C. Therefore, the presence of the water cores contributes to a 4–6 °C/min rise in temperature in the bulk solution. This increase in bulk temperature did not lead to phase separation,<sup>24</sup> and was the basis for choice of the 300 W of microwave power (2.45 GHz) for the 2-min time interval.

The procedure for the synthesis of the Au particles involved mixing two reverse micelles solutions containing varying concentrations of hydrazine (0.5–2 M) and  $\text{HAuCl}_4$  (0.5 M). The characteristics of the reaction system were  $[\text{AOT}] = 0.1$  M and water/AOT = 6 ( $R_o$ ). Microwaving at 300 W for 2 min was started within 19 s of mixing. The nonmicrowaved samples are labeled as nMW $m$ , where  $m$  represents the concentration of hydrazine used to reduce the gold source, and all reactions (both microwave and nonmicrowave) were carried out for a total of 4 min, at which point hexadecanethiol was added to cap off the gold particles. The TEM images for the nMW2, nMW1, and nMW0.5 samples are shown in Figure 1 and compared to the microwaved samples MW2, MW1, and MW0.5. The gold particles appear spherical, and the size distributions of the Au

particles prepared with various hydrazine concentrations are presented in Figure 2 and reported in Table 1. These data show that microwaving increases the particle size, ranging from 33 to 58%; for example, for  $[\text{hydrazine}] = 0.5$  M, the size increased from 7.9 to 10.6 nm upon microwaving.

A plot of the average size of the Au particles for two nonmicrowaved systems ( $[\text{hydrazine}] = 1$  M) that were halted after 4 and 15 min of growth is shown in Figure 3. The size of the Au particles grows with time, along with a broadening of the size distribution. After 4 min, the particle size is approximately  $4.8 \pm 0.85$  nm, and at 15 min, it is  $8.1 \pm 2.6$  nm. The experiment was repeated with microwaving. The sizes of the Au particles recovered after microwaving for 2, 4, 6, and 15 min are also shown in Figure 3, with the bulk temperature in the variable microwaving time experiments reaching 37, 47, 56, and 81 °C, respectively (for the last sample, phase separation was observed). The particle size for the Au was  $10 \pm 1.9$  nm, regardless of the length of the microwaving period.

The electronic spectra of the particles recovered from the 2 M hydrazine treatment shows a red shift from 536.5 to 547.2 nm upon microwaving (data not shown). The position and intensity of the plasmon band is known to be sensitive to particle size and correlates well with the growth in size of the gold nanoparticles.<sup>25</sup>

**Effect of a Microwave on the ZnPO-X Reverse Micelle System.** Figure 4a shows the particle sizes during the growth of ZnPO-X in a nonmicrowaved reverse micelle system over a 22 h time period. For the first 4 h, little to no growth occurs. After growth begins, it continues for the next 4–5 h, followed by declining particle size, as larger particles settle out of the system. The size of the entities remaining after growth is completed is an order of magnitude larger (68 nm) than in the nucleation stage (6.7 nm). From 12 to 22 h, the system is fairly stable, and the reaction is considered to be complete. The mother liquor from the system after 22 h remains stable, with no precipitation for at least 2 months. Products isolated after the reaction are pure ZnPO-X, as indicated by capillary XRD<sup>26</sup> (not shown) and SEM (Figure 5a).

Microwave radiation was introduced briefly for 1 min at the times shown in Table 2, at various stages during the growth of ZnPO-X, including nucleation, growth, and after crystal growth is complete (Figure 4). Reverse micelles were stable after microwave treatment, and no phase separation was observed. The average temperature increase of the bulk solution was 22 °C by the end of the 1-min microwave pulse to a final temperature of 45 °C. The water-loading level in these experiments corresponds to  $R_o = 6$ , where  $R_o = [\text{H}_2\text{O}]/[\text{DODMAC}]$ . This is similar to the water-loading level for the gold growth, but the overall concentration of DODMAC is almost twice the concentration of AOT in the gold growth study. Therefore, the amount of water used is nearly double the amount of water used in the gold synthesis, and the increased surfactant and water content is proposed as the reason for the larger increase in solution temperature upon microwaving for the zincophosphate growth.

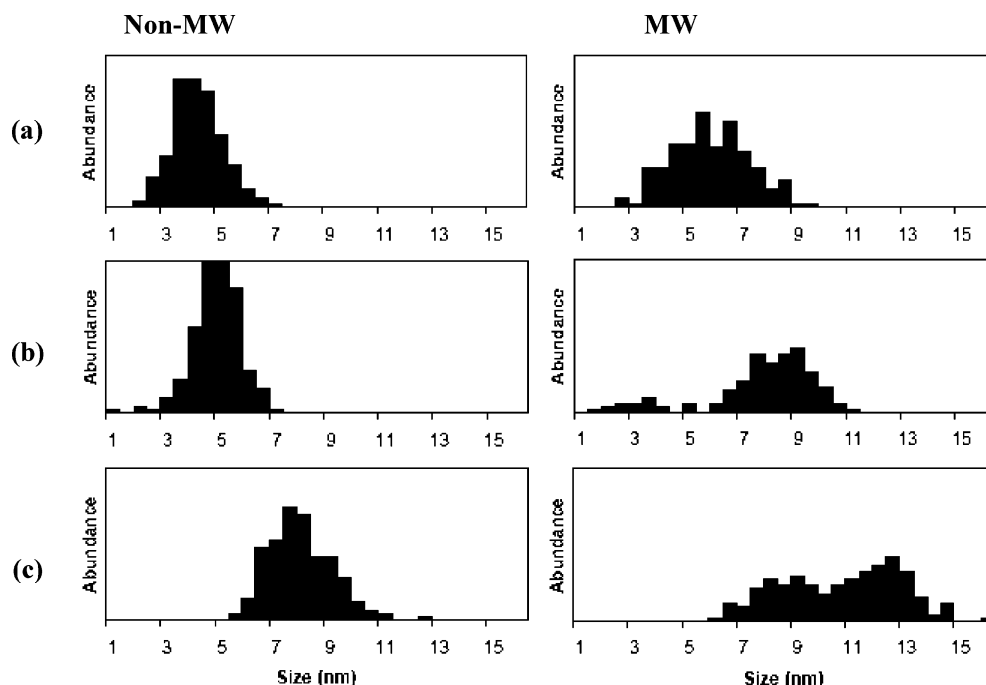
The products of the reactions (microwave pulse at different times, Table 2) were isolated after 48 h of total reaction time, washed, dried, and sealed in a glass capillary tube. The powder diffraction pattern and electron microscopy of all 14 samples were obtained, and the major products identified from the patterns were ZnPO-X (an analogue of zeolite X)<sup>26</sup> and P6 (a hexagonal form).<sup>27,28</sup> A scanning electron micrograph of the material

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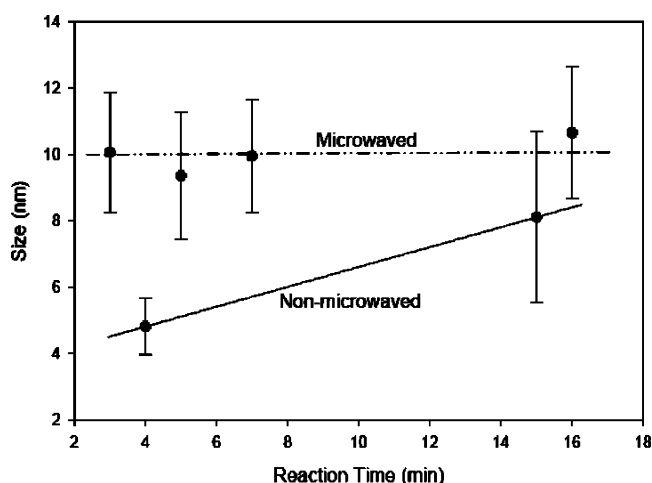


**Figure 2.** Particle size distributions of Au particles (determined from TEM micrographs) recovered from microwaved and nonmicrowaved reverse micelle samples (AOT) using different amounts of hydrazine: (a) 2 M, (b) 1 M, (c) 0.5 M (MW = microwaved).

**Table 1. Summary of the Particle Size Distributions Determined from the Transmission Electron Micrographs**

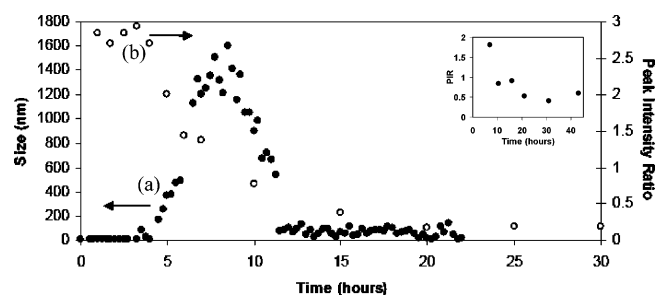
sample <sup>a</sup>	avg size (nm)	median size (nm)	$\Delta$ average (% increase)
nMW2	4.2	4.1	+1.6 nm
MW2	5.8	5.7	(39%)
nMW1	4.8	4.9	+2.8 nm
MW1	7.6	8.1	(58%)
nMW0.5	7.9	7.9	+2.7 nm
MW0.5	10.6	10.9	(33%)

<sup>a</sup> MW $m$  in the sample name depicts microwaved samples, nMW $m$  is the nonmicrowaved samples, and  $m$  represents the concentration of the hydrazine used to reduce the tetrachloroaurate.



**Figure 3.** Growth curves of Au particles for nonmicrowaved and microwaved reverse micelle (AOT) grown samples as a function of total reaction time. For the microwaved samples, the time in the microwave is 1 min less than the reaction time (lines just connect the points).

obtained with the microwave pulse at 1 h is shown in Figure 5b, and the hexagonal morphology of the crystals due to P6 is evident. Two of the diffraction patterns, obtained from samples with the

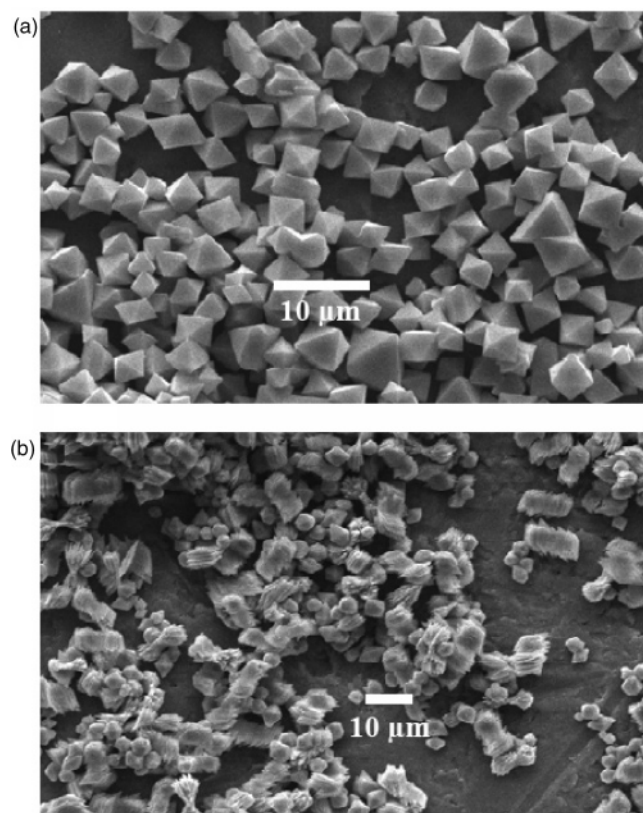


**Figure 4.** (a) Particle size determined by DLS during the growth of ZnPO-X from a DODMAC nonmicrowave reverse micelle system (axis corresponds to the left). (b) Plot of the ratio of XRD peaks of P6 (26.7  $2\theta$ ) to ZnPO-X (26.3  $2\theta$ ) (axis corresponds to the right) obtained from samples that were subjected to 1 min of microwave radiation at the times indicated (all samples recovered after 48 h). Inset: Nonmicrowaved reaction was set up, and the mother liquor was recovered at the times shown. The mother liquor was subjected to 1 min of microwave radiation and the experiment was allowed to continue for 48 h. The plot of the ratio of XRD peaks of P6 (26.7  $2\theta$ ) to ZnPO-X (26.3  $2\theta$ ) for samples that were recovered are shown.

microwave pulse at times 1 and 25 h, are shown in Figure 6, with the peaks of ZnPO-X and P6 marked as X and P, respectively (inset shows a blown up region between 26 and 27  $2\theta$ ). The general observation is that as the microwave pulse is delayed, and the amount of ZnPO-X relative to P6 was increased. To quantify this trend, the ratios of several of the peaks (for ZnPO-X,  $2\theta$  values of 6, 26.3, and 31.6°; for P6,  $2\theta$  values of 11.4, 26.7, and 31.9°) were measured and are reported in Table 2. Figure 4b overlays on the growth curve the ratio of the 26.7 and 26.3°  $2\theta$  peaks. If the 1-min pulse of microwave radiation is introduced during the nucleation phase (first 4 h of Figure 4a), the major product is P6. However, once growth of the ZnPO-X

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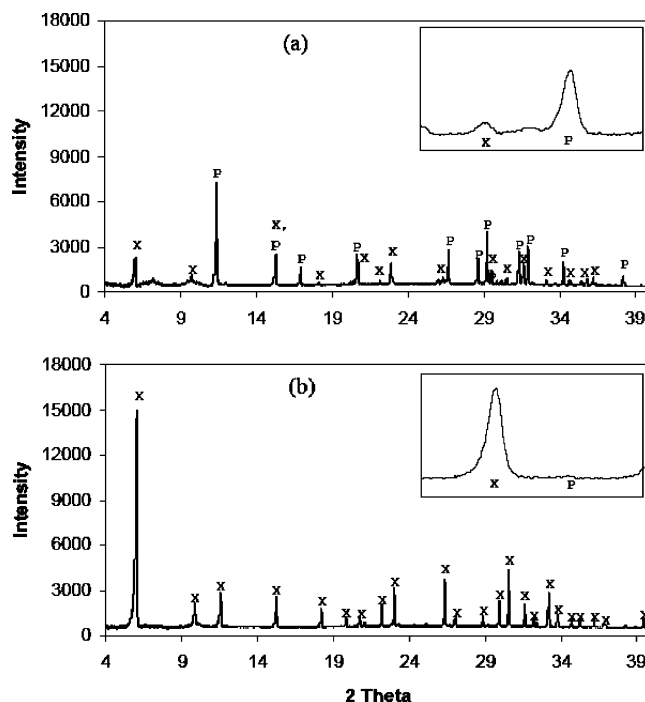
**Figure 5.** SEM micrographs of samples recovered from (a) a nonmicrowave DODMAC reverse micelle solution and (b) a similar solution that was subjected to 1 min of microwave radiation at 1 h. (All samples were recovered after 48 h of reaction).

**Table 2.** Ratios of Three Sets of  $2\theta$  XRD Peaks Corresponding to P6 (11.4, 26.7, 31.9) and ZnPO-X (6.0, 26.3, 31.6) for Samples that Were Subjected to 1 min of 150 W Microwave Radiation at Times Shown on the Table and Then Recovered after 48 Hours of Total Reaction Time

time (hours)	11.4/6.0	26.7/26.3	31.9/31.6
1	3.18	2.84	1.53
1.75	2.49	2.70	1.53
2.5	2.79	2.85	1.48
3.25	3.24	2.94	1.53
4	2.63	2.71	1.54
5	2.07	2.01	1.37
6	0.95	1.43	1.31
7	0.85	1.37	1.21
10	0.43	0.77	0.96
15	0.18	0.38	0.59
20	0.06	0.18	0.31
25	0.07	0.19	0.33
30	0.06	0.19	0.33
42	0.06	0.17	0.30

is initiated after 4 h, the effect of the microwave pulse in the disruption of ZnPO-X growth is gradually minimized. After about 15 h of reaction time, ZnPO-X is the major product, and the microwave pulse at later points does not lead to the formation of P6. Microwave radiation also improves yields: for a typical reaction, a 5-fold increase was observed in yield upon microwaving (2 to 10 mg).

In a separate series of experiments, the mother liquor was removed from a nonmicrowaved reaction at the various times shown in Table 2 by centrifugation and exposed to microwave radiation for 1 min, and the reaction was allowed to continue for 48 h. The products were analyzed by capillary XRD, and the ratio of the  $2\theta$  (26.7/26.3) peaks are shown in the inset of Figure



**Figure 6.** Capillary powder XRD patterns of samples recovered from DODMAC reverse micelle systems that were subjected to 1 min of microwave radiation at (a) 1 h and (b) 25 h. All reactions were continued for 48 h. (X = ZnPO-X, P = P6). Inset: blow up of 26–27  $2\theta$  region.

4. The relative ratio of ZnPO-X versus P6 also increases as a function of reaction time.

## Discussion

The electron microscopy studies of gold particles clearly show that microwaving leads to larger particles compared to those of nonmicrowaved control samples (Figures 1 and 2). The average sizes of particles made with 2, 1, and 0.5 M hydrazine increased from 4.2, 4.8, and 7.9 to 5.8, 7.6, and 10.6 nm, respectively, upon microwaving. For the ZnPO-X system, a short period (1 min) of microwave radiation, although negligible in duration compared to the 48-hour total reaction time, changes the products, and the positioning of the microwave pulse along the synthesis route also plays a role in the final product and their yields.

**A Possible Model.** As two reverse micelle solutions mix, a distribution of concentrations develops in the reverse micelles, being controlled by the solubilize exchange rate between reverse micelles via collisions. Fletcher et al. defined this as an interdroplet transfer of reacting species, controlled by a second-order rate constant of  $10^6$ – $10^8$   $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ .<sup>24</sup> The distribution of reactants within the reverse micelle under steady-state conditions via interdroplet transfer is expected to have a Poisson distribution.<sup>29</sup>

In the present study, the volume of water in the reaction system is small; for example, for the Au synthesis experiments, ~0.26 mL of water is dispersed in 24 mL of heptane. Heptane, with a permanent dipole moment of ~0.2 D should have little absorption in the microwave.<sup>30</sup> The AOT-surrounded water clusters should couple well with the radiation and result in dielectric heating. There are three possible absorption processes of the 2.45 GHz radiation for the AOT reverse micelle system

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that can result in heating.<sup>31</sup> These include diffusion and counterion motion involving the AOT molecules, ionic drift within the aqueous core giving rise to Joule heating, as well as relaxation processes involving bulk water.

Thus, it can be approximated that the observed average 6 °C/min increase in temperature of the bulk heptane solution primarily arises from the microwave radiation absorbed by the AOT and the water core and subsequent heat transfer to the bulk. Using the expression for power absorption,  $P = mC_p\rho(\Delta T/\Delta t)$ , where  $m$  is the mass,  $C_p$  is the heat capacity,  $\rho$  is the density, and  $(\Delta T/\Delta t)$  is the heating rate. From the temperature change of the heptane solution, we can estimate the heating rate of the water cores to be 148 °C/min ( $C_p$  (cal g<sup>-1</sup>deg<sup>-1</sup>) = 1.0 (water), 0.5 (heptane);  $\rho$  (g/cm<sup>3</sup>) = 1.0 (water), 0.73 (heptane)).<sup>32</sup> The heat is transferred from the water core to the hydrocarbon by diffusion.

Fletcher et al. examined the temperature increases of AOT-based reverse micelles with 2.45 GHz microwave radiation at a lower power of 25 W and observed a 2.7 °C/min increase in temperature of the entire solution ([AOT] = 0.298 M, H<sub>2</sub>O/AOT = 15) and a 1.1 °C/min increase for a second reverse micellar solution ([AOT] = 0.239 M, H<sub>2</sub>O/AOT = 25.2). Spectroscopic investigation with *p*-nitroaniline as solute showed no changes in the distribution within the microemulsion (oil versus interfacial pseudophase) upon microwave radiation.<sup>33</sup>

**Implications of the Model for Gold Growth.** The reduction of HAuCl<sub>4</sub> with hydrazine is as follows:



Application of microwave radiation began 19 s after mixing the micelles. Considering that the reduction occurs rapidly, nucleation begins within these 19 s. Increasing the reducing agent concentration in the reverse micelle leads to smaller Au particles, as shown in Figures 1 and 2. With an increasing amount of reducing agent per reverse micelle, faster nucleation is promoted, resulting in larger numbers of nuclei. With microwave radiation, larger particles are formed since there is an enhanced rate of growth due to the heating of the water core, the site of reduction. This is the reason the particle sizes are larger in the microwaved samples, as shown in Figures 1 and 2. At no time in these experiments does the temperature of the bulk solution exceed 40 °C, ensuring that reverse micelle integrity is maintained.

Figure 3 shows that, for the nonmicrowaved system nMW2.0, the gold particle size increases from about  $4.8 \pm 0.85$  to  $8.1 \pm 2.6$  nm when the system is allowed to react for 15 instead of 4 min. The increase in growth suggests that, after nucleation, crystals grow as micelles continue to collide and provide nutrients to the growing crystals. Longer microwave times on the MW2.0 system shown in Figure 3 had no effect on the average particle size. It appears that the reaction is complete within the first two minutes, reaching a size of ~10 nm. Longer microwave times (15 min) led to a rise in bulk temperature to 79 °C and to the destruction of reverse micelles, but since the growth is accelerated and over within 2 min, heating longer and to higher temperatures has no effect on the particle size. These results are consistent with the water core heating model, which provides a higher growth rate of the gold particles.

**Implications of the Model for ZnPO-X Growth.** A typical collision-driven reverse micelle reaction presents a nutrient

exchange environment that allows for nucleation and eventual growth of the ZnPO-X product. In the early stages of the ZnPO-X reverse micelle growth, the application of a 1-min pulse of microwave radiation disrupts the nucleation of ZnPO-X and promotes the formation of a condensed zincophosphate, P6. Rani et al. suggested that the nucleation phase for microporous materials can be separated into two parts: a prenucleation step for formation of primary particles (not nuclei), followed by a period over which those primary particles evolve into nuclei.<sup>34</sup> The microwave radiation applied in the early stages of the reaction could be destroying the ZnPO-X prenuclei structures due to the heat and also promoting the formation of condensed P6. However, once the ZnPO-X nuclei are formed, microwave radiation enhances the growth by providing local heating to speed up the growth. Microwave radiation actually seemed to promote the additional growth of ZnPO-X, as a 2–5-fold increase in yield was noted.

After a reaction is “complete” in a reverse micelle system, there are still reactants encased in the reverse micelles. Singh and Dutta reported that solutions recovered after a reverse micelle synthesis will cause the immediate growth of ZnPO-X to commence if nutrients are provided by adding a fresh supply of reverse micelles.<sup>15</sup> The application of microwave radiation to the mother liquors resulted in the continued growth of the particles/nuclei. Heating of the water core promotes further reaction in the micelle, resulting in yield improvements, an overall effect similar to adding extra nutrients.<sup>15</sup>

Vibrational excitation of the OH stretches of water in the reverse micelle by infrared lasers has also been proposed as a method to heat the water core without disrupting the reverse micelles.<sup>35</sup>

## Conclusions

The synthesis of gold nanoparticles and microporous ZnPO-X in reverse micelles was studied with microwave radiation, paying particular attention to the fact that the bulk temperature of the solution did not exceed 40–45 °C. The gold particles were formed from an H<sub>2</sub>O–AOT–heptane reverse micelle system by hydrazine reduction of HAuCl<sub>4</sub>. At 300 W of microwave radiation and a 2-min duration, the reverse micelle phase was stable. For all hydrazine concentrations studied (0.5–2 M), the presence of microwave radiation led to an increase in the particle size of Au by 33–58%. In a nonmicrowaved reverse micelle system, the Au growth continued with time (~15 min), whereas, upon microwaving, growth was complete in 2 min. The second system examined was the growth of microporous ZnPO-X (an analogue of the faujasite structure) synthesized from an H<sub>2</sub>O–DODMAC–heptane reverse micelle system. Typical growth of ZnPO-X occurs with a 4 h nucleation period, followed by crystal growth over the next 4–5 h and an eventual settling of crystals. Microwave radiation was applied for 1 min at 150 W at various stages of the nucleation and growth process, and did not disrupt the reverse micelles. Product analysis after 40 h of reaction showed that the 1 min microwave pulse, if applied during the nucleation stage (first 4 h), promoted the formation of P6 over ZnPO-X. The effect of the microwave pulse at the crystal growth stage was to promote the formation of ZnPO-X. The model proposed to explain the effects of the radiation involves absorption of the microwave radiation by the water core and surrounding polar surfactant molecules, leading to a rapid rise in temperature (predicted to be ~150 °C/min for the AOT system). Under these conditions, the reaction rates in the reverse micelle are increased.

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Such a model explains the increased size and rapid formation of the Au particles. In the ZnPO-X synthesis, the rapid heating of the water core during the nucleation period destroys the ZnPO-X prenuclei and nucleates a more condensed phase P6. After the nucleation of ZnPO-X has been established, the microwave promotes the growth of ZnPO-X, much like the Au growth. Thus, the effects of microwave radiation are manifested in this study in two ways under conditions in which the overall stability of the reverse micelle is not compromised by keeping the bulk temperature below the phase transformation threshold.

Rapid heating of the water core promotes faster reaction among the contents of reverse micelles. Second, for thermally sensitive nucleation events such as that in microporous materials synthesis, prenuclei can be destroyed, as is reported with zincophosphates, whereas, in the crystal growth stage, the microwave promotes the growth.

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