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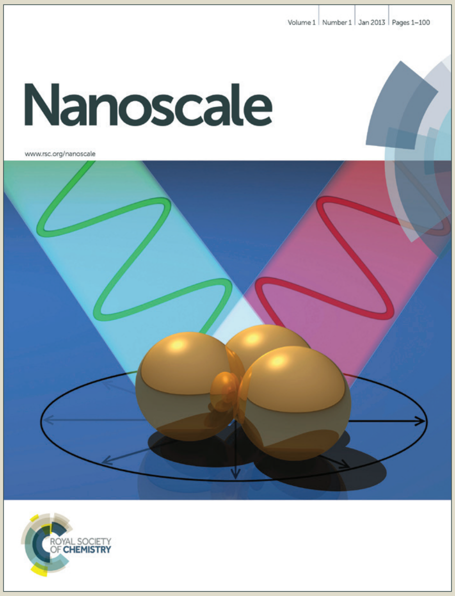

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COMMUNICATION

Size control of noble metal clusters and metallic heterostructures through the reduction kinetics of metal precursors

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Eight precious metal salts/complexes were reduced in propylene glycol at temperatures ranging between 110 and 170 °C. We found that the reduction temperature and the size of precipitated metallic nanoparticles formed were significantly affected by the structure and reactivity of the metal precursors. The choice of noble metal precursor offers flexibility for designing, fabricating and controlling the size of metallic heterostructures with tunable properties.

The 'seeds-mediated' growth approach has shown significant potential for the synthesis of highly dispersed uniform particles, and its importance and versatility in preparing novel advanced nanomaterials with controlled particle size has been amply documented.[1] Thus, this strategy has become quite popular in the design and development of novel materials with exciting properties, such as binary nanocrystals,[2,3] advanced fuel-cells electrocatalysts,[4–6] bio-catalysts[7,8] for green chemistry and pharmacy, environmentally benign and recyclable heterogeneous catalysts[9] as well as quantum dots for bio-analysis, optics, and photovoltaics.[10,11] Further, refinements of the 'seeding' approach are expected to provide additional new opportunities in the preparation of uniform metallic crystals,[12] bio-related functionalized materials,[13] complex heterostructures involving quantum dots (QD)[14–17] and core-shell (CS) architectures.[18–21]

The core of this study describes a methodology for preparing uniform dispersed noble metal nanoparticles (NPs) with controllable size in the 1–7 nm range. These entities may be used for electronic and opto-electronic applications in complex heterostructures involving suitable QDs as well as heterogeneous nucleation sites ('seeds') in the precipitation of multi-component metallic heterostructures. Thus, in regard to the former, Kramer et al.[22] and Hatef et al.[23] have shown that positioning QDs near metallic nanostructures strongly affects the light emission at the single photon level. To exhibit exciton quantum confinement properties, the size of the whole heterostructure should not exceed 20 nm. The method revealed here is capable of generating noble metal particles in the size range highly suitable for the synthesis of such structures. In regard to the latter, as a case study, we prepared Ni-Cu core-shell (CS) nanoparticles that can be used as recyclable coupling agents in click reactions[9,24] for the synthesis of triazoles[25] and in Ullmann coupling reactions.[26,27]

Precipitation from homogeneous solutions is one of the most effective approaches for controlling nucleation and growth of the metallic phase that yields uniform particles in the desired size range. Since first employed by Fievet[21] for precipitation of dispersed metals and alloys, the polyol system has been further refined to allow the synthesis of metallic nanoparticles with controlled size and shape.[22] In this study we adopted this route to obtain dispersions of uniform metal clusters of 1–7 nm size, which served as starting cores for growing complex heterostructures. The wide range of reaction temperatures (ambient to >200 °C), offered by the polyol process, is usually the main parameter used for controlling the reduction kinetics of a metal, the nucleation rate, and, thus, the size of the final particles. A parameter that also has a significant importance, but has not been studied systematically, is the reactivity of the metallic precursor. It is well known that involving the metal ions in complexes of increased stability reduces the rate of the electron transfer between the reductant and the metallic species. The result is a decrease in the nucleation rate, which yields progressively larger particles. This study contributes to a better understanding of this phenomenon, while offering a viable methodology for synthesis of metal clusters suitable for growing hierarchical structures. In particular, this method relies on reactivity properties of different salts involved in polyol reduction. This offered flexibility for controlling the growth of complex heterostructures from homogenous mixtures ('one-pot-reaction') severally with the reaction temperature.

Precious metal compounds were supplied by Umicore AG (Germany/USA) along with their structural formula and composition, while analytical grade propylene glycol (PG) was used as both dispersion medium and reductant. Identical sample preparation, reduction, and isolation routines were used for all eight noble metal salts. Specifically, 50 ml of PG and an amount of metal complex needed to yield a concentration of 2,500-ppm metal were introduced in a 150 ml spherical flask placed in an electrically heated mantle. The pH of the resulting solutions, which varied with the nature of the ligand, was not adjusted. Under continuous stirring, the mixtures were heated at a rate of 2 °C/min until the reduction of the noble metal occurred. In all cases, the color of polyol changed gradually with the increase in temperature before the metallic nanoparticles formed. The precipitation of metal particles was indicated by a sudden increase in turbidity and, eventually, the formation of a black dispersion. These stages in the formation of precious metal seeds are consistent with the predictions of existing models describing the formation of dispersed metals in homogenous solutions.[28–31] After rapid cooling, the metal particles were separated from the polyol and were inspected by electron microscopy to assess the size, shape, and dispersion. The relevant experimental parameters used in the precipitation process are summarized in Table 1.

Table 1. Reduction temperature, time, and size of noble metal clusters formed in propylene glycol (EA and ETA stand for ethanolammonium and ethanolamine, respectively)

Metal complex formula (metal wt%)	Reduction temperature (°C)	Reduction time (min)	Particle size range, d_{seed} (nm)
$[Pt(II)(NH_3)_4](OC_2H_3O_2)_2$ (6.17%)	162–165	2	6.1±0.9
H_2PtCl_6 (30.06%)	125–130	5–10	5.0±0.8
$[(EA)_2Pt(IV)](OH)_6$ (8.99%)	113–115	2	2.2±0.6
$Pt(II)(NH_3)_4\ (HCO_3)_2$ (50.19%) (powder)	145–148	2–3	5.5±0.8
$[(ETA)_4Pt(II)](CO_3)$ (10.06%)	152–153	2	6.0±0.9
$[(ETA)_2[Pt(IV)](OH)_6$ (9.22%)	168–170	2	6.6±0.9
H_2IrCl_6 (20.44%)	110	150	1.6±0.6
$IrC_6H_9O_6$ (4.22%)	125	15–20	2.1±0.6

Electron micrographs of the largest (~7 nm) and smallest (~1.5 nm) noble metal particles obtained are shown in Figure 1a,b. Electron diffractograms (Figure 1a,b, inserts) indicate that metallic phases of platinum (JCP 004-0802) and iridium (JCP 006-0598) were formed. The plot in Figure 1c shows the final size of the noble metal particles and the corresponding reduction temperatures for all metal complexes tested.

For a given metal, the data in Figure 1c point to a general trend between the complex stability (as reflected by the reduction temperature) and the final size of metallic nanoparticles. The largest nanocrystals (~7 nm) were formed in the presence of the most stable platinum complex $\{(ETA)_2[Pt(IV)(OH)_6]\}$ (Figure 1a), while the least stable Pt precursor $\{(EA)_2[Pt(IV)(OH)_6]\}$ yielded particles of only ~2 nm. The nature of the noble metal has a noticeable impact on its size as well. For the same ligand (Cl^-) and complex structure (octahedral H_2MeCl_6), iridium generated smaller metal clusters (1–2 nm) than platinum. In terms of particle dispersion, both Pt and Ir nanoparticles were more aggregated when the solution of the metal precursor was acidic, and well dispersed in alkaline complex solutions. For the former case, the use of a dispersing agent such as polyvinylpyrrolidone (PVP) was necessary to maintain the satisfactory dispersion of the 'seeds'.

The Pt seeds were next used to grow multilayered Pt/Ni/Cu particles in a controllable manner. Stage one was the preparation of Ni nanocrystals. The procedure (disclosed in a previous study[32]) consisted of heating a mixture of nickel basic carbonate (Sheppard Chemical Co., USA) and $(EA)_2[Pt(IV)(OH)_6]$ in PG at 180 °C, maintaining the temperature for 12 hours. At this temperature, basic-$NiCO_3$ is slowly reduced to Ni^0 and deposited on the platinum seeds that were formed at lower temperature (~115 °C, Table 1). Slow reduction of Ni at 180 °C governs its heterogeneous nucleation and Ni crystal growth driven by a diffusional mechanism.[29,33,34] This allows for control of the final size of the Ni particles through the amount of Pt seeds added, i.e. Ni/Pt weight ratio. Indeed, assuming that the size of the Pt seeds formed remains essentially the same for a given Pt precursor and only their number increases with the amount of salt added, the final nickel particle size is determined by:

$$d_{Ni} = d_{seed}\left(1+\frac{\rho_{seed}}{\rho_{Ni}}\times\frac{m_{Ni}}{m_{seed}}\right)^{1/3}, \qquad (1)$$

where d, m, and ρ are the diameter (nm), mass (g), and density (g/cm^3) of the metals used. Thus, Figure 2a shows uniform 20–40 nm Ni particles (Figure 2a) formed by seeding with the Pt clusters obtained with $(EA)_2[Pt(IV)(OH)_6]$ at 0.25 wt.% of Pt (by nickel weight). Figure 2b indicates that Ni particle size distribution follows the Gaussian fit. From Eq. (1) it follows that selecting a different Pt complex from Table 1 allows proportional tuning of the Ni size without alternating the $NiCO_3$ amount or concentration.

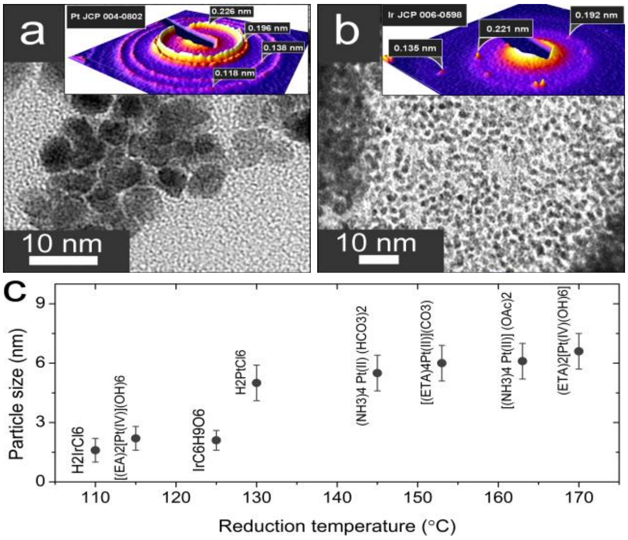

Figure 1. a) TEM image of precipitated Pt metal particles (6.6±0.9 nm) obtained from ethanolamine-Pt-hydroxide; b) TEM image of Ir particles (1.6±0.6 nm) obtained from Ir-chloride complex; c) the reduction temperature for the noble metal complexes vs. the final size of metallic nanoparticles.

To prepare the Ni/Cu core-shell NP's, copper carbonate ($CuCO_3$, Ames Goldsmith Corp., USA) was added into the Pt/Ni dispersion which had been cooled to 160 °C. This temperature was selected to provide for the slow reduction of copper favoring its epitaxial growth on Ni particles. The powder XRD pattern in Figure 2c indicates that two metallic phases of Ni and Cu were formed without alloying. Assuming that the Ni particles have a spherical shape and Gaussian size distribution, the amount of copper added theoretically translates to a 3.8 nm thick shell. Indeed, the electron micrographs (Figure 2d) reveal a distinct uniform shell of copper approximately 2–4 nm in thickness over

Ni particles. High resolution TEM in Figure 2e indicates that CuO patches were also formed, likely after the sample was dried in air. Preventing the access of moisture and oxygen to the particles would preclude their oxidation and render them suitable for intended applications.[25–27]

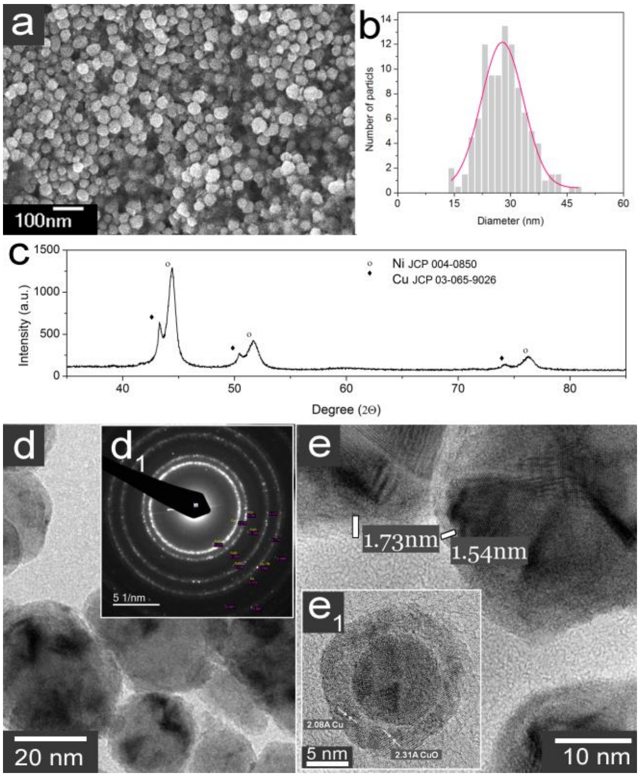

Figure 2. a) Ni core particles prepared via 'seeding' method with the $(EA)_2[Pt(IV)(OH)_6]$ precursor; and b) their Gaussian fitted size distribution (insert); c) XRD pattern of Ni/Cu core-shell particles; d) TEM of the Ni core particles coated with continuous copper shell; d1) their electron diffractogram; e, e1) high resolution TEM indicates 2–4 nm Cu and CuO shell was formed

In conclusion, we showed that by controlling the stability of the metal complex through a suitable ligand selection, the reduction temperature in PG could be varied over the range of 60–70 °C. The changes in the nucleation rate due to complex reactivity permit the preparation of uniform dispersed noble metal nanocrystals in the 1–7 nm size range. These nanocrystals are well suited to act as seeds for the growth of larger heterostructures tailoring their size based on Eq. (1) instead of alternating any critical experimental condition. As an example of this, we showed that Ni/Cu core-shell particles can be prepared on Pt seeds. This method also can be easily adopted for preparation of other complex nanosystems.

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Notes and references

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‡ The size and shape of the particles were determined by transmission (TEM JEM-2010) and scanning (SEM JEOL-7400) electron microscopy, and XRD aquired with Bruker-D8.

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