

Facile synthesis of porous Ag microspheres via Cu^{2+} -mediated reduction of AgCl

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Published in Micro & Nano Letters; Received on 30th July 2015; Revised on 28th October 2015; Accepted on 29th October 2015

A facile approach to producing silver (Ag) microspheres with a porous structure via a one-pot synthesis is described. The success of this work relies on the use of Cu^{2+} to mediate the reduction of silver chloride by oleylamine. The type of additives, amount of copper(II) chloride, type of Ag precursor and reaction temperature were systematically investigated to reveal their roles in the formation of the unique porous structure. The method described provides a convenient route for fabricating porous Ag micro/nanocrystals and could be potentially extended to similar synthesis of other noble metals.

1. Introduction: Silver (Ag) micro/nanocrystals have attracted significant research interest in the past decades due to their unique physiochemical properties and potential applications in the fields of optics and catalysis [1–9]. It has been widely accepted that the physiochemical properties of Ag micro/nanocrystals are highly dependent on their sizes and/or shapes [10]. For example, when their size was reduced to nanometre range, the suspension of Ag nanocrystals usually exhibited the colour of yellow or green. This is caused by the localised surface plasmon resonance effect, where resonant oscillation of electrons at the interface stimulated by incident light [11]. In addition to the size, the shape (e.g. anisotropic structure, sharp feature on the surface etc.) was also found to be another important parameter in influencing their optical performances [12, 13]. To this end, developing synthetic route for fabricating Ag micro or nanocrystals with desired sizes and shapes has been of great importance for their further application.

Thanks to research efforts contributed by many groups, it is now possible to synthesise Ag micro/nanocrystals with tunable shapes and sizes via a one-pot wet-chemical method. Generally, the Ag precursor was either reduced or decomposed to zero-valent atoms in the presence of capping agent, followed by nucleation and growth to form large-sized particles. The final product would exhibit different morphologies under thermodynamically or kinetically-controlled conditions. Typical examples include polyhedra (cube, cuboctahedron, octahedron, right bipyramid, decahedron and icosahedron), wires/rods, plates/flakes among others [14–22]. For part of these demonstrations, the size of products can also be tuned in a relatively wide range.

Despite these successful demonstrations, it is worth noting that most of the products are of solid interiors. There has been very few reports about fabricating Ag micro/nanocrystals with a porous structure via a simple one-pot synthesis. Generally, in order to obtain a porous structure, Ag products with uniform shapes or sizes usually have to be prepared initially, followed by the reaction with a second metal precursor via galvanic replacement reaction (GRR) under proper conditions [23]. For example, Xia and co-workers synthesised several hollow nanostructures by reacting Ag cubes and nanowires with metal precursors, including Au, Pd and Pt [24, 25]. However, the second metal tends to deposit on the Ag surface and form core-shell or alloyed structure. As a result, the product obtained using GRR method often contains more than one type of metal. In a sense, it has still remained

grand technical challenge to fabricate porous micro/nanocrystals composed of pure Ag via a convenient method, especially a one-pot approach.

The use of metallic cations to mediate the shape-controlled synthesis of noble metals has attracted enormous research attentions. Typically, the addition of a secondary metal precursor with trace amount will react with the major metal during the synthesis and thus change the size and/or morphology of final products. The most typical example would be the seed-mediated synthesis of single-crystal gold nanorods, which was developed initially by Murphy, El-Sayed, Mirkin among others [26–28]. In a typical reaction, Au seeds were prepared first, followed by seeded growth mediated with the Ag ions. It is believed that the one-dimensional (1D) preferential growth was attributed to the underpotential deposition of Ag layer on the Au surface. This mechanism was further extended to other systems and contributed to the successful preparation of noble metal nanocrystals with thermodynamically unfavoured shapes, such as concave/convex Au cubes/rods, Au bipyramids and rhombic dodecahedra, concave Ag octahedra among others [29–32].

Herein, we describe a facile synthesis of pure Ag microspheres with a porous structure. The success of this work relies on the use of Cu^{2+} to mediate the reduction of silver chloride (AgCl) by oleylamine at an elevated temperature [33–36]. To understand the mechanism, the type of additives, amount of copper(II) chloride (CuCl_2), type of Ag precursor and reaction temperature were systematically investigated to reveal their roles in the formation of final products. It was found that the reaction kinetics played an important role in promoting the formation of such unique morphology. The current approach provides a convenient route for fabricating Ag microspheres with a porous structure and could find important use in the synthesis of other noble metals.

2. Experimental section

2.1. Chemicals: Ag(I) chloride ($\text{AgCl} \geq 99.5\%$), anhydrous CuCl_2 (CuCl_2 99%) and hexane were obtained from Sinopharm Co. Ltd. and used as received. Anhydrous nickel(II) chloride (NiCl_2 99%) was obtained from Alfa and used as received. Anhydrous iron(III) chloride ($\text{FeCl}_3 \geq 99.99\%$) and oleylamine (OAm 80–90%) was obtained from Aladdin Chemical Co. Ltd. and used as received.

2.2. Standard procedure for porous Ag microspheres: A total of 430 mg of AgCl and 200 μL of CuCl_2 (0.3 mg/mL) were mixed

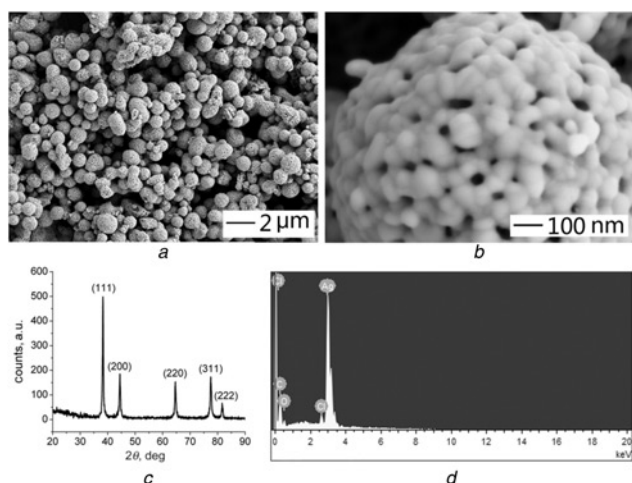


Fig. 1 Morphology, structure and composition characterisation of porous Ag microspheres

a Low-magnification SEM image
b high-magnification SEM image
c XRD pattern
d EDS pattern

with 30 mL of OAm at room temperature in a 250 mL three-neck round-bottom flask. The mixture was then heated in an oil-bath kept at 180°C for 6 h with magnetic stirring. The mixture was cooled down to room temperature by placing the flask in an ice-bath. The products were washed with hexane twice via centrifugation at 3000 rpm for 10 min and the precipitates were collected for further characterisation and use.

2.3. Characterisation: Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDS) patterns were captured using an Ultra Plus microscope operated at 3.0 kV (Zeiss, Oberkochen, Germany). The samples were prepared by dropping aqueous samples onto Cu foils. X-ray diffraction (XRD) patterns were recorded by using a diffractometer with filtered Cu K_{α} radiation at 0.154 nm.

3. Results and discussion

3.1. Morphology, structure and composition characterisation: Figs. 1*a* and *b* show SEM images of porous Ag microspheres. The resultant products exhibited a porous spherical shape in high purity. The size of these porous microspheres was $1.05 \pm 0.14 \mu\text{m}$ in diameter statistically and the pore size was measured to be around 40 nm. It is worth pointing out that such Ag microspheres could be routinely synthesised in high purity (>98%) without involving any additional purification/separation process. To figure out their crystal structures and compositions, we performed XRD and EDS analysis of these products. Figs. 1*c* and *d* show XRD and EDS patterns of the porous Ag microspheres, respectively. As displayed in Fig. 1*c*, the diffraction peaks occurring at 38.1° , 44.3° , 64.5° and 77.5° are indexed as (111), (200), (220) and (311) facets, respectively, being consistent well with an fcc Ag crystalline structure (JCPDS 04-0783). No peak for other crystal types was observed. The sharp diffraction peaks indicated the sample had a high crystallinity. EDS pattern confirmed there is no other metallic element involved in the product (Fig. 1*d*). Taken together, we can conclude that the as-obtained products were composed of pure Ag, together with a porous spherical shape with hollow interiors.

3.2. Effect of additives on product morphology: In the current synthesis, Cu^{2+} ions were added to promote the formation of porous Ag microspheres. To elucidate the mechanism involved in

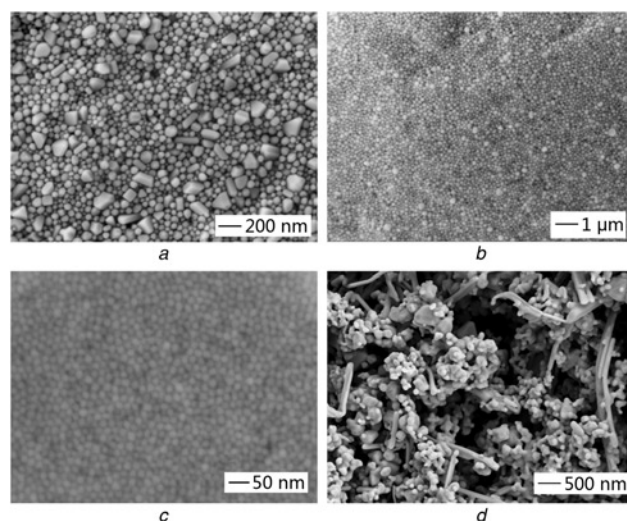


Fig. 2 Effect of additives on the morphology of final products. SEM images of products obtained using the standard procedure, except that the 0.06 mg of CuCl_2 was replaced by

a 0.06 mg of FeCl_3
b 0.06 mg of NiCl_2
c 0 mg of CuCl_2
d 3 mg of CuCl_2

the synthesis, we conducted a set of experiments using the standard procedure, except for the use of different additives and concentrations for CuCl_2 . For instance, we tried to replace the CuCl_2 with two other common metallic additives in the noble metal synthesis while keeping other reaction parameters the same. As shown in Figs. 2*a* and *b*, when either FeCl_3 or NiCl_2 was added in the reaction systems, respectively, the resultant products no long exhibited the porous spherical shape. Instead, polyhedral nanoparticles were dominated. We also manipulated the amount of CuCl_2 to observe its impact on the morphology of final products. As shown in Fig. 2*c*, if there is no CuCl_2 , polyhedral Ag nanocrystals with an average size of 10 nm were obtained. When the amount of CuCl_2 was increased from 0.06 mg in the standard procedure to 3 mg, no porous sphere can be obtained (Fig. 2*d*). All these results suggested the formation of Ag microspheres with a unique porous structure in high purity relies on the use of CuCl_2 with an appropriate concentration in the system.

As indicated in previous studies, the use of secondary metallic additives in the synthesis of noble metal nanocrystals can significantly vary the size and/or the shape of final products. In this Letter, Cu^{2+} can be reduced to Cu^+ and/or $\text{Cu}(0)$ by oleylamine at an elevated temperature [37]. However, as $\text{Cu}(0)$ could be easily oxidised back to Cu^+ and/or Cu^{2+} by oxygen in the air, the Cu species in the system should be dominated by a mixture of Cu^{2+} and Cu^+ . This mechanism was quite different from the concept of underpotential deposition reported by Murphy, El-Sayed, Mirkin among others, for manipulating the growth habit of Au nanostructures with Ag^+ ions [38, 39]. This is because no zero-valent Cu atoms deposited on the surface of Ag. In addition, such redox cycle occurred to Cu should have consumed the oxygen that could have reacted with Ag species if there is no CuCl_2 was added [40]. In this case, the growth pattern could have changed since the oxidative etching strength was dampened. Instead of nucleation and growth into individual particles, newly-generated Ag(0) atoms could deposit on the surface of AgCl quasi-spheres to form small islands and these Ag islands could connect to each other due to surface atomic migration. Meanwhile, AgCl was continually reduced to supply Ag(0) atoms and make the spheres interior hollow. All the processes contributed to the formation of such unique porous structure.

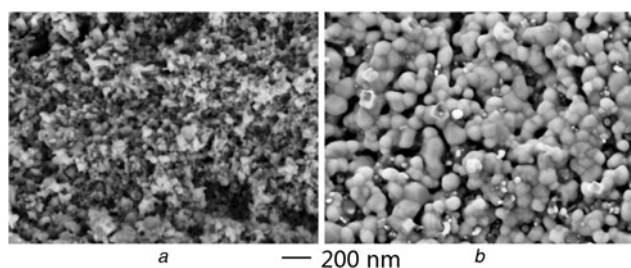


Fig. 3 Effect of reaction temperature on the morphology of final products. SEM images of products obtained using the standard procedure, except that the reaction temperature was tuned to
a 160°C
b 200°C

3.3. Effect of reaction temperature on product morphology: To evaluate the effect of reaction temperature on product morphologies, we conducted a set of control experiments. Fig. 3 shows SEM images of products obtained using the standard procedure, except that the reaction temperature was changed. As reaction temperature tuned from 180–160 to 200°C, the resultant products no longer exhibited the shape of porous microspheres. It is not unreasonable to expect that increasing/decreasing the reaction temperature will vary the reduction rate for AgNO₃ and thus the deposition rate for Ag atoms. The synergetic effect of oxidative etching and crystal growth played an important role in the formation of porous Ag microspheres in high purity. When the temperature varied, the oxidative etching strength would be either enhanced or dampened. In short, these results of control experiments showed that an appropriate reaction temperature was essential for the formation. Either higher or lower temperature may cause the change of reduction rate of Ag and also the oxidative etching strength, which led to the variation of crystallinities and shapes of final products.

3.4. Effect of Ag precursor on product morphology: We also evaluated the effect of Ag precursor on the final product morphologies. As shown in Fig. 4, when AgCl was replaced by AgNO₃ and AgBr, the resultant products were dominated with the shape of polyhedron and wire, respectively. It indicated that the anions involved in the precursor played an important role in influencing the final product morphologies. Compared with AgCl/Ag, the standard potential of Ag⁺/Ag and AgBr/Ag are different (AgCl/Ag 0.2223 V; Ag⁺/Ag 0.7996 V; and AgBr/Ag 0.07133 V). As a result, the variation of Ag precursor can significantly cause the change of reduction rate of Ag precursor, which may impact the concentration of Ag atoms in the system and thus growth pattern and morphology of final products.

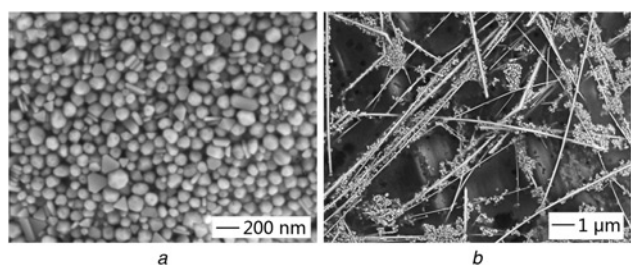


Fig. 4 Effect of Ag precursor on the morphology of final products. SEM images of products obtained using the standard procedure, except that the AgCl was replaced by same amounts of
a AgNO₃
b AgBr

4. Conclusion: In summary, Ag microspheres with a porous structure have been successfully prepared via a simple, one-pot synthesis. The use of Cu²⁺ to mediate the reduction of AgCl by oleylamine was found to be essential to promote the formation of such unique structure. We conducted several control experiments to reveal the effects of type of additives, amount of CuCl₂, type of Ag precursor and reaction temperature on product morphologies. The method described in this Letter that using metallic cations to mediate the reduction of metal halide could be potentially extended to similar synthesis of other noble metals.

5. Acknowledgments: This work was supported by the foundation of the National Natural Science Foundation of China (grant no. 21175059).

6 References

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