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Shape-Controllable Synthesis of Crystalline Ni Complex Particles via AOT-based Microemulsions

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This article presents a simple method for the fabrication of shape-controllable Ni complex particles via an AOT-based single microemulsion. In this approach, Ni^{2+}/N_2H_4/EG solution is used as the dispersed phase, and cyclohexane is used as the continuous phase to obtain a microemulsion by the aid of the anionic surfactant AOT. The primary Ni complex particles with diameters of 20−30 nm were first formed in the reverse micelles and then self-organized into spindle-like, ellipse-like, cuboid, and cubic morphologies, depending on the reaction conditions. When aged at 100 °C for 24 h, these Ni complex particles changed into crystalline Ni. A possible evolution mechanism of the Ni complex particles with different morphologies is also discussed.

Introduction

In the past several decades, considerable attention has been devoted to the surfactant-assisted synthesis of nano- and microstructured materials for their soft template effects, reproducibility, and simple maneuverability.[1–3] Several methods based on the soft template technique are available for preparing inorganic nanomaterials, including those based on bubbles,[4] emulsion droplets,[5] miniemulsion droplets,[6] and reverse micelles or microemulsions.[7] Among these methods, those using reverse micelles or microemulsions have already been verified as effective approaches for synthesizing ultrafine inorganic particles.[8–19] It is well-known that certain surfactant molecules such as the anionic surfactant AOT [sodium bis(2-ethylhexyl)sulfosuccinate] or other nonionic surfactants, dissolved in organic solvents, are capable of solubilizing water droplets in their polar cores, and these entities are called reverse micelles or microemulsions. The dispersed water droplets behave as nanoreactors for the production of inorganic particles, and the reactions for the formation of particles are limited to occur only inside the dispersed water droplets. Thus, the particle size and corresponding size distribution can be readily controlled by reaction confinement.[20–22]

The formation of particles in reverse micelles can be achieved in either single-microemulsion or multimicroemulsion routes. In the single-microemulsion approach, one microemulsion is prepared, and the precursor or reactant is then added, diffusing through the oil phase into the micelles. This method is frequently used in space-confined sol−gel processes for the synthesis of oxide nanoparticles by hydrolysis and condensation of alkoxide precursors within the nanosized water droplets. Therefore, in most cases, only spherical particles, including TiO_2 and SiO_2, are prepared within the polar cores of the microemulsions.[23,24] A second process, namely, the multimicroemulsion route, takes advantage of two or more separately prepared microemulsions of the same water/surfactant/oil ratio, but with each microemulsion containing one of the necessary reactants for particle synthesis. After the microemulsions have been mixed together, particle formation occurs through the intermicellar exchange of the reactants. Moreover, further growth and aggregation of the initially formed nanoparticles from the multimicroemulsion-based approach can result in the formation of higher-order structures such as $PbWO_4$ nanorods,[3] $BaSO_4$ fibers,[19] and $CaSO_4$[22] and $BaCO_3$[25] nanowires. For instance, Mann et al.[26] synthesized $BaSO_4$−surfactant filamentous structures through the reaction of $Ba(AOT)_2$ reverse micelles with NaAOT microemulsion droplets containing Na_2SO_4 at a Ba^{2+}/SO_4^{2-} molar ratio of 5:1. Tang et al.[3] prepared $PbWO_4$ nanostructures using two separate AOT/EG/H_2O microemulsion systems containing Pb^{2+} or WO_4^{2-} in equivalent amounts. The morphologies of the as-prepared nanostructures could be controlled as dipyramids, bundles of rods, or nanorods by varying the concentration of AOT in the microemulsion formulations. These studies suggest that microemulsion-based approaches can be not

TABLE 1: Summary of the Ni Complex Particles Prepared at Different Reaction Conditions

run	AOT (g)	Ni/N_2H_4/EG solution (mL)	reaction temperature (°C)	morphology of the products
1	1.5	1.0	60	unstable system
2	2.5	1.0	60	spindle-like, coexist with primary particles
3	3.0	1.0	60	spindle-like
4	4.0	1.0	60	ellipse-like
5	5.0	1.0	60	cuboid
6	6.0	1.0	60	cubic
7	5.0	0.5	60	cubic
8	5.0	1.5	60	ellipse-like
9	5.0	2.0	60	spindle-like, coexist with primary particles
10	5.0	1.0	40	irregular morphology
11	5.0	1.0	50	spindle-like, coexist with primary particles
12	5.0	1.0	75	cubic

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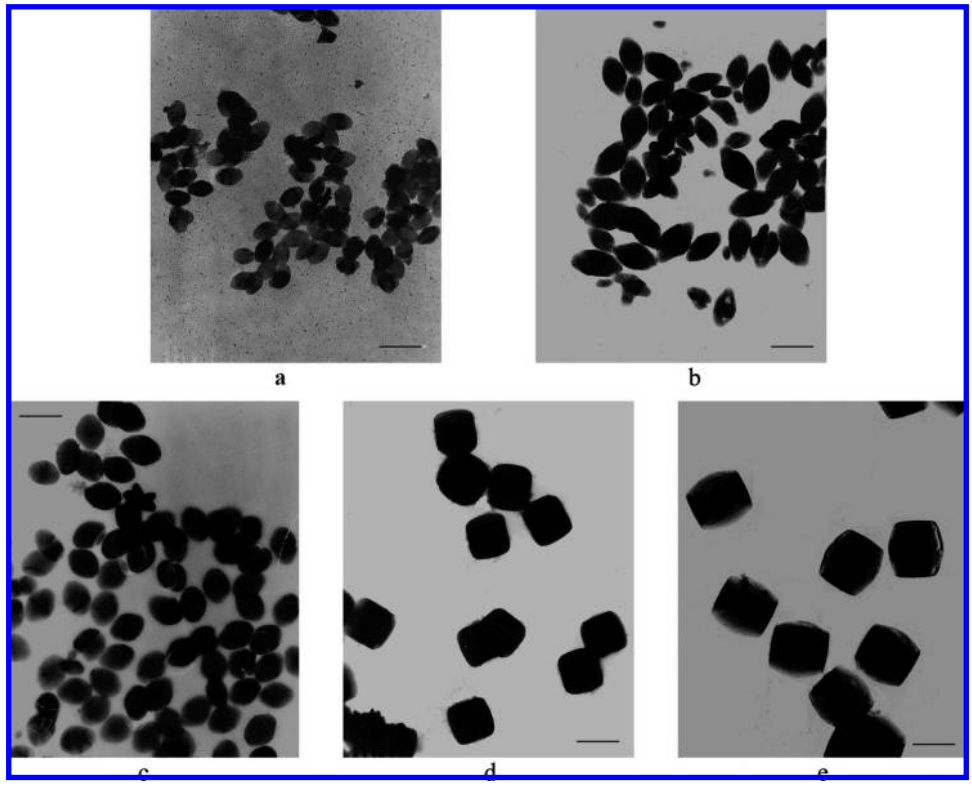

Figure 1. TEM images of the Ni complex particles prepared at various ATO contents (runs 2−6 in Table 1). The scale bar is 1 μm.

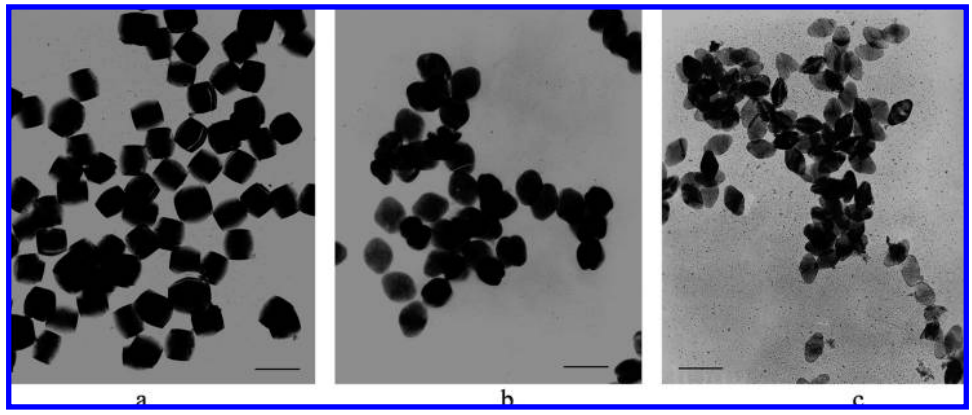

Figure 2. TEM images of the Ni complex particles prepared at various contents of Ni/N_2H_4/EG solution (runs 7−9 in Table 1). The scale bar is 1 μm.

only used to control the size and shape of inorganic nanoparticles, but also to form dynamical systems for the spontaneous organization of inorganic materials beyond the mesoscopic length scale. However, to the best of our knowledge, very few studies have focused on the formation of higher-order structures via the single-microemulsion approach.

In this article, we report the synthesis of crystalline Ni complex particles via an AOT-based single-microemulsion approach. Very interestingly, these Ni complex particles could be a spindle-like, ellipse-like, cuboid, or cubic in morphology, depending on the AOT concentration, content of the water phase, and reaction temperature. When aged at 100 °C for 24 h, these Ni complex particles changed into crystalline Ni. Thus, it is very easy to synthesize shape-tunable crystalline Ni complex particles via the AOT-based single-microemulsion approach.

Experimental Section

Materials. The anionic surfactant AOT [sodium bis(2-ethylhexyl)sulfosuccinate], hydrazine hydrate (85%, $N_2H_4 \cdot H_2O$), nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$], ethylene glycol (EG), absolute ethanol, and cyclohexane of analytical reactant grade were purchased from Shanghai Chemical Reagent Company (Shanghai, China) and used as received. The water used in this work was distilled and deionized.

Preparation of Ni/N_2H_4/EG Solution. Initially, 1.16 g of $Ni(NO_3)_2 \cdot 6H_2O$ and 50 g of ethylene glycol (EG) were charged into a 250-mL three-neck flask equipped with a mechanical stirrer, a thermometer with a temperature controller, and a Graham condenser; this mixture was stirred at room temperature for 30 min to obtain a homogeneous green solution. Then, 4.71 g of $N_2H_4 \cdot H_2O$ was added dropwise at room temperature under simultaneous agitation. The Ni/EG solution immediately turned violet upon addition of $N_2H_4 \cdot H_2O$, and then the solution was stirred for 24 h at room temperature to obtain a homogeneous Ni/N_2H_4/EG solution.

Synthesis of Ni Complex Particles via Microemulsion. Ni complex particles with various morphologies, such as spindle-like, square-like, cuboid, and cubic, were prepared in the a AOT-

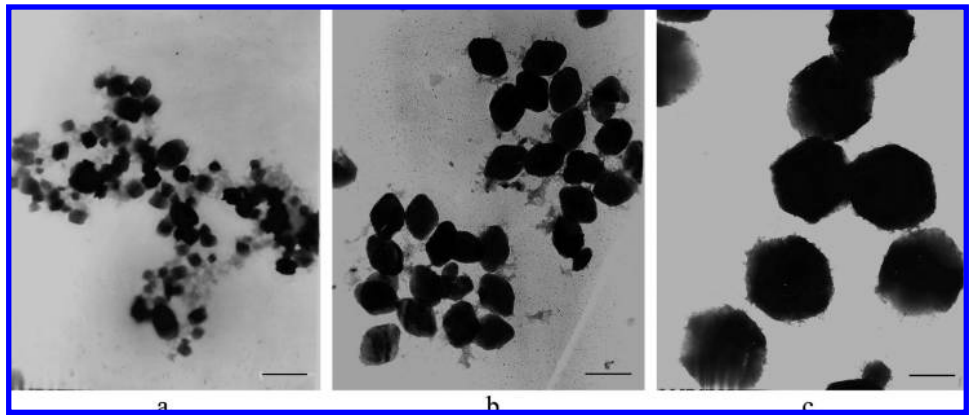

Figure 3. TEM images of the Ni complex particles prepared at various reaction temperatures (runs 10−12 in Table 1). The scale bar is 1 μm.

based single-microemulsion system. Typically, 5.0 g of AOT was first dissolved in 30.0 g of cyclohexane, and the mixture was stirred for 1 h to obtain a homogeneous solution. Then, 1 mL of the above-prepared Ni/N_2H_4/EG solution was added under vigorous stirring at 20 °C, and stirring was continued for about 30 min until the mixture appeared transparent, indicating the successful preparation of a microemulsion. The mixture was then heated to 60 °C under stirring at a rate of 100 rpm for 24 h, during which the color of the solution gradually changed to deep brown, indicating the formation of Ni complex particles. After the reaction had completed, the as-prepared products were separated from the reaction medium by centrifugation at ~15000 rpm, washed twice with absolute ethanol, and redispersed in distilled water. By modulating some parameters, such as the AOT content, the content of the Ni/N_2H_4/EG solution, and the reaction temperature, a series of Ni complex particles with shape-tunable morphologies could be prepared, as reported in Table 1.

Characterization of the Ni Complex Particles. ***Morphology.*** A transmission electron microscope (TEM Hitachi H-600; Hitachi Corporation, Tokyo, Japan) was used to observe the morphology of the as-prepared Ni complex particles. The particle dispersions were diluted and ultrasonicated at 25 °C for 10 min and then dried onto carbon-coated copper grids before examination.

XRD Analysis. The Ni complex particles were separated from the reaction medium by centrifugation and redispersed in ethanol three times and then dried in a vacuum oven at 25 °C for 24 h before XRD analysis. Some powders were further heated to 100 °C for 24 h and then examined with a Rigaku D/Max-RA X-ray diffraction meter using Cu Kα radiation (λ = 0.15418nm).

Results and Discussion

Formation of Ni Complex Particles. During the preparation of the Ni/N_2H_4/EG solution, the color of Ni/EG solution turned from green to violet immediately upon the addition of $N_2H_4 \cdot H_2O$. This was due to the formation of $[Ni(N_2H_4)_2](NO_3)_2$ when Ni^{2+} reacted with N_2H_4, as follows[27]

$$Ni(NO_3)_2 + 2N_2H_4 \rightarrow [Ni(N_2H_4)_2](NO_3)_2$$

Then, the as-prepared Ni/N_2H_4/EG solution was used as the water phase, and cyclohexane was used as the continuous phase to prepare a microemulsion using AOT. The initial microemulsion was lilac and completely transparent at room temperature. When the temperature was increased to 60 °C, the microemulsion turned deep brown within 24 h, indicating the formation of Ni complex particles, as reported previously

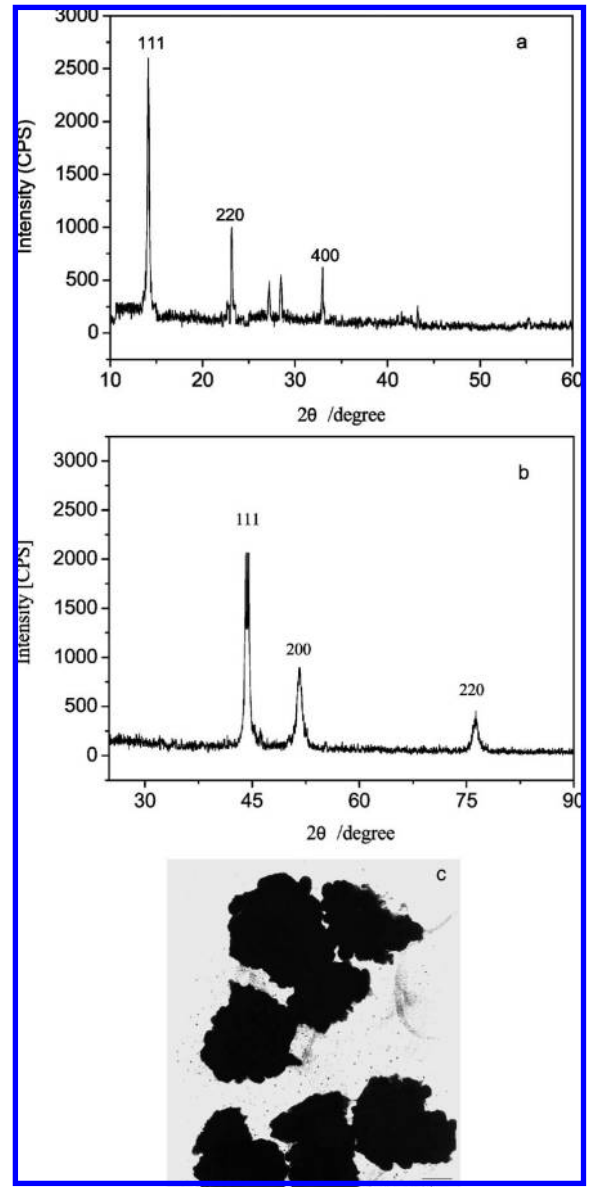

Figure 4. Typical XRD patterns of Ni complex particles (a) before and (b) after being aged at 100 °C for 24 h. (c) TEM image of crystalline Ni after being aged at 100 °C for 24 h. The scale bar is 500 nm.

$$2[Ni(N_2H_4)_2](NO_3)_2 + 5N_2H_4 \rightarrow 2[Ni(NH_3)_6](NO_3)_2\downarrow + 3N_2\uparrow$$

This reaction was confined inside the AOT-stabilized Ni/N_2H_4/EG droplets dispersed in cyclohexane, causing primary

Ni complex particles with rather small particle sizes. However, these primary Ni complex particles could grow and self-organize during the reaction, ultimately resulting in higher-order Ni complex particles. These Ni complex particles could be spindle-like, square-like, cuboid, and cubic in morphology, depending on the reaction conditions.

Effect of AOT Concentration. In the conventional single-microemulsion approach, the concentration of AOT or other surfactant basically has little effect on the morphology of the inorganic nanophases obtained.[8,28] However, in this work, the concentration of AOT was found to have a significant impact on the morphology of the Ni complex particles. Figure 1 presents the TEM images of the synthesized Ni complex particles as a function of AOT content. When the AOT content in the formulation was 1.5 g (run 1 in Table 1), phase separation was observed for the mixture of the $Ni/N_2H_4/EG$ solution and cyclohexane even after 24 h of stirring, as a result of the relatively low surfactant concentration, which encumbered the formation of the microemulsion. When the AOT content was increased to 2.5 g, a transparent microemulsion was prepared, and Ni complex particles with a spindle-like morphology were obtained, as shown in Figure 1a. However, from this image, one can see that some very small particles with a mean size of 20−30 nm are also present; these should be the primary particles formed according to the theory of microemulsions. From this observation, one can deduce that the final Ni complex particles are formed via the self-assembly of the primary particles obtained from the microemulsion droplets. When the AOT content was further increased to 3.0 g, spindle-like Ni complex particles without any primary particles were obtained (Figure 1b), and the average particle size increased markedly compared to the sample prepared with 2.5 g of AOT. Furthermore, when the AOT content was increased to 4.0 g, ellipse-like Ni complex particles with a rather narrow size distribution were obtained (Figure 1c). Continuing to increase the AOT content to 5.0 g resulted in the formation of Ni complex particles with a typical cuboid morphology (Figure 1d), both the shape and size of which were quite homogeneous. Figure 1e further shows a cubic morphology when 6.0 g of AOT was used in the formulation. Therefore, products with different morphologies could be easily synthesized in the AOT-based single microemulsions by tuning the surfactant concentration.

Effect of $Ni/N_2H_4/EG$ Solution Content. In addition to the AOT concentration, the content of $Ni/N_2H_4/EG$ solution in the microemulsion formulations also had an effect on the morphology of the products (runs 7−9 in Table 1 and Figure 2). When only 0.5 mL of $Ni/N_2H_4/EG$ solution was used as the dispersed phase to prepare microemulsion, Ni complex particles with a typical cubic morphology were obtained (Figure 2a). However, if 1.5 mL of $Ni/N_2H_4/EG$ solution was used, ellipse-like Ni complex particles with a uniform diameter were synthesized (Figure 2b). Further increasing the $Ni/N_2H_4/EG$ solution volume to 2.0 mL resulted in Ni complex particles with a spindle-like morphology, as indicated in Figure 2c. However, the TEM images show that the mean particle size was smaller and many primary particles remained compared to the samples prepared with less $Ni/N_2H_4/EG$ solution. This was probably because the volume of the dispersed phase was relatively higher and fewer surfactant molecules adsorbed onto the surfaces, which encumbered the further self-assembly of the primary particles.

Effect of Reaction Temperature. Figure 3 illustrates the effect of the reaction temperature on the morphology of the Ni complex particles obtained (runs 10−12). For a reaction temperature of 40 °C, the TEM image shows an irregular morphology with a relatively small size (Figure 3a). However, some small primary particles can also be seen in this image, which indicates the incomplete self-assembly of the primary particles at such a low temperature. When the reaction temperature was increased to 50 °C, spindle-like Ni complex particles were obtained (3b), and when the reaction temperature was further increased to 70 °C, Ni complex particles with a cubic morphology and increasing particle size appeared. This was probably because the high kinetic energy of the primary particles at high temperature led to the complete assembly of the primary particles into Ni complex particles with larger particle sizes.

XRD Analysis. The as-prepared Ni complex particles by examined with X-ray diffraction (XRD), as shown in Figure 4a. The diffraction peaks in the range of $10° < 2\theta < 60°$ can be indexed as the cubic structure of $[Ni(NH_3)_6](NO_3)_2$, by comparison with the standard powder XRD pattern (JCPDS 45-0027). Further XRD examination of the sample after it had been aged at 100 °C for 24 h was carried out and indicated that the Ni complex particles were converted to crystalline Ni, as shown in Figure 4b. The diffraction peaks in the range of $25° < 2\theta < 85°$ can be indexed as face-centered-cubic Ni, which is in good accordance with the standard XRD pattern (JCPDS 04-0850). TEM observation of the aged sample indicated that the crystalline Ni had an irregular sphere-like morphology (Figure 4c), which is similar to the original findings of Guo et al.[27] in the preparation of nickel complex nanotubes at 197 °C.

Possible Formation and Evolution of Ni Complex Particles. On the basis of the above results and discussion, the formation and evolution of the Ni complex particles could be described as shown in Figure 5. First, reverse micelles with $Ni/N_2H_4/EG$ solution as the dispersed phase and cyclohexane as the continuous phase form with AOT as the surfactant. After the temperature is increased to 60 °C, primary Ni complex particles with an average diameter of 20−30 nm gradually form in the reverse micelles. According to the literature,[29–31] these sphere-like primary particles can then collide and fuse, and simultaneously, rapid intramicellar nucleation can occur, which results in the displacement of AOT molecules and the formation of a surfactant bilayer between the complex particles. The further self-organization of the nucleus leads to the formation of Ni complex particles with a spindle-like morphology through the Ostwald ripening process. Because of the flexibility of the microstructure interface, Ni complex particles can continue to grow at the base of the formed spindle-like particles, leading to Ni complex particles with ellipse-like, cuboid, or cubic morphologies. Increasing the AOT content or decreasing the content of $Ni/N_2H_4/EG$ solution allows for the formation more micelles in the system and, hence, the cuboid or cubic morphology. Increasing the reaction temperature also favors self-assembly of the primary particles through increased Brownian motion, hence leading to higher-order morphologies.

Conclusions

As shown in this study, Ni complex particles with controllable morphologies can be obtained easily in an AOT-based single-microemulsion system by modulating the reaction parameters. As the AOT content increases, the Ni complex particles evolve from a spindle-like morphology to ellipse-like, cuboid, and cubic morphologies. Decreasing the content of $Ni/N_2H_4/EG$ solution or increasing the reaction temperature promotes the formation of Ni complex particles with higher-order structures. These Ni complex particles can be converted into crystalline Ni upon aging at 100 °C for 24 h. Thus, shape-tunable crystalline Ni complex particles can be prepared via this AOT-based single-

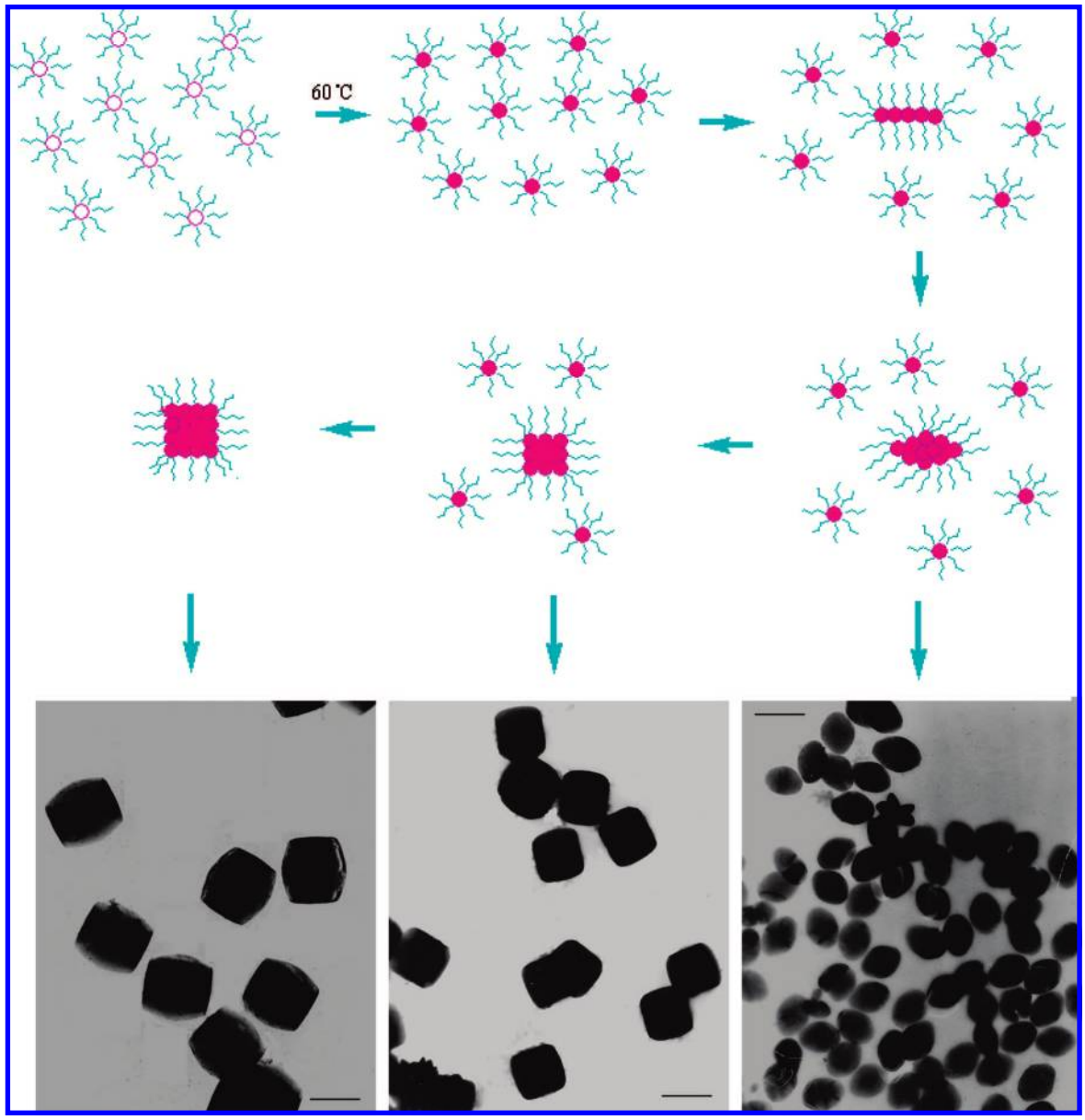

Figure 5. Proposed model for the evolution of Ni complex particles via the AOT-based microemulsion process.

microemulsion approach. Moreover, this approach might represent a promising method for the preparation of other metal oxide particles or inorganic complex particles with desired morphologies, for materials including Ag, Au, Pb, and so on.

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