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## Communications

### Size-Tunable Synthesis of Metallic Nanoparticles in a Continuous and Steady-Flow Reactor

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A multitude of nanoparticles including metal<sup>1–4</sup> and oxide,<sup>3,5,6</sup> semiconductor,<sup>3,7,8</sup> core–shell composite architectures,<sup>9,10</sup> and organic polymers<sup>11</sup> nanoparticles have been developed to date that exhibit novel properties and potential applications as nanotechnological building blocks.<sup>12–15</sup> Fundamental and applied research on synthetic methods and

properties of these nanoscale objects has attracted sustaining passion during the past decade as scientists strive toward perfection. However, at present, a general synthetic strategy in a continuous manner and in a way that can produce particles with size and monodispersity tuning, economy or facility, and environmental friendliness is still not available.

In this paper, we demonstrate a completely new chemical–mechanical metallic nanoparticles synthesis strategy: hydrodynamically and mechanically assisted metal displacement reduction in a continuous and steady-flow reaction system. The method is based on the heterogeneous reduction of metal precursor ion by a piece of active metal foil with the aid of deplating and mass transport resulting from mechanical and hydrodynamic forces. The method allows simple and green synthesis and continuous production. Size selectivity and size distribution control can be acceptably realized in a straightforward manner by adjusting particle average residence time in the continuous flow system.

Based on the universal oxidoreduction principle that a metal ion or ion complex can be reduced to corresponding atomic state in solution by another metal with relatively lower reduction potential, we, in the first instance, exploit bulk metal foil as a heterogeneous reducing medium and therefrom metal displacement reduction as a new approach for nanoparticles generation. The relatively active metals with low reduction potentials ( $E^{\circ}_{\text{Al}^{3+}/\text{Al}} = -1.67 \text{ V}$ ;  $E^{\circ}_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$ ;  $E^{\circ}_{\text{Ni}^{2+}/\text{Ni}} = -0.25 \text{ V}$ ) can reduce metal ions with higher reduction potentials, such as silver ( $E^{\circ}_{\text{Ag}^{+}/\text{Ag}} = 0.80 \text{ V}$ ) and copper ( $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$ ) in solution phase. The reduced metallic atoms then grow into nanosize particles in the presence of capping agent through a series of nucleation and kinetic coagulation processes. Unlike traditional homogeneous-phase reduction, here metal ions in solution are reduced on the metal foil surface. Due to intermolecular forces, the

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reduced atoms and resulting nuclei and particles have a tendency to accumulate on the foil surface, leading to plating and bulk formation. This physical process prevents the generated nuclei from entering the solution phase and subsequently forming nanoparticles. Severe foil surface coverage from plating and deposition stops the reduction reaction completely, and no colloidal particles can be achieved. We have previously reported a technique to overcome deposition by means of ultrasonic wave-generated agitation to dislodge particulates from the metal foil to successfully produce metal nanoparticle colloids including Au and Pt.<sup>16</sup>

In this work, we engineered another method to overcome deposition, which is inspired by chemical–mechanical planarization (CMP). We employ a “scrubbing” brush functioning like a “polishing” pad in constant contact with the rotating metal foil. This hairy brush (commercially available scrubbing brushes with polymer bristles were employed in the experiment) immediately removes newborn atoms or atom clusters from the foil surface during the reduction process. In addition, turbulent agitation resulting from high-speed rotation of a substrate disk and attached foil in the solution further helps ejecting the particle species from the foil, transferring them into the bulk phase and creating a well-mixed, uniform suspension. In this way, a synthesis condition is created to optimize the growth of particle.

It is well-known that controlled size and structure of nanoparticles are critical to achieve tunable physical and chemical properties of nanoparticles.<sup>2,12,17</sup> For instance, in “structure sensitive” catalytic reactions there is an ideal size and morphology for metallic nanoparticles on the catalyst surface for optimum reaction conditions. Much higher catalytic efficiency can be achieved if a monomodal distributions can be produced. Moreover, advanced application of nanoparticles as building blocks for bottom-up assembly and construction of nanoscale device requires the ability to process and maneuver particles, which exerts more strict demand for size selection. Currently predictable control of particle size and size distribution remains an important challenge, although some strategies have been performed and proven successfully. These strategies include, but are not limited to, controlling the concentration of capping agents,<sup>18</sup> employing reverse micelles as microreactor,<sup>19</sup> and using dendrimer,<sup>20</sup> or nano- or meso-porous matrices<sup>21,22</sup> as encapsulation templates. However, reverse micelles and the porous templates are hard to remove after syntheses and are not ideal for producing pure and uncontaminated nanoparticles. Decomposition of organometallic precursors is also

typically effective to obtain uniformly dispersed nanoparticles; however, it is still not desired in terms of cost and environmental perspectives.

More recently, microfluidic or microchannel reactors for continuous synthesis of metal and semiconducting nanoparticles have attracted significant interest due to the possibility to control nanoparticle growth and thereby particle dimensions by adjusting flow parameters.<sup>23–26</sup> The advantage of microreactors with continuous flow over conventional macroreactor batch processes relies on the fact that simply scaling down the reaction system is often sufficient to lower the polydispersity. Furthermore, the temperature and concentration can be varied promptly and reproducibly on the scale of micrometers and milliseconds, as desired for nanocrystal synthesis.<sup>23,24</sup> However, these continuous-flow processes usually require prior well-mixed solutions in order to form narrowly dispersed nanoparticles if several reactants are involved, otherwise the micromixing mediated by slow and spontaneous molecular diffusion is not sufficient.<sup>25</sup> In hydrodynamically and mechanically assisted metal displacement reduction, the mechanical and hydrodynamic forces not only effectively prevent plating and bulk formation by the scrubbing action but also facilitate mass transport and well-mixing, providing more favorable conditions for particle nucleation and growth. Our method in continuous flow also circumvents the intrinsic drawback in the microfluidic reactors—reactor fouling, which is due to the aggregates’ settling on the inner surface of the tube wall.<sup>24,25</sup>

For desired size and size distribution, the synthesis is performed similarly to industrial MSMRP (mixed suspension, mixed product removal) crystallizers.<sup>27</sup> The continuous and steady-state operating MSMRP vessel, characterized by a feeding stream of precursor ionic solution and an exit stream of mixed reaction solution, allows regulated control of average residence time of suspended nanoparticles, providing particles with selective growth time and size tunability.

As an example of the synthesis strategy, silver nitrate (AgNO<sub>3</sub>, anhydrous, 99.9+%, Alfa Aesar) is mixed with poly(vinyl pyrrolidone) (PVP, weight-average molecular weight of 58 K, Acros Organics) in deionized water at room temperature at various reported concentrations. Nickel foil, iron foil, and cobalt foil (all 0.5 mm thick, 50 × 50 mm, Alfa Aesar) are employed as a heterogeneous reducing medium respectively for the generation of silver nanoparticles in the reactor. The molar ratio of AgNO<sub>3</sub>/PVP (in repeating unit) is fixed at 1:1 for Ni and Fe reduction and 10 for Co reduction. The AgNO<sub>3</sub>/PVP solution is put into the reaction vessel (150 mL in vessel) and an inlet reservoir. The volume of reaction solution remains constant at 150 mL during the whole procedure because of the balanced input and exit volumetric flow rate. The foil, immersed in the solution, rotates at high speed together with the substrate holder, and a hairy brush fastened to the vessel bottom remains in

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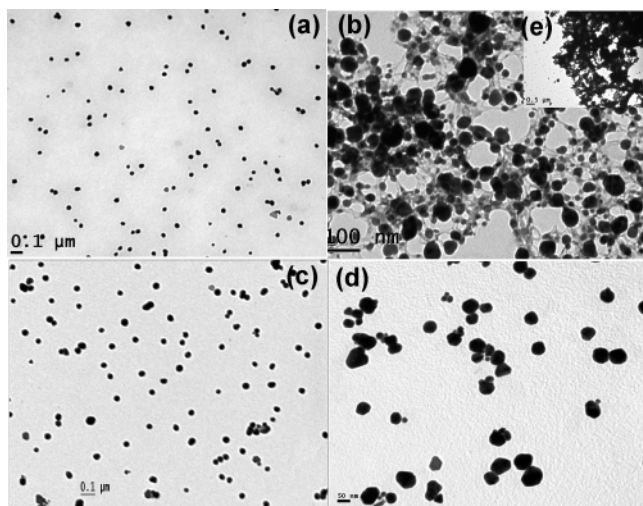
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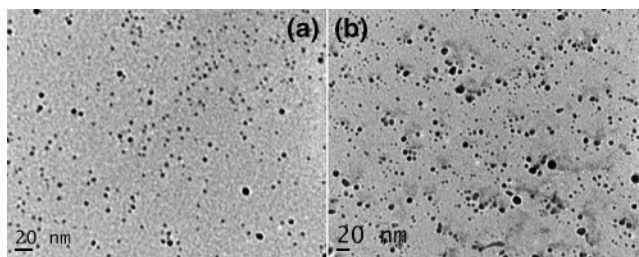


**Figure 1.** Representative TEM images of Ag nanoparticles synthesized by Ni foil with 0.05M  $[Ag^+]$ :  $\tau = 60$  min (a);  $\tau = 120$  min (b); zero flow rate (e); and by Fe foil at  $\tau = 30$  min:  $[Ag^+] = 0.05$  M (c); with Co foil with  $\tau = 30$  min,  $[Ag^+] = 0.5$  mM (d). The average sizes are  $29.4 \pm 5.4$  nm,  $35.8 \pm 9.9$  nm,  $35.4 \pm 6.0$  nm, and  $47.1 \pm 11.2$  nm (all SD,  $n = 50$ ) respectively, from panel a to panel d. The scale bars are  $0.1 \mu\text{m}$ ,  $100$  nm,  $50$  nm, and  $0.5 \mu\text{m}$  respectively from panel a to panel e.

constant contact with the foil surface to perform the polishing function. The inlet flow is controlled through a funnel, and the exit flow is controlled by a plastic tube with a regulatory clamp. After steady flow state is reached (usually 1–2 average residence time), solution mixture was sampled for further characterization and analysis.

The concentration of the metal salt precursor, the flow rate, and thus corresponding particle average residence time (due to fixed balance volume) were investigated as regulatory factors for particle dimension and distribution control. Figure 1 shows TEM images of synthesized Ag nanoparticles reduced by Ni, Fe, and Co foil at varied flow rate.

The results show that average size and size distribution can be selectively modulated by particle average residence time ( $\tau$ ). For Ni reduction, the increased  $\tau$  leads to increased average size and broader distribution from  $29.4 \pm 5.4$  ( $\tau = 60$  min) to  $35.8 \pm 9.9$  nm ( $\tau = 120$  min) (Figure 1a,b). When reducing the flow rate to zero, as in a batch system, severe agglomeration occurs, and almost no individual particle can be identified (Figure 1e). The reason why the average residence time  $\tau$  serves as a size and size distribution control strategy is apparent in this specific process; a characteristic “progressive” reduction and nucleation governs the particle formation due to the foils’ relatively weak reducing ability as compared to strong reducing agent such as  $N_2H_4$  and  $NaBH_4$  and other factors such as limited reaction sites on the foil surface. Thus nucleation cannot be separated from particle growth in time, and the growth durations for individual particles have a distribution with time.<sup>28</sup> Thus a broad size distribution results. Consequently, the average residence time balances the negative effect of progressive nucleation and creates approximately equal particle growth duration although it cannot provide absolutely synchronous growth for each particle. Too long average residence time cannot effectively offset progressive nucleation, hence a



**Figure 2.** Representative TEM images of Cu nanoparticles synthesized by Co foil with 0.01 M  $[Cu^{2+}]$ :  $4.0 \pm 1.1$  nm (SD,  $n = 50$ ),  $\tau = 30$  min (a);  $4.9 \pm 3.1$  nm (SD,  $n = 50$ ),  $\tau = 60$  min (b). The scale bars are 20 nm for both panel a and panel b.

larger size and broader distribution is obtained with long residence times.

It is interesting to compare the reduction by Ni, Fe, and Co foils. With Fe as the reducing agent, the Ag particles size is  $35.4 \pm 6.0$  nm (Figure 1c) with a residence time of 30 min and a concentration of 0.05 M. With Co as the reducing agent, the Ag particles size is  $47.1 \pm 11.2$  nm (Figure 1d) with a residence time of 30 min and a concentration of only 0.5 mM. This shows that the reduction rate plays a more important role in determining the average particle size. Further, it was observed that the slow reduction by using Ni and Fe foils leads to a smaller yield of less than 5%, while the yield with a faster reduction rate (using Co foil) can be much higher ( $>30\%$ ). The effect of the reduction rate implies that the reduction rate is not proportional to the standard potential difference between the metal ion–metal pairs, as  $E^{\circ}_{Fe^{2+}/Fe} = -0.44$  V  $< E^{\circ}_{Co^{2+}/Co} = -0.28$  V  $< E^{\circ}_{Ni^{2+}/Ni} = -0.25$  V.

Figure 2 shows another synthesis example. Copper nanoparticles are reduced by Co foil using copper(II) nitrate 2.5-hydrate ( $Cu(NO_3)_2 \cdot 2.5H_2O$ , Acros Organics) plus PVP and a fixed molar ratio of  $[Cu^{2+}]/[PVP] = 0.2$ . Under same precursor concentration of  $[Cu^{2+}] = 0.01$  M, the average size and distribution goes up from  $4.0 \pm 1.1$  ( $\tau = 30$  min) to  $4.9 \pm 3.1$  nm ( $\tau = 60$  min). The average residence time is again successfully employed as an adjustment parameter for size selectivity. It should be noted that Co is also an excellent reduction agent, and the yield is approximately 20%.

In conclusion, we have successfully developed a new general route for metal nanoparticles production by using metal foil as heterogeneous reducing medium with the deplating and mass transporting aid of mechanical and hydrodynamic forces. Particle average residence time are proven effective adjustable parameters for tunable particle size and distribution. These techniques open new horizons for exploitable scalability of continuous industrial production of an array of metallic nanoparticles with tunable size.

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**Supporting Information Available:** Schematic diagram of the experimental setup and XRD patterns of synthesized Ag and Cu nanoparticles. This material is available free of charge via the Internet at <http://pubs.acs.org>.