

Novel Syntheses of Silica-Gold Core-Shell Particles

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ABSTRACT

Methods for the synthesis of silica-gold core-shell particles presented in literature are not considered commercially viable due to the need for unacceptably high reaction temperatures, the use of light-sensitive reagents and the use of *ex-situ* gold seeding adding an undesirable number of steps to the syntheses. We have developed two novel syntheses that eliminate these issues.

Syntheses initially require the formation and capping of silica spheres with (3-mercaptopropyl)-trimethoxysilane (MPTMS). The first method involves only these MPTMS capped silica spheres and the reduction of AuCl_4^- at slightly elevated temperatures which leads to the formation of thick gold shells on the silica spheres. The second method involves these MPTMS capped silica spheres and the reduction of AuCl_4^- at lower temperatures with external reducing agents NH_2OH and NaBH_4 , to control the seeding and growth of the gold shells around the spheres and allow more control over the resulting thinner gold shells.

Keywords: gold nanoparticles, core-shell, silica, surface plasmon resonance

1 INTRODUCTION

Gold nanoparticles exhibit different properties to those of the bulk metal. One of the most notable differences between the two is the gold nanoparticles' interesting optical properties due to surface plasmon resonance (SPR) effects. This SPR phenomenon is also observed in gold shell particles. The wavelength of these SPR absorptions and hence the observed colour of such particles is dependent on the dielectric constant of the gold metal and that of the surrounding medium, as well as the size and shape of the particles. Hence, by manipulating the size and shape of the particles, the absorption characteristics and observed colour can be changed.

The synthesis of silica-gold core-shell particles has been presented in literature many times before [1–5]. However, the syntheses set out previously, involve parameters that compromise the processes' commercial attractiveness. These parameters include factors such as the use of undesirably high temperatures [1,4], the use of light-sensitive reagents [2–4], and the use of *ex-situ* seeded gold nanoparticles [3–5]. High temperatures are required in these

syntheses for the calcination of silica spheres to facilitate the binding of the gold shells [1], and to promote and speed up the nanoparticle synthesis reactions [4]. A commonly used reagent in previously devised syntheses is the solution known as "K-gold". This solution is used as a gold precursor for the growth of a gold shell onto a surface already decorated with gold nanoparticle seeds and must be used in conjunction with other reducing agents such as NaBH_4 [2,3] or formaldehyde [4]. This "K-gold" solution is commonly used as it has been shown to produce full gold shells with varying thicknesses, but it is light-sensitive and must be stored in the dark and used promptly, thus complicating the overall synthesis process. The use of *ex-situ* seeded gold nanoparticles is involved in many syntheses [3–5], often in conjunction with "K-gold" solution, but the formation of these seed particles *ex-situ* complicates the synthesis by preventing a one-pot approach from being used.

Two novel methods of silica-gold core-shell particle synthesis have been developed and are described in this work. These methods were devised to increase the commercial viability of silica-gold core-shell particle synthesis. The first synthesis requires slightly elevated temperatures but few reagents and few steps. Due to its simple nature, this synthesis does not allow for much control over the resulting particles. However, it does represent an important development in the synthesis of these particles as it is much simpler than syntheses reported previously and does not require temperatures over 100 °C or the use of light-sensitive reagents. The second synthesis requires only lower temperatures less than 50 °C but does involve a number of steps which afford much more control over the resulting particles. While this synthesis does involve the use of NaBH_4 , the need for "K-gold" solution has been removed and the synthesis can be carried out at lower temperatures.

Although these new methods themselves require some optimisation and scale up work before they can be commercially viable, they do present a development towards a more commercially viable process of achieving these silica-gold core-shell particles.

2 MATERIALS AND METHODOLOGY

All chemicals were used as received and were of analytical grade unless otherwise stated. All water used was distilled and the ethanol was absolute unless otherwise specified. Sodium borohydride powder ≥98%, (3-mercaptopropyl)-trimethoxysilane (MPTMS) 95%, and tetraethylorthosilicate (TEOS) ≥99%, were purchased from Sigma-Aldrich. Hydroxylammonium chloride ≥99% was purchased from AnalaR. Ammonia solution 35% AR was purchased from Pure Science.

2.1 Preparation of MPTMS Capped Silica

Silica spheres were prepared via a modified Stöber process [5,6]. 1.0 mL of water and 1.5 mL of TEOS were added to 50 mL of ethanol and heated to 40 °C under continuous stirring. When the solution reached 40 °C, 4.2 mL of NH₃ was added and the solution was stirred and kept at 40 °C for 3 hours. Another 1 mL of TEOS was added and stirring and heating continued for a further 3 hours. This reaction mixture was added to approximately equal volume of drum acetone and shaken vigorously to break the microemulsion state before being centrifuged at approximately 2500 rpm for 30 minutes. The sample was then washed with ethanol three times and washed once with water before being redispersed in water.

Approximately 0.5 g of silica (dispersed in water) was added to 1.56 mL of MPTMS and left in a shaking water bath at 50 °C for 7 days [7]. The reaction mixture was centrifuged at approximately 2500 rpm for 30 minutes. The sample was washed with ethanol three times before being redispersed in ethanol.

2.2 First Synthesis Method

1mL of 1 wt% MPTMS capped silica and 50 µL of 0.156 M AuCl₄⁻ solution were added to 19 mL of water and stirred and heated to 98 °C for 2 hours.

2.3 Second Synthesis Method

1 mL of 1.2 wt% MPTMS capped silica spheres and 50 µL of 0.156 M AuCl₄⁻ solution were added to 9 mL of ethanol and left at room temperature for 24 hours. 10 µL of 0.0074 M NaBH₄ solution in ethanol was then added and left at room temperature overnight. The sample was washed in ethanol via centrifugation, 0.209 mL of 0.19 M NH₂OH was added and then put in a shaking water bath at 50 °C for 6 hours until the yellow colour of the AuCl₄⁻ was lost. The sample was cooled and another 50 µL of 0.156 M AuCl₄⁻ solution was added and the sample was returned to the shaking water bath at 50 °C for another 6 hours until the yellow colour was lost again, this addition was repeated so the sample contained a total of 150 µL of AuCl₄⁻ solution. The sample was removed from the shaking water bath 6 hours after the final addition.

2.4 Characterisation

UV-Visible absorption spectroscopy was carried out on a Varian Cary 100 scan spectrometer.

Scanning electron microscopy (SEM) was performed on a JEOL-6500F Field Emission Scanning Electron Microscope and a JEOL-JSM-6610LA Scanning Electron Microscope.

3 RESULTS AND DISCUSSION

The prepared silica was characterised using SEM to confirm that the desired MPTMS capped silica spheres were obtained before gold shell syntheses were carried out. The capped spheres were found to have an average particle diameter of 200 nm.

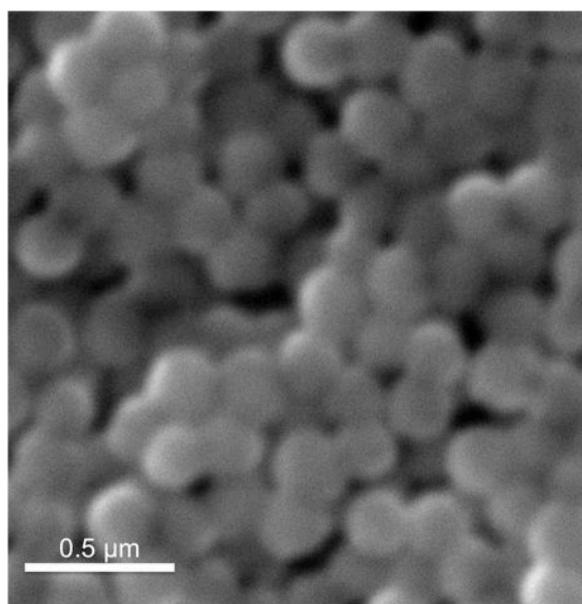


Figure 1: SEM image of MPTMS capped silica.

3.1 First Synthesis Method

The first synthesis method required slightly higher temperatures but was quick and simple to perform, requiring only three reagents. This method eliminated the need for any light-sensitive reagents and minimised the time and work needed to produce silica-gold core-shell particles.

During the synthesis a distinct colour change was observed; the sample lost its yellow colour and developed a dark orange/brown colour. It was also observed that the resulting sample appeared different colours in reflected light and transmitted light, appearing orange in reflected light and blue in transmitted light, as seen in Figure 2.



Figure 2: Sample synthesised via the First Synthesis Method appearing orange in reflected light (left) and blue in transmitted light (right).

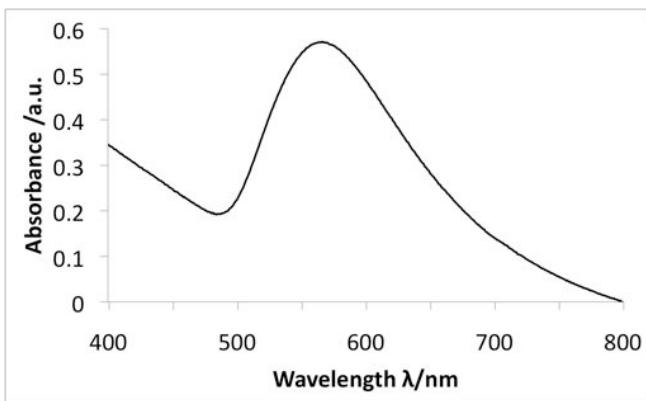


Figure 3: UV-Vis absorption spectrum of sample synthesised via the First Synthesis Method.

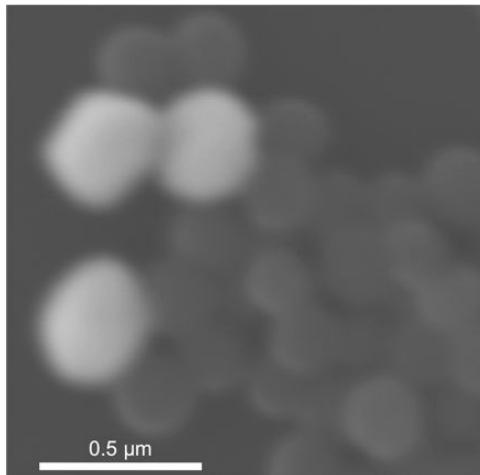


Figure 4: SEM image of sample synthesised via the First Synthesis Method, showing gold shells (white) on MPTMS capped silica spheres (grey).

SEM imaging of the sample revealed the size and composition of the core-shell particles formed. The core-shell particles were found to have an average diameter of 375 nm.

3.2 Second Synthesis Method

The second synthesis method involves many more steps than the first method, but allows for more control over the resulting gold shells, and requires lower temperatures. The synthesis is carried out in a one-pot approach by utilising *in-situ* seeding of gold nanoparticles. The synthesis also eliminates the need for the light-sensitive reagent “K-gold” but still involves sodium borohydride.

The initial AuCl_4^- present in the synthesis must be left for 24 hours to allow for the gold to fully adsorb into the MPTMS capping layer on the silica spheres. From here, the strong reductant NaBH_4 can be added to seed the gold nanoparticle growth on the surface of the core particles. As hydroxylamine will only reduce gold onto a surface that already has gold on it [8], if it is the only reductant in the system, the gold will be reduced onto the silica surfaces. Hence, the washing step involved in this synthesis after the reduction by NaBH_4 is important to ensure the additional gold precursor is reduced by hydroxylamine onto the surface and not into the solution, forming large gold aggregates.

The sample synthesised via the second synthesis method was observed to have a similar colour and the same dichroic behaviour of the previously synthesised sample, shown in Figure 5. However, the UV-Vis absorption spectrum of this sample showed a slightly higher wavelength absorbance peak at 570 nm, as shown in Figure 6.

SEM imaging showed the size and composition of these core-shell particles. The gold shells were found to be quite smooth and the average particle diameter of this sample was found to be 220 nm, as the MPTMS capped silica spheres were found to have a diameter of 200 nm, the shells were deemed to have a thickness of approximately 10 nm. This indicates that the resulting shells are considerably thinner than those in the sample synthesised via the first synthesis method. This suggests that the additional steps involved in this second synthesis method allows for more control over the resulting particles to afford thinner shells.



Figure 5: Photograph of sample synthesised via Second Synthesis Method in ambient lighting (mostly reflected light).

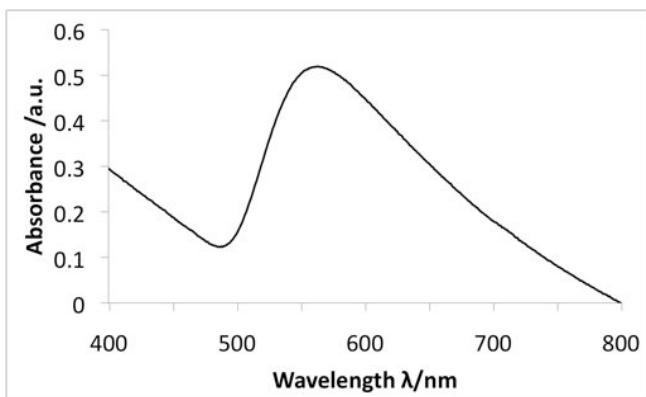


Figure 6: UV-Vis absorption spectrum of sample synthesised via the Second Synthesis Method.

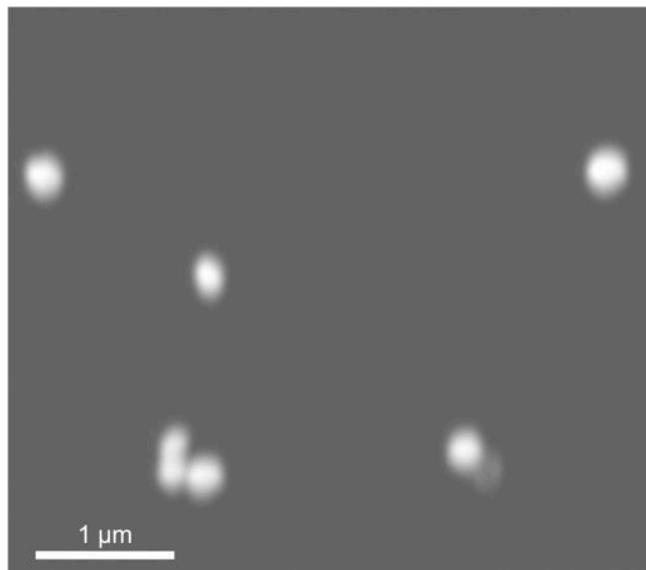


Figure 7: SEM image of the sample synthesised via the Second Synthesis Method.

4 CONCLUSIONS

Two methods for synthesising silica-gold core-shell particles were devised which address some factors identified in previously reported syntheses that compromise those syntheses from becoming commercially viable.

The first novel method involves only few reagents and few steps and does not require temperatures over 100 °C. This synthesis has little control over the thickness of the resulting particles but is much simpler and likely to be more cost effective than previously reported syntheses.

The second novel method involves a number of steps but this provides much more control over the resulting particles. Also the synthesis does not require temperatures over 50 °C and eliminates the need for “K-gold” solution.

Both syntheses successfully produced smooth, spherical gold shells of either 10 nm or 90 nm thickness surrounding MPTMS capped silica spheres of 200 nm diameter.

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