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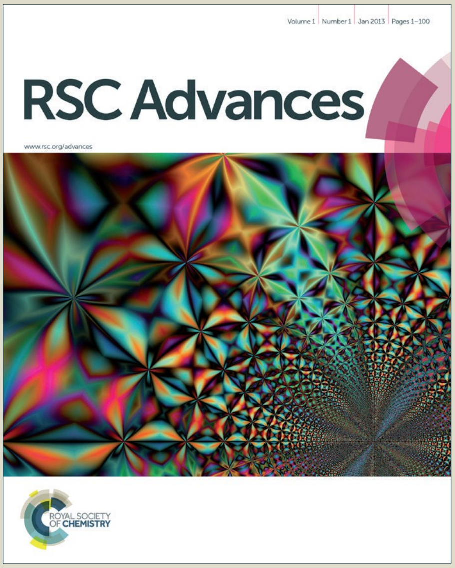

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Direct synthesis of size-tailored bimetallic Ag/Au nano-spheres and nano-chains with controllable compositions by laser ablation of silver plate in $HAuCl_4$ solution

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Abstract:

The direct conversion of bulk silver metal to size-tailored bimetallic silver-gold (Ag/Au) nano-spheres and nano-chains with controllable compositions has been achieved by laser ablation of Ag target in $HAuCl_4$ solution. Taking advantage of the replacement reaction between Ag and Au ions, the average sizes of the bimetallic Ag/Au nano-particles substantially decreased from tens of nanometers to sub-2 nm with the increasing of $HAuCl_4$ concentration(0.12~4.59mM). Meanwhile, the relative ratio of Ag and Au elements in individual Ag/Au nano-particles has been systematically changed from about 9:1 to 1:9. The UV-visible absorption spectra of the Ag/Au nano-particles significantly red shifted from about 400 nm to 785 nm. The designed simplistic, single-step, versatile strategy does not require seed preparations, intermediate workup process and any potential toxic surfactants. This will offer a convenient and valuable new way to fabricate bimetallic nano-particles with desired structures and functions.

Electronic Supplementary Information (ESI) available: The elemental mapping images of Ag and Au in bimetallic nano-particles. UV-visible absorption spectra of the pure Ag and Au nano-particles by laser ablation of Ag and Au target in liquid.

Introduction

Constructed by more than one component and intergraded with the two-phase hybrids, bimetallic nano-particles (NPs) have received increasing attention as attractive multifunctional materials.[1-6] Compared with pure nano-particles, bimetallic nanostructures with controllable structures exhibit remarkable electron transport, improved catalytic performance, and excellent luminescent properties, *etc*.[4-7] In particular, bimetallic nano-objects with exceptionally small crystal size of a few nanometers show strong localized surface Plasmon resonance (LSPR) absorption in visible or near-infrared (NIR) region. This has significant implications for super-active catalysts, faster responsive biosensor, photodynamic-therapy, and novel light-emitting devices, *etc*. Increasing evidence has shown that the excellent properties of bimetallic NPs are strongly dependant on their compositions, sizes, and shape structures. Consequently, tremendous efforts have been devoted to the controllable synthesis of bimetallic NPs. The most common strategy is based on the reduction of the metal precursors in the presence of stabilizing agent. It requires the simultaneous and uniform reduction to occur at similar temperature. Xie *et al*. fabricated Ag/Au nano-boxes with sizes ranging from 70~80nm by the co-reduction of $AgNO_3$ in $HAuCl_4$ solution.[5] Novel trimetallic Au_{oct}@PdPt core-shell nano-particles with length of ~61 nm have been generated by using the simultaneous reduction of multiple metal precursor with ascorbic and hydrazine.[4] By using sodium borohydride, dodecylamine, hexadecanediol, oleic acid, oleylamine, and octadecene, *etc*, the sub-10nm Au/Ag nano-particles were synthesized by the reduction of $HAuCl_4$ and $AgNO_3$ by $NaBH_4$.[3,6-7] It should be noted that these reports mainly focused on the synthesis of bimetallic NPs with large-sizes or the formation of smaller nano-colloids via some potential toxicity issues. The toxicity issues arise from inevitable purification procedures of nano-particles via standard chemical fabrication based on the reduction of a precursor in complicated stabilizers. The schemes which are environmentally friendly or have negligible toxicity for the preparation of bimetallic NPs with controlled structures remain incomplete.

Laser ablation in activated liquid is an attractive green technique for the fabrication of novel nano-structures.[14-17] It is a new approach with high non-equilibrium processing character. It offers a unique hot plasma and high pressure. Herein, a versatile and simple strategy has been designed by use for the controllably synthesis of bimetallic Ag/Au nano-particles directly from Ag target based on laser ablation in $HAuCl_4$ solution. The $HAuCl_4$ concentration plays an import role in the synthesis of size-controlled bimetallic Ag/Au nano-spheres during laser ablation of Ag target in anhydrous alcohol solution. The mean diameters of the mono-disperse bimetallic nano-structures decrease from about 32.5nm to 1.8nm with the increasing of $HAuCl_4$ from 0.12 to 4.59mM. Meanwhile, the relative ratio of Ag and Au elements in individual Ag/Au nano-spheres changed from about 9:1 to 1:9 with decreasing the particles sizes. In the case where distilled water used as solvent, the size-controlled bimetallic Ag/Au nano-chains can be fabricated by laser ablation of Ag target in different concentration of $HAuCl_4$ solutions. The UV-visible absorption spectra of the Ag/Au nano-chains red shifted from about 408nm to 785nm as the $HAuCl_4$ concentration increased from 0.12 to 4.59mM. Meanwhile, a detailed discussion of the relevant mechanism has been addressed. The aim of this work is to extend a novel method of synthesizing the bimetallic NPs with controllable structures. This strategy can be used to generate other noble complex nano-structures by laser fabrication.

Experimental setup

In a typical experiment, different amounts (0.12~4.59mM) of $HAuCl_4$ were separately added into 20mL liquid solvent to make a series of solutions by stirring and ultrasonic treatment. A well polished pure (99.99%) Ag plate was placed on the bottom of a rotating glass dish (*X-Y* stage) with speed of ~600rpm filled with 5mm depth of liquid solution. If the target is stationary, the pulses laser induced damage will appear on the metal target. We have found that the modified spot can lead to an enhanced absorption of the following laser energy.[18-19] This is unfavorable for the synthesis of homogeneous bimetallic nano-particles._A Q-swithed Nd-YAG (yttrium aluminum garnet) laser (Quanta Ray, Spectra Physics) beam operating at a wavelength of 1064 nm with a pulse duration of about 6ns and 10Hz repetition rate was focused onto the Ag target surface. The laser beam was focused on the target by a quartz lens with 70mm focal length. The average spot size of the laser beam at the target was about 400μm. The laser beam power density was about 4 GW/cm^2, and the ablation lasted 50 minutes. The laser power density was adopted to induce effective ablation yet not too high to cause splashing of the solution layer. After laser fabrication, the products were carefully washed, and centrifuged at 18000 rpm for 15 min in an ultracentrifuge. The sediments were dropped on a copper mesh and dried in an oven at 60^{o}C for observation by transmission electron microscopy (JEOL-JEM-2100F). To determine the diameter distribution of the obtained Ag/Au nano-particles based on TEM images, and more than 300 particles were measured with the aid of the graphics editing program of Macromedia Fireworks 8. The UV-visible absorption spectra of bimetallic Ag/Au NPs were measured with a UV-Vis-IR spectrometer (UV-1800, Shimadzu).

Result and discussion

After pulse laser ablation of pure Ag plate in solution containing 0.12mM $HAuCl_4$ and 20mL anhydrous alcohol, the low-magnification and high resolution morphologies of the nano-particles are analyzed with transmission electron microscopy (TEM; Fig.1 (a) and (b), respectively). The TEM image in Fig.1(a) clearly shows that numerous liquid-dispersed nano-particles with the mean size of about 32.5nm are well-defined spherical-like structures. The nano-spheres with solid interiors are not hinge joined, but are fabricated individually. The HRTEM image in Fig.1 (b) provides a typical structural detail of the nano-sphere. The representative areas marked by red lines in Fig.1(b) with a periodicity corresponding to a *d*-spacing of 0.238nm could be indexed to the Ag(111) plane structure. On the other hand, the selected regions marked by yellow lines with a *d*-spacing of 0.235nm can be indexed to be the (111) plane of the Au structure. Because of similar lattice constants, the Ag and Au plane structures in HRTEM image are miscible phases in the rest regions. Moreover, the elemental mapping image in Fig.S1(a)† also clearly displays that the well dispersed Ag and Au elements are homogeneously alloyed within a nano-sphere. The relative ratio of Ag to

Au in the bimetallic nano-composites is calculated to be 9:1. Moreover, increasing the $HAuCl_4$ concentration to 4.59mM result in ultra-small bimetallic Ag/Au nano-spheres (Fig.1(b)). In addition to the well-dispersed bimetallic Ag/Au nano-structures, the mean size drastically drops from about 32.5 nm to 1.8nm as the $HAuCl_4$ concentration increases from 0.12 mM to 4.59mM. In brief, the $HAuCl_4$ controls the size of the bimetallic Ag/Au NPs even down to sub-10 nm mono-dispersed structures. The (111) planes in the Ag and Au crystal structures are also indeed found in the HRTEM image (Fig.1(d)). The uniform ultra-small bimetallic nano-particles has an Ag/Au ratio of about 9:1, which can be simply confirmed by the elemental mapping image in Fig.S1(b)†. It is reasonable to deduce that the replacement reaction between Ag and Au ions indeed occurred during laser ablation of Ag target.

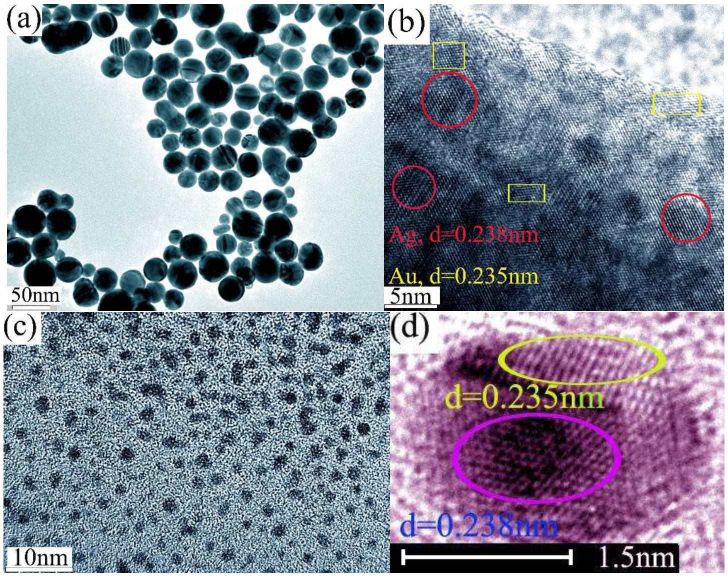

Fig.1 (a, b) The representative low-magnification and enlarge TEM images of the nano-spheres by laser ablation of Ag target in liquid containing 0.12mM $HAuCl_4$ and ethanol solution. (c, d) the typical morphology and HRTEM iamge of the ultra-small Ag/Au nano-spheres fabricated by laser ablation in 4.59mM $HAuCl_4$ solution.

To reveal the possible growth of bimetallic Ag/Au nano-spheres, laser induced plasma and the rapid nucleation process have been proposed. At the moment of laser arriving at Ag target, the outmost surface layers of the target absorb well the laser energy, rapid boiling, superheating, melting and vaporization of Ag element will occur simultaneously.[21-22] This will then lead to the formation of hotter and denser Ag plasma on the irradiated spot. Moreover, the explosive plasma-induced pressure will be enhanced in $HAuCl_4$ liquid condition. The extreme conditions characterized by the highly non-equilibrium feature include high temperature (~ thousands Celsius) and high pressure (~tens Gpa).[21-22]This will enable the replacement reaction between the ablated Ag and Au ions to be significantly improved in the pulse ablation process. The nucleation of bimetallic Ag and Au will take place in the stages of rapid condensation of the plasma, and sharply terminate due to the expiration of the pulse and exhaustive expansion of the vapor. The composition of bimetallic nano-particles should be highly related to the degree of replacement reaction during laser ablation. A higher concentration of $HAuCl_4$ in the liquid solution should improve the degree of the replacement reaction. This will then lead to a higher mole fraction of Au in bimetallic NPs. On the other hand, the required energy for the replacement reaction should mainly derive from the hot plasma in activated solution, which will be increased at higher $HAuCl_4$ concentration. This can accelerate the plasma cooling and nano-particles nucleation processes. In this way, the size of bimetallic Ag/Au NPs should gradually decrease with increasing the concentration of $HAuCl_4$ in activated solution.

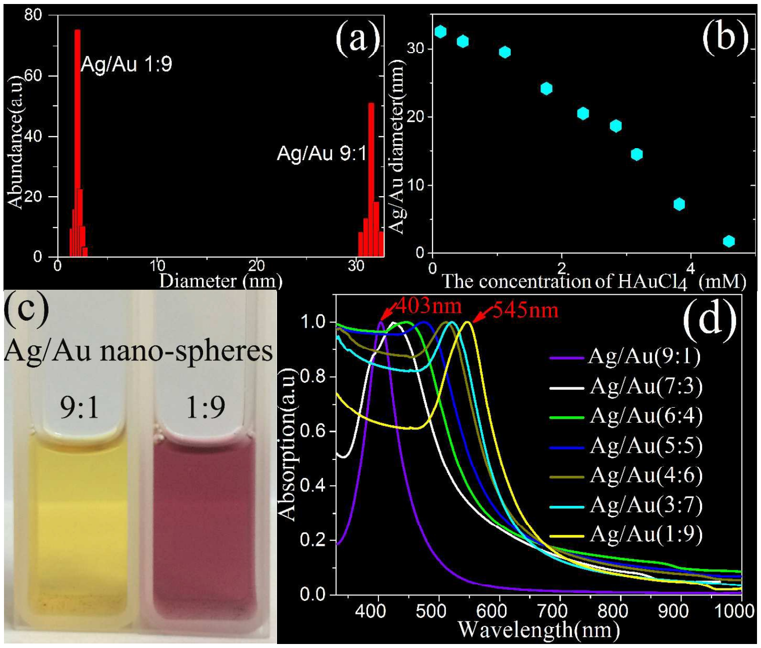

Fig.2 (a) The mean size distribution histograms of bimetallic Ag/Au at ratio of 9:1 and 1:9. (b) The size reduction behavior of bimetallic Ag/Au nano-spheres *versus* the $HAuCl_4$ concentration. (c) Direct photographs of Ag/Au nano-spheres colloidal suspensions by laser ablation in 0.12 and 4.59mM $HAuCl_4$-ethanol solution, respectively. (d) The UV-visible absorption spectra of the bimetallic Ag/Au nano-spheres.

To get more information of the size-controlled bimetallic Ag/Au nano-spheres, the size-distribution histogram is shown in Fig.2(a). Each size distribution is obtained by measuring the diameters of more than 300 nano-particles in sight on the TEM images. The result reveals that the ultra-small bimetallic Ag/Au nano-spheres have narrow size dispersion. Moreover, Fig.2(b) clearly illustrates that the size reduction of bimetallic Ag/Au nano-spheres with increase of $HAuCl_4$ concentration (0.12~4.59mM in 20mL solution). The size reduction can be described as a nearly linear-function. The direct photographs of bimetallic Ag/Au nano-spheres are shown in Fig.2(c). The higher Au content in bimetallic nano-structure leads to a significant change in the solution color from the bright yellow to light red. Moreover, the unique optical properties of bimetallic Ag/Au nano-sphere were illustrated by the UV-visible absorption spectra. The absorption spectra of bimetallic Ag/Au nano-spheres in Fig.2 (d) significantly red shifted from ~ 403nm to 545nm with increase of Au fraction in bimetallic NPs. The peak positions are strongly dependent on the composition of the Au fraction, which have been verified in previous work.[14] As shown in Fig.2 (d), the single peak of absorption spectra in each solution indicates the fabrication of bimetallic or alloyed Ag/Au nano-materials instead of a simple mixture of Ag and Au products after laser ablation, which is consist well with the previous reports.[3,23-24]

The nucleation process of bimetallic NPs during laser ablation involved the basic interaction in liquid, which is also sensitively dependent on the high pressure generated by the laser-induced plasma.[13-16] Based on previous reports, it is generally believed that the pressure is proportional to the liquid density.[20-22] It is found that the bimetallic Ag/Au nano-structures indeed have different morphologies if the pressure of laser-induced plasma was increased by simply adopting distilled water ($1.0 g/cm^3$) instead of anhydrous alcohol ($0.8 g/cm^3$) as liquid solvent. The typical morphology of the products by laser ablation of Ag target in 20mL distilled water containing 0.12mM $HAuCl_4$ is shown in Fig.3(a). The low-magnification image clearly shows that numerous nano-particles are interconnected and accreted with each other. They form short curvilinear groups with chain-like structures. It is distinct from the mono-disperse Ag/Au nano-sphere obtained in ethanol condition. The HRTEM image in Fig.3(b) indicates that the bimetallic nano-chains with diameter of tens of nanometers are Ag core/Au shell structures. As shown in Fig.3(b), the core region marked by yellow line with a *d*-spacing of 0.238nm is indexed to be as the (111) plane of the Ag structure. On the other hand, the outer region marked by red line with a periodicity corresponding to a *d*-spacing of 0.204nm should be indexed with reference to (200) plane in Au structure. As the $HAuCl_4$ concentration increases to 4.59mM, the mean size of the bimetallic nano-chains drastically dropped from tens of nanometers to sub-10nm (Fig.3(c)). The HRTEM image in Fig.3(d) illustrates that the interconnected structures of the ultra-small bimetallic nano-chains. The region with a *d*-spacing of 0.238nm is indexed as the (111) plane in the Ag structure. The area with a *d*-spacing of 0.235nm can be indexed with reference to the Au (111) plane structure. On the other hand, the shell region with a *d*-spacing of 0.204nm is indexed as (200) plane in the Au structure. The above results confirm that there is a regularity of orientation between the different domains in bimetallic Ag/Au NPs fabricated by laser ablation of Ag metal in $HAuCl_4$ solution. Because of the similar lattice constants, the preferential alignment of the Ag (111) and Au (111) orientation will be formed in bimetallic Ag/Au NPs. The shell of bimetallic Ag/Au nano-chains only contain the (200) plane of the Au structure, which may be generated by laser sintering of the assembled particles.

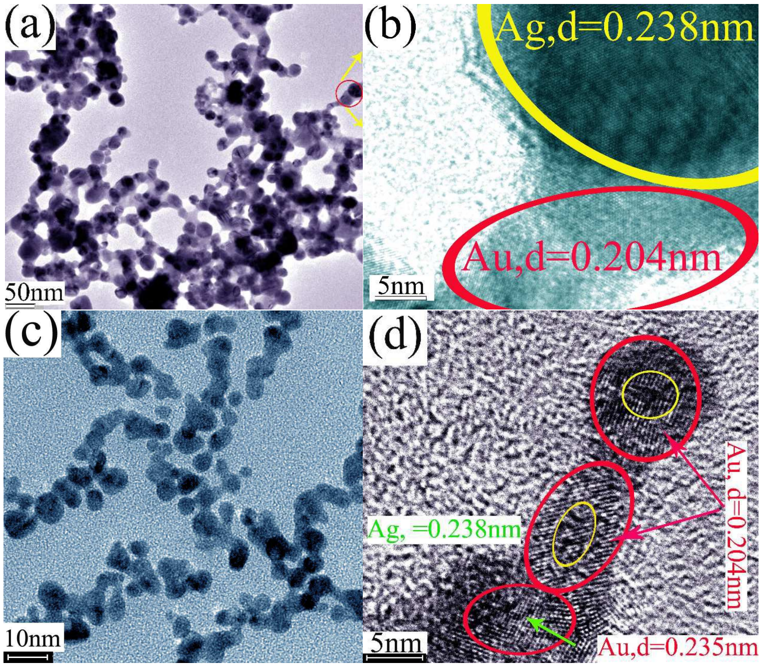

Fig.3 (a, b) The typical low- and high- magnification TEM images of bimetallic Ag/Au nano-chains fabricated by laser ablation in distilled water with $HAuCl_4$ concentration of 0.12mM. (c, d) The low- magnification and enlarge TEM images of ultra-small Ag/Au nano-chains generated in solution of 4.59mM $HAuCl_4$.

Compared with the well-dispersed Ag/Au nano-spheres, the bimetallic Ag/Au nano-chains with an interconnected structure should be highly related to the fact that higher pressure generated by laser-induced plasma in distilled water. The higher pressure will lead to a stronger interaction between Au and Ag metal ions. Then, the interconnection and accretion can take place in nucleation process. This results in the formation of nano-chain structures due to the laser sintering of the assembled particles.

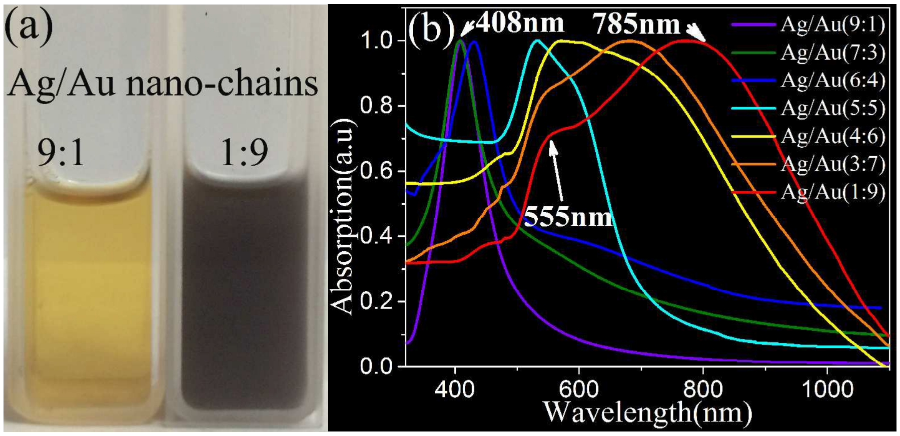

Fig. 4 (a) The photographs of bimetallic Ag/Au nano-chain colloidal suspensions by laser ablation in 0.12 and 4.59mM $HAuCl_4$-distilled water solution, respectively. (b) UV-visible absorption spectra of the as-prepared bimetallic Ag/Au nano-chains.

On the other hand, the compositions of bimetallic Ag/Au nano-chains are very similar to that of nano-spheres fabricated under the same $HAuCl_4$ concentration in each solution. Fig.4(a) shows the photographs of the bimetallic Ag/Au nano-chains colloidal suspensions fabricated by laser irradiation of Ag target in distilled water with the $HAuCl_4$ concentration of 0.12 and 4.59mM. The higher Au composition in bimetallic NPs leads to significant change in the solution color from yellow color to grey brown. Finally, the UV-visible absorption spectra of bimetallic Ag/Au nano-chains solutions are illustrated in Fig.4 (b). It is interesting to note that the absorption spectra drastically red shifted from about 408nm to 785nm with the increase of the Au composition in bimetallic Ag/Au nano-chains. Meanwhile, the absorption spectra of bimetallic Ag/Au nano-chains become broader, and exhibit another peak at about 555 nm. Compared with the UV-visible spectra of pure Ag and Au nano-particles (Fig.S2; ESI†), the observed broadening spectra may be attributed to the plasmon hybridization caused by the agglomeration of ultra-small bimetallic Ag/Au nano-chains.[16] Two absorption peaks at 555 and 785nm can be attributed to latitudinal and longitudinal plasmon wavelengths of the nano-chain structures, respectively. The results illustrate the tuning of LSPR in the range of 408-785 nm. This would be applicable to photodynamic therapy, biological imaging, *etc*.

Conclusions

In summary, bimetallic Ag/Au NPs with good controllable structures have been carefully devised through laser ablation of bulk Ag target in $HAuCl_4$ solution. The sub-10 nm bimetallic Ag/Au NPs can be obtained by simply increasing the $HAuCl_4$ concentration in liquid solvent to 4.59mM. The related mechanism is proposed based on the high non-equilibrium processing character during laser ablation in liquid. The UV-visible absorption spectra of bimetallic Ag/Au nano-chains demonstrated the possible tuning of LSPR in the range of 408-785nm. This has significant implications in biological imaging and biomedicine. The simple, versatile, and rapid strategy will be very suitable for developing other bimetallic complex nano-structures.

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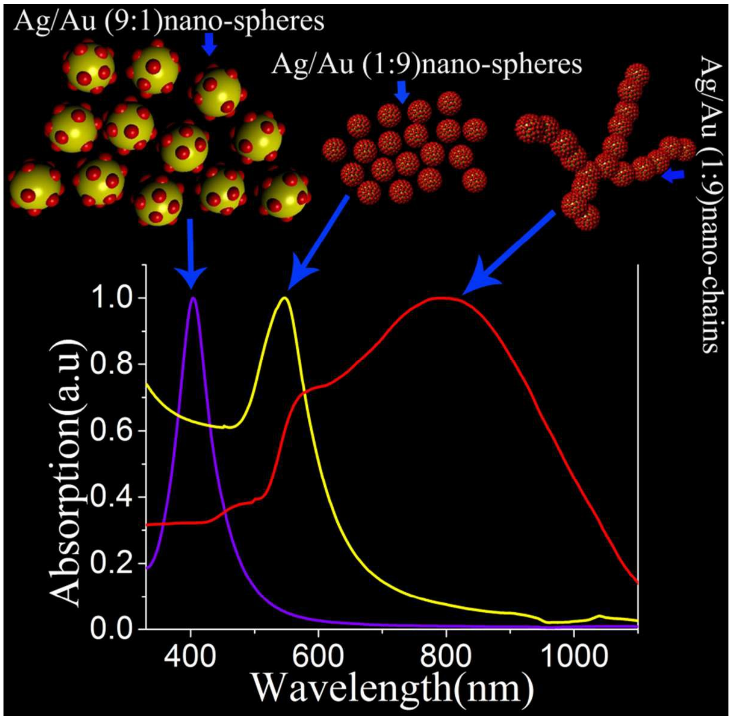

TEXT: Bimetallic Ag/Au nano-spheres and nano-chains with controllable structures fabricated by laser ablation of Ag in $HAuCl_4$ solution without any potential toxic surfactants or adding extra reductants.