Synthesis of Au doped Ag nanoclusters and the doping effect of Au atoms on their physical and optical properties

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Abstract
Bimetallic noble metal nanoclusters (NCs) are an emerging topic of metal clusters due to their distinguishing characteristics compared to monometallic clusters. Doping of different noble metals in other clusters is an effective strategy for tailoring their functionalities for specific applications and synergistic effects. Obtaining single-heteroatom doping is desirable but still very challenging to date. Herein, 2,4-dimethylbenzenthiol (2,4–DMBT) protected Ag/Au alloy NCs (ca. 2–3 nm) were synthesized via a wet chemical one-pot process. The effect of the number of Au atoms in Ag NCs on their optical properties and bandgap was investigated. We found that the change of the absorption peak positions of the Ag NCs was influenced by the presence of Au atoms. Besides, we found that the HOMO–LUMO peak has appeared without a significant change in cluster size during synthesis. Ag/Au alloy NCs are characterized by UV–visible spectroscopy, transmission electron microscopy (TEM) and scanning electron transmission microscopy (STEM).

1. Introduction
Since the last decade nanoclusters (NCs) have become a flourish research topic in catalysis, biomolecule-sensing, bio-labeling, medical therapy, drug delivery, and sensors, due to their interesting optical and electronic properties and chemical stability [1–8]. The noble metal clusters are interesting in technological applications due to free electronic cloud and good electronic conductivity, or strong resonance effect (Mie surface plasmon resonance) [9]. Clusters in principle, are the combination of two to thousands of atoms bounded by interatomic force [10, 11]. These NCs have a finite number of atoms and exhibit molecule-like properties with discrete electronic states arising from carrier confinement effects [12]. Additionally, it has been suggested the photoemission from these alloy NCs may arise from the electronic transitions in the metallic core (singlet-singlet), or at the surface, the charge transfer from ligand- to-metal be equally involved [13]. The bimetallic instead of monometallic noble metals have enhanced catalytic activity based on size, shape, interaction with supporting materials, oxidation state, and quantum size effects [9, 14–16].

The specific optical properties of the atomic cluster making them unique physical objects which differ from molecules and bulk matters [17, 18]. By changing the number of atoms, constituents, and surface to volume ratio, surface plasmon resonance (SPR) and other properties of NCs can be tuned due to quantum confinement effect [19, 20]. Alloy NCs are more favorable than single metal NCs because of its synergistic effect and the easy tunability of its optical and physical properties by changing the number, size, structure, types and surrounding environment of its constitutents [6, 15, 17, 21–23]. For the electronic and optical perspective, making the heteroatoms by doping it will be more prominent, if dopant can take place into the kernel of NCs, as the kernel...
dictates the HOMO–LUMO gap and optical properties of NCs [20]. By doping a single foreign atom into an opposite cluster the magnetic, catalytic, physical, optical and electronic properties of NCs dramatically changes [24–26].

There are plenty of physical and chemical methods to synthesis alloy NCs (i.e. sputtering technique, helium droplet, Ligand-exchange and galvanometric, etc), but most commonly been produced in aqueous solutions [16, 19, 27]. However, it is still challenging to synthesis alloy NCs of controllable size and composition [20]. From the theoretical point of view, synthesizing nanoalloys was a great challenge due to the complexity of their energy landscape [17]. In case of pure Au and Ag clusters to be replaced by any atoms of them is feasible [6], because of isomorphism of Ag (1.34 Å) and Au (1.34 Å) atoms, their crystalline lattice parameters are very similar (4.0786 Å for Au; 4.0862 Å for Ag) [28], in face-centered cubic lattice. Both elements have a single s valance electron [25, 29]. The high advancement of Au and Ag accentuated differences in their chemical and physical properties exist. Comparatively, Au is more biocompatible and is used for bio-medicine while Ag is mostly used as an antibacterial and anti-fungal agent for its cytotoxicity [14, 30]. The catalytic activity of Au is comparatively high than Ag and that is why it has been used for the catalytic reduction of aldehyde and CO oxidation [29, 30].

Herein, we used a wet chemical method to produce Ag/Au alloy NCs with few Au atoms to form Ag rich alloy NCs. The synthesized NCs have different optical properties than monometallic Ag NCs (figure S1 is available online at stacks.iop.org/MRX/7/016506/mmedia). There is plenty of work that has been done by substituting either Au or Ag atoms in any of the clusters of the other element to form alloy NCs, which leads to dramatic changes in the optical and electronic properties [6, 14]. However, according to our knowledge, very rare studies about short route synthesis of alloy NCs and their HOMO-LUMO peak appearances during synthesis (figure 1(b)). According to theoretical calculation, we doped one Au atom with 628 Ag atoms (equation (1)) (figure 1(a)) [16]. By the addition of a single foreign atom in another cluster can vary its properties [26]. The absorption peak shifts from the UV region for Ag NCs (figure S1) to the visible region for Ag/Au alloy NCs (figures 1(a), (b)), due to Au atoms embedment into Ag clusters. The bandgap of these alloy NCs was found (figure 1(c)). We also found that by the further increment of Au precursor not only the peak further shifted to higher wavelength but also HOMO–LUMO peak has appeared during synthesis (figure 1(b)), without any significant change in particle sizes (figure 3). Besides, different characterization i.e. UV–visible, SPR, TEM, STEM, and EDS were carried out to elucidate the NCs and evaluate their properties.
2. Experimental

2.1. Materials
All materials used in this study were of analytical grade and used as such without purification. Tetrachloroauric (III) acid (HAuCl₄·3H₂O) (Shanghai Kefeng Industry & Commerce Co. Ltd), silver nitrate (AgNO₃, ≥98%) (From Sinopharm Chemical Shanghai), sodium borohydride (NaBH₄, 99%) (from Aladdin, Shanghai, China) 2,4-Dimethylebenzenethiol (From MACKLIN Shanghai, China) were purchased.

2.2. Synthesis of NCs
AgNO₃ (162 mg) was dissolved in 12 mL ethanol and stir in an ice bath, then an aqueous solution of HAuCl₄·3H₂O (0.1 mol L⁻¹, 40 μl) was added. After 40 min 300 μl 2,4-dimethylebenzenethiol was added with constant stirring. The color of the solution changed quickly from yellow to yolk. After 3 h of continue stirring the ice bath was removed and added 77 mg NaBH₄ dissolved in 5 mL ice-cold ethanol with agitation. The color of the solution changed from the yolk to dark brown which indicates the synthesis of NCs. The solution was stirred for 24 h. The sample was centrifuged for 10 min at 10 k rpm to remove the supernatants from green color precipitates, which was dried in the furnace at 50 °C for 24 h. The color of the NCs changed from greenish to yellow color after complete dryness. It may be due to the wrapping of gold by silver atoms, which means Ag covered the whole surfaces of NCs with a small Au internal core [22, 29].

2.3. Instrumentation
All glassware and Teflon-coated magnetic stirrer bar were thoroughly cleaned with aqua regia, rinsed with deionized water, and then dried in an oven prior to use. The UV--visible absorption spectra were recorded on a JASCO V-550 UV-vis spectrophotometer in a glass cuvette at ambient temperature. For SPR Omni−λ300 tuneable light source with uniform light output from zolix supplier was used. PL (photoluminescence) study was carried out on an F-7000 fluorescence spectrophotometer (Hitachi, Japan). Transmission electron microscope (TEM) images were recorded with a TECNAI 200KV instrument (FEI USA). The dispersion was diluted with ethanol, drop cast on a carbon-coated copper grid and dried at ambient conditions. STEM (Scanning Transmission Electron Microscope): (FEI Titan Themis Z, America) were used for HAADF-STEM images and for EDS (Energy-dispersive x-ray spectroscopy).

3. Results and discussion

3.1. UV-visible spectroscopy
The absorption peak of Ag/Au alloy NCs at 473 nm arises from a combination of several transitions levels that fall in the range of 450–500 nm [1]. These high energy transitions can be mainly classified as interband transitions, where most transitions arise from p atomic orbitals of the ligand S atoms into orbitals with a primary character from the p atomic orbitals of the core Au and Ag atoms. The presence of Au atoms in Ag rich alloy NCs caused a significant difference in optical properties (figure S1). Similar results were observed in the case of a single Ag atom incorporation into Au clusters [2]. On the other hand, further, an increase in Au atoms into Ag clusters, the absorption peak shifted to a higher wavelength (ca. 490 nm) (figure 1(b)). The absorption peak of the as-synthesized Ag/Au NCs shifts to the ultraviolet region (figure 1(a)). This manifests two phenomena, the first one is due to the higher molar ratio of Ag with respect to Au precursor [15, 31]. As for pure Ag NCs absorption peak is in the UV region (ca. 360 nm, figure S1a). According to Kumara et al as the ratio of Ag increasing with respect to Au the peaks at visible region disappear and shifting towards the UV region [2]. Conversely, the peak will shift from 396 to 520 by increasing the amount of Au and vice versa [16, 28]. In the case of Au as a core while Ag as a shell the absorption band will be at the visible region around 400 nm [28]. Herein, we observed the sharp peak at UV region which makes this statement strong that Au is a core whilst Ag is the shell. Due to the small amount of Au precursor with respect to Ag, the peak at visible region shifts and a sharp peak at the UV region was observed (figure 1(a)). Whilst, the peak broadness at 450 nm probably due to the segregation of Ag atoms on the clusters surfaces [29, 32]. By increasing the Au atoms quantity into Ag NCs the absorption peak further shifts to longer wavelength (ca. 490 nm+) (figure 1(b)) [33]. In the case of only Au atoms, the peak for NCs is at 520 nm [8].

The absorption band in the visible region is due to surface plasmon resonance (SPR) which is related to the two constituents elements of the alloy NCs [29]. In contrast, small molecular clusters with low electron density require high energy for electrons excitation (quantum confinement effect). The wide peak observed at 450 is due to clusters 2–4 nm (polydispersity) (figure 1(a)), while the peak at 370 is very sharp (monodispersity) representing the clusters less than 2 nm in size (figure S2). By the same experiment, we elucidated time-dependent optical properties of Ag/Au alloy NCs via UV-visible spectroscopy and compared them with the
corresponding clusters sizes at each time (figure 1(b)). We found that there is no dominant change in the size of clusters between 2 h and 24 h during synthesis via magnetic stirring at ambient temperature, as well as in the main absorption peak (ca. 490 nm). However, another peak emerged after 10 h during synthesis at (ca. 640 nm), which illustrates HOMO-LUMO transitions in the clusters. The enhancement of this peak caused by Localized Surface Plasmon Resonance (LSPR) [21]. That is also the manifestation of surface charges that have been produced on the clusters with the passage of time during synthesis.

The optical bandgap of the Ag/Au alloy nanoclusters showed in figure 1(c). Bandgap energy for insulators is greater than 4 eV while for semiconductors is less than 3 eV [34]. In bulk, metal conduction occurs due to the overlap of valance and conduction bands, whilst decreasing size up to quantum dot (less than 5 nm) then these NCs behave as semiconductors and conduction will occur due to crossing of electrons from valance to conduction band means an energy gap exist [10]. This is the manifestation of quantum confinement effect for these clusters.

3.2. Surface plasmon resonance (SPP)
Plasmon is the coherent collective oscillation moment of the electronic cloud of the NCs in the presence of electromagnetic field [29]. When there is resonance between the frequency of alternating electric field of the electromagnetic radiation and the oscillation of free electrons then absorption occurs due to the fulfillment of plasmon resonance condition [22]. The final extinction cross-section in the case of SPP composed of absorption and scattering is given as a summation of all-electric and magnetic multipole oscillations [16, 35].

The SPR band observed at 396 nm for Ag/Au alloy NCs clusters due to a high concentration of Ag. On the other hand, by increasing the concentration of Au, peak will shift towards 520 nm [16, 21, 29]. The SPR peak at 472 nm represents the exact composition of Ag/Au alloy NCs (figure 1(a)) [1, 21]. Zheng et al reported that the extinction peaks for Ag, Au-Ag alloy and Au NCs locate at 396, 470 and 522 nm, respectively [21]. The absorbance peak for Ag NCs at 396 is due to SPP [16]. Plasmon resonance not only depends on the main constituents of the sample but also depends on protecting the medium and solvent due to different refractive indexes [10].

Comparatively, Ag exhibits intense SPR whilst Au shows a broad and damped one because of their different electronic configuration of d orbitals [29]. As metal NCs show interesting optical properties due to SPP at visible light with specific frequency [22]. In the case of bimetallic NCs, the outer shell determines the optical properties of noble metal atoms [7]. Besides, the SPR peak position also depends on the ratio of starting precursors of the alloy Ag and Au [14].

3.3. Photoluminescence (PL)
The optical properties of metal NCs are due to the interaction between the incoming light and the free electrons [22], which depend on the constituents and size of alloy NCs (confinement effect). The Ag and Au are two interesting and well-studied elements which are famous for their distinctive optical properties [22]. By doping, even a single atom of Au or Ag in consecutive clusters can change their PL property [6]. By changing the molar ratio of Au or Ag, the properties of alloy clusters i.e. PL, toxicity and other properties can be tuned [36].

In PL spectroscopy, the maximum emission spectrum centered at 570 nm was observed when the sample was excited at 365 nm (figure 1(d)). The effect on the emission spectrum was observed by changing the excitation wavelength with a 20 nm increment (figure 1(e)). As the excitation wavelength increases from 320 to 360 nm the PL intensity increases, beyond that the PL intensity decreases without a change in the peak position. The occurrence of PL peak at the same wavelength even though at different excitation wavelengths points the monodispersity of the particles and also shows that the emission from a single source.

3.4. TEM, STEM, and EDS
The size and morphology of these clusters were examined via TEM and STEM. The agglomeration tends the particles to a relatively large size. Some clusters of size less than 2 nm, but the ratio of these clusters is small as compared to the clusters from 2 nm to 4 nm. The histogram of these NCs count distribution versus size shows that the NCs of size 2 to 3 nm are much more (figure 2(c)). Which may be counted via theoretical and experimental calculations [37]. From the molar ratio of gold precursor, Au atoms can be calculated from equation (1).

\[ \chi_{Au} = \frac{n}{m - 2n} \]  \hspace{1cm} (1)

Whereas, m and n are the moles of Ag and HAuCl₄, respectively [16]. The result shows the presence of one Au atom in 628 Ag atoms for clusters. The molar ratio of Au with respect to Ag is less than 1:100, that’s why a specific peak for Au in EDS was not seen (figure 2(f)). In figure 4, STEM images through HAADF show Ag/Au alloy composition by addition of more Au atoms incorporation in Ag clusters to form Ag/Au alloy NCs via the same
Figure 2. TEM images at a different magnification of Ag/Au NCs stabilized by 2,4-Dimethylbenzenethiol as a ligand. Scale bar (a) 50 nm (b) 4 nm. HAADF-STEM images at different magnification. Scale bar (c) 5 nm (d) 10 nm, (e) Histogram of the concern nanoclusters. (f) EDS spectrum of Ag/Au alloy NCs.

Figure 3. (a)–(d) TEM images at a different time during synthesis with scale bar 3 nm, 2 nm, 3 nm, and 3 nm, respectively. (e) EDS spectrum of Ag/Au alloy NCs.

protocols in a different experiment. These images are the clear manifestation of Ag rich Ag/Au alloy NCs. Eventually, not only the absorbance peak further shifted towards higher wavelength, but by which also clarified the plasmon peak at ca. 640 nm (figure 1(b)).
4. Conclusion

Herein, the Ag/Au alloy NCs was synthesized through the one-pot wet chemical method with a small amount of Au precursor for the sake of few Au atoms incorporations to form Ag rich alloy NCs. Different techniques (i.e. UV-vis, SPR, PL, TEM, STEM, and EDS) have been used for interpretation of Ag/Au alloy NCs size, composition, physical and optical properties. A significant effect on optical properties by emerging of few Au atoms to form Ag rich alloy NCs have been observed. The absorption peak shifted from UV region to visible region by incorporation of few Au atoms into Ag clusters. The increase of the Au atoms into Ag clusters to form Ag/Au alloy NCs the peak shifted further towards higher wavelength. We also observed that during synthesis HOMO-LUMO peak has appeared at ca. 640 nm, without significant change in cluster size. Moreover, the optical bandgap of Ag/Au alloy NCs through UV-vis absorption spectrum was found, which can be tuned by varying the size and number of different constituents in alloy NCs.

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Note

There is no conflict of interest.

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References

[1] Wang Z, Senanayake R, Aikens C M, Chen W-M, Tung C-H and Sun D 2016 Nanoscale 8 18905–11
[2] Kumara C and Dass A 2012 Nanoscale 4 4084–6
[3] Du W, Jin S, Xiong L, Chen M, Zhang J, Zou X, Pei Y, Wang S and Zhu M 2017 JACS 139 1618–24
[4] Wang S, Jin S, Yang S, Chen S, Song Y, Zhang J and Zhu M 2015 Science Advances 1 e1500441
[5] Tong L, Cobley C M, Chen J, Xia Y and Cheng J X 2010 Angew. Chem. Int. Ed. 49 3485–8
[6] Negishi Y, Iwai T and Ide M 2010 Chem. Commun. 46 4713–5
[7] López Lozano X C, Mottet C and Weisgerber H-C 2013 J. Phys. Chem. C 117 3062–8
[8] Zvyagin A I, Perepelitsa A S, Ovchinnikov O V, Smirnov M S and Ganeev R A 2019 Mater. Res. Express 6 11

Figure 4. STEM-EDX elemental mapping images of Ag and Au through HAADF of Ag/Au alloy NCs stabilized by 2,4-dimethylbenzenethiol as a ligand.
[9] Bucceta D, Piñeiro Y, Vázquez-Vázquez C, Rivas J and López-Quintela M A 2014 *Catalysts* **4** 356–74
[10] Corain B, Schmid G and Toshima N 2011 *Metal Nanoclusters In Catalysis And Materials Science: The Issue of Size Control* (Amsterdam: Elsevier) eBook ISBN: 9780080555003
[11] Yang H, Lei J, Wu B, Wang Y, Zhou M, Xia A, Zheng L and Zheng N 2013 *Chem. Commun.* **49** 300–2
[12] Heer W A D 1993 *Rev. Mod. Phys.* **65** 611
[13] Mishra D, Lobodin V, Zhang C, Aldeek F, Lochner E and Mattoussi H 2018 *Phys. Chem. Chem. Phys.* **20** 12992–3007
[14] Kumara C and Dass A 2011 *Nanoscience* **3** 3064–7
[15] Wang A-Q, Liu J-H, Lin S, Lin T-S and Mou C-Y 2005 *J. Catal.* **233** 186–97
[16] Zhang Q, Lee I Y, Yang J, Boothroyd C and Zhang J 2007 *Nanotechnology* **18** 245605
[17] Ferrando R, Jellinek J and Johnston R L 2008 *Chem. Rev.* **108** 845–910
[18] Jin R, Zhao S, Xing Y and Jin R 2016 *Cryst. Eng. Comm.* **18** 3996–4005
[19] Liu S, Chen G, Prasad P N and Jin R 2011 *Nanoscale* **3** 3064–7
[20] Wang A-Q, Liu J-H, Lin S, Lin T-S and Mou C-Y 2005 *J. Catal.* **233** 186–97
[21] Rodríguez-González B, Burrows A, Watanabe M, Kiely C J and Marzín I. M. I. 2005 *J. Mater. Chem.* **15** 1755–9
[22] Campos A, Troc N, Cottancin E, Pellarin M, Weissker H-C, Lermé J, Kociak M and Hillenkamp M 2018 *Nat. Phys.* **15** 275–80
[23] Guodong S, Xi K, Shan J, Xiaowu L, Daqiao H, Shuxin W and Manzhou Z 2017 *Acta Physico-Chimica Sinica* **34** 799–804
[24] Tlahuice-Flores A 2013 *J. Nanopart. Res.* **15** 1771
[25] Martins M and Wurth W 2016 *J. Phys. Condens. Matter* **28** 503002
[26] Dou X, Yuan X, Yu Y, Luo Z, Yao Q, Leong D T and Xie J 2014 *Nanoscale* **6** 157–61
[27] Guisbiers G, Mendoza-Cruz R N, Bazán-Díaz L, Velázquez-Salazar J S, Mendoza-Perez R, Robledo-Torres J A, Rodríguez-Lopez J L, Montejano-Carrizales J M, Whetten R L and José-Yacaman M 2015 *ACS Nano* **10** 188–98
[28] Wei L, Qi W, Huang B and Wang M 2013 *Comput. Mater. Sci.* **69** 374–80
[29] Mingos D M P and Broda J 2014 *Gold Clusters, Colloids And Nanoparticles I* (Berlin: Springer) ppISBN 978-3-319-07848-9
[30] Dharma J, Piala A and Shelton C 2009 Simple Method of Measuring the Band Gap Energy Value of TiO2 in the Powder Form using a UV/Vis/NIR Spectrometer (Application Note)
[31] Link S, Wang Z.L and El-Sayed M 1999 *J. Phys. Chem.* **B** 103 3529–33
[32] Ganguly M, Jana J, Pal A and Pal T 2016 *RSC Adv.* **6** 17683–703
[33] Hu K-J, Plant S R, Ellis P R, Brown C M, Bishop P T and Palmer R E 2015 *JACS* **137** 15161–8