NUCL SCI TECH (2018) 29:158
https://doi.org/10.1007/s41365-018-0505-y

Solvent effects on gold nanoparticle formation from photochemical reduction of Au(III) by UV irradiation

Ming Yuan[1] · Yu-Bo Li[1] · Jun Guo[2] · Rui-Bo Zhong[2] · Li-Ping Wang[3] · Feng Zhang[1,4]

Received: 21 May 2018 / Revised: 22 June 2018 / Accepted: 28 July 2018 / Published online: 27 September 2018

Abstract Colloidal gold nanoparticles (AuNPs) have attracted more and more attention in areas of materials science, biotechnology and organic chemistry due to their unique functions as molecular markers and their applications in diagnostic imaging and catalysis. The AuNP synthesis approaches have been well developed; however, the solvent effects have not been systematically studied yet. Here we analyzed and compared solvent effects on AuNP formation using UV irradiation of Au(III) without adding any other ligands. By monitoring the surface plasmon resonance absorption of Au(III)-containing solutions, results showed that both ketone and alcohol solvents can induce Au(III) to form gold nanospheres; on the other hand, solvents like ACN and THF can induce Au(III) to form nanostructures with longer dimensions. The possible mechanism was discussed, which could facilitate efficient photochemical synthesis of AuNPs and might apply to other metal NP synthesis.

Keywords Solvent effect · Gold nanoparticle · UV irradiation · Photochemical reduction

1 Introduction

Considerable attention has been focused on AuNPs due to their unique optical, catalytic and electronic properties. AuNPs are known to have a strong plasmon resonance absorption in the visible region (called surface plasmon resonance, SPR) due to the collective oscillation of free electrons in the conduction band, and therefore, they are being used for optical sensors, surface-enhanced Raman scattering (SERS) [1]. Generally speaking, the more is understood about the properties and the mechanism of formation of AuNPs, the better control of their sizes, shapes and applications can be achieved.

A number of synthetic methods have been developed to prepare monodispersed AuNPs, such as thermal reduction of Au(III)-containing salts (like $AuCl_4^-$) including traditional citrate reduction [1] and the widely employed Brust–Schiffrin method of two-phase synthesis with thiol stabilization [2], and photochemical reduction methods [3]. The photochemical synthesis of AuNPs offers the possibility of controlling the rate of NP formation as well as the spatial

---

This work was supported by the Program Funded by University for Fostering Distinguished Young Scholars, National Natural Science Foundation of China (No. 51763019, U1832125), China Postdoctoral Science Foundation (No. 2018M630937), Inner Mongolia Grassland Talent, Distinguished Young Scholars of Inner Mongolia Autonomous Region, and Yong Scientist Foundation of Inner Mongolia Autonomous Region.

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s41365-018-0505-y) contains supplementary material, which is available to authorized users.

✉ Li-Ping Wang
lpingwang@sjtu.edu.cn

✉ Feng Zhang
fengzhang1978@hotmail.com

[1] School of Life Science, Inner Mongolia Agricultural University, 306 Zhaowuda Road, Hohhot 010018, China

[2] Department of Biomedical Engineering, School of Basic Medical Sciences, Guangzhou Medical University, Guangzhou 511436, China

[3] School of Biomedical Engineering, Shanghai Jiaotong University, Shanghai 200241, China

[4] Affiliated Stomatological Hospital of Guangzhou Medical University, Guangzhou 510150, China

and temporal control that characterized many photochemical reactions [3–5]. Various agents and approaches have been used in photochemical reductions, such as photosensitizers, dendrimers (as stabilizers) and the placement of metal salts in polymer films [3]. The most common precursor ($HAuCl_4$) shows a strong absorption at ∼ 320 nm and significant absorptions at shorter ultraviolet wavelengths, which matches the emissions of common UV lamps (center around 350 nm), so it provides a useful region for photochemical synthesis of AuNPs.

Reactive intermediates can be photochemically generated in intermolecular reactions involving triplet ketones [3, 5]. Ketyl radicals, one of powerful reducing agents, normally are involved in metal ion reduction as reducing species, in that the redox potentials of ketyl radicals are thermodynamically favorable in gold ion reduction process [3]. Zhao et al. [6] attributed formation of NPs to a multiphoton process of 800 nm fs irradiation light to form electrons capable of reducing $AuCl_4^-$ to Au(0). Kurihara et al. [7] generated AuNPs with γ-irradiation and laser irradiation to study transient absorption spectrum and the presence of intermediates. Malone et al. [8] discussed possible mechanisms of formation inside polymer gels by photochemical reduction.

It has also been suggested that the surfactants play an important role in the formation of NPs through micelle formation, and preformed NPs are able to catalyze disproportionation [4]. Anisotropic AuNPs have been prepared by the photochemical reduction in the room-temperature ionic liquid without any additional capping agents, in which the ionic liquid can act as a reaction medium, template and capping agent [9]. Sporadic researches showed that different solvents (like acetone and methanol) affect the AuNP synthesis, too [10].

However, the effect of solvents on the AuNP synthesis has not been studied yet, so this paper aims to point out the significance of solvent effects on photochemical reduction based on synthesis method. Here we found that continuous-wave (cw) UV irradiation was able to reduce Au(III) at room temperature in most of common solvents, and a mechanism was presented in which AuNPs formed from Au(0), which are proposed to be produced from the disproportionation of the gold ions in their higher oxidation states.

2 Experimental section

2.1 Instruments and agents

UV–Vis spectrophotometer (U-2900, Hitachi) was used to record the absorption spectra. Transmission electron microscopy (TEM) images were taken using JEM-1400 Plus at 100 kv. $HAuCl_4$ was purchased from Alfa Aesar. Other organic solvents, such as acetone (ACTN), isopropyl alcohol (IPA), ethanol (EA), methanol (Me), acetonitrile (ACN), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), and acetic acid (HAc), were purchased from SCRC. All the agents were used directly without further purification.

2.2 Methods

The mixtures of 500 μL $HAuCl_4$ aqueous solution and 10% different organic solvents were added in the 24-well quartz plate. The absorption spectra were recorded after UV irradiation (365 nm) for 20, 40 and 60 minutes.

3 Results and discussion

Previous researchers proposed the mechanism for the formation of AuNPs using UV irradiation, in which they suggested that Au(III) is firstly excited by UV radiation, and then reduced into Au(II) which is unstable, so Au(II) further reacted disproportionately to form Au(I) and Au(III) (the starting state) [4]. The Au(I) can be photoreduced into Au(0) by absorbing photons. The Au(0) atoms are formed homogeneously throughout the solution, in that the binding energy between two metal atoms is much stronger than the atom-solvent binding energy, and followed by a multi-step process, these atoms progressively coalesce into clusters and further become AuNPs [3, 5]. The photochemical reduction of Au(III) to Au(0) has already been studied by many researchers, but almost none considered the effect of solvents on the formation of AuNPs. In our experiment, there were not any reducing or protective agents added in solutions at all, and it is clear that different solvents have significant effects on the

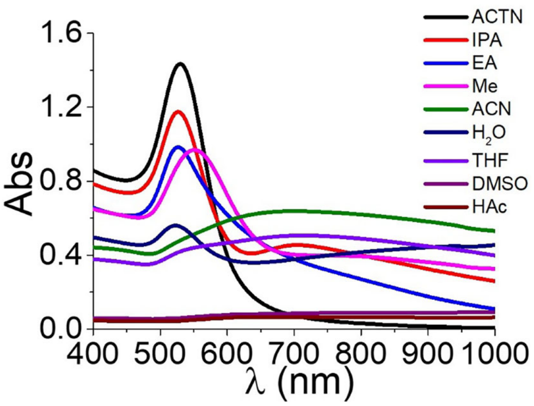

Fig. 1 (Color online) Absorption spectra of chloroauric acid solutions mixed with different organic solvents after 1-hour UV irradiation

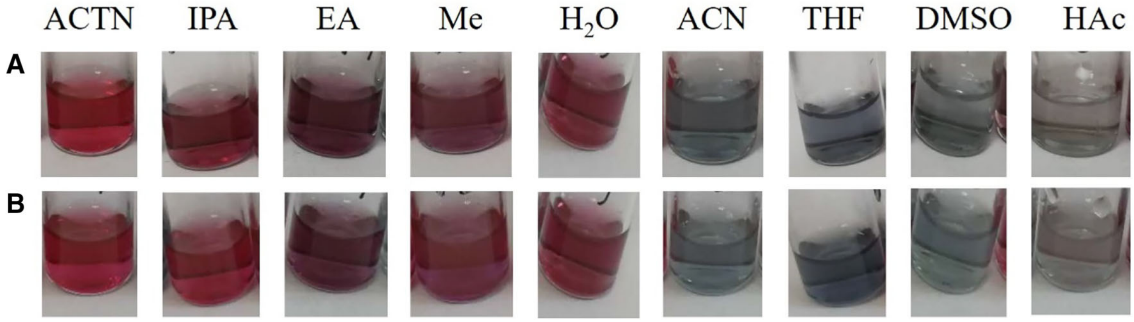

Fig. 2 (Color online) Photographs of Au(III) reaction solutions mixed with different solvents after 1-hour UV irradiation (**a**) and again 1-hour sitting under sunlight (**b**)

formation of AuNPs, which can be seen from absorption spectra, the color changing of reaction solutions and TEM observation as well.

After the Au(III) solutions were irradiated under UV light for an hour, their absorption spectra were recorded (Fig. 1). Except for DMSO and HAc, all of $HAuCl_4$ solutions mixed with other organic solvents exhibited the reduction of Au(III), since the absorption spectrum of Au(III) disappeared progressively. And in the meanwhile, the $HAuCl_4$ solutions mixed with ACTN, IPA, EA and Me showed a typical SPR peak around 520 nm, which indicated the formation of AuNPs. And the absorbance peak intensity increased with the prolonged reaction time (Fig. S1). For a control experiment, the aqueous solution of $HAuCl_4$ also forms AuNPs. The $HAuCl_4$ solution mixed with ACN and THF did not show any apparent specific absorption peaks, but they have wide absorption from 500 to 1000 nm, indicating some nanostructures with longer dimensions or large aspect ratio formed [11], and also some aggregation of AuNPs was observed, which might be due to the absence of surfactants in solutions, a compromise to avoid any new effects on morphological modulation of gold nanostructures. For DMSO and HAc solutions, they both showed a very weak peak at around 520 nm at 20 min, but both peaks disappeared at 40 min and 1 hour, respectively.

The photographs of solutions after UV irradiation in Fig. 2 gave us a more intuitional understanding on the formation of AuNPs. All the colors of these solutions matched with the absorption spectra that are shown in Fig. 1. Those red solutions represent gold nanospheres, and the blue solutions represent other kind of gold nanostructures which normally have at least one longer dimension or a large aspect ratio (such as nanorods, triangles and nanosheets, Fig. 2a). ACTN, IPA, EA and Me solution color changed from colorless to red and deep red with the increasing time, but for ACN and THF solutions color changed from colorless to light blue to deep blue, and no red color was observed during 1 hour (Fig. S2). After leaving these solutions under sunlight for another hour, gold nanospheres in the red solution remained stable, but aggregation and precipitation began to appear in the blue solution (Fig. 2b).

Ketones are good photosensitizers for NP synthesis not only because of the energy they can absorb or deliver but rather because of the reducing free radicals they can generate [3]. Under UV irradiation, acetone will dissociate into $CH_3\cdot$ and $CH_3CO\cdot$ which could been used for the reduction of $HAuCl_4$ [5]. The concentration of $HAuCl_4$ in the initial solution of all reactions is the same and the reaction time is also kept the same, but from the spectra in Fig. 1, it can be seen that the final yield of gold nanospheres in acetone is obviously more than those in others, which is consistent with those reported from previous experiments. Typical gold nanospheres were also produced in solutions containing Me, EA and IPA, indicating that hydroxyl groups also have an effect on the reduction of $HAuCl_4$. It can be inferred that carbonyl has a stronger effect than hydroxyl. For ACN and THF, we thought they are not reductive, but they can affect the shape of the gold nanostructures, also they can affect the degree of AuNP aggregation. Furthermore, ketones and alcohols may be also served as protective agents to stabilize the gold nanospheres.

TEM tests were taken to characterize the structure of the AuNPs (Fig. 3). From the TEM results, we could see that more longer-dimension AuNPs were observed, such as triangle, nanorod rhombic and irregular shape of AuNPs appeared in the TEM images. TEM results were consistent with the color of the solution and the UV–Vis absorbance. And the TEM results could be as the persuasive and supplementary data to the UV–Vis absorbance and color change of the solution. According to these results and the TEM data, we deduced that the blue color was the combination result of the longer dimension and the aggregation of AuNPs.

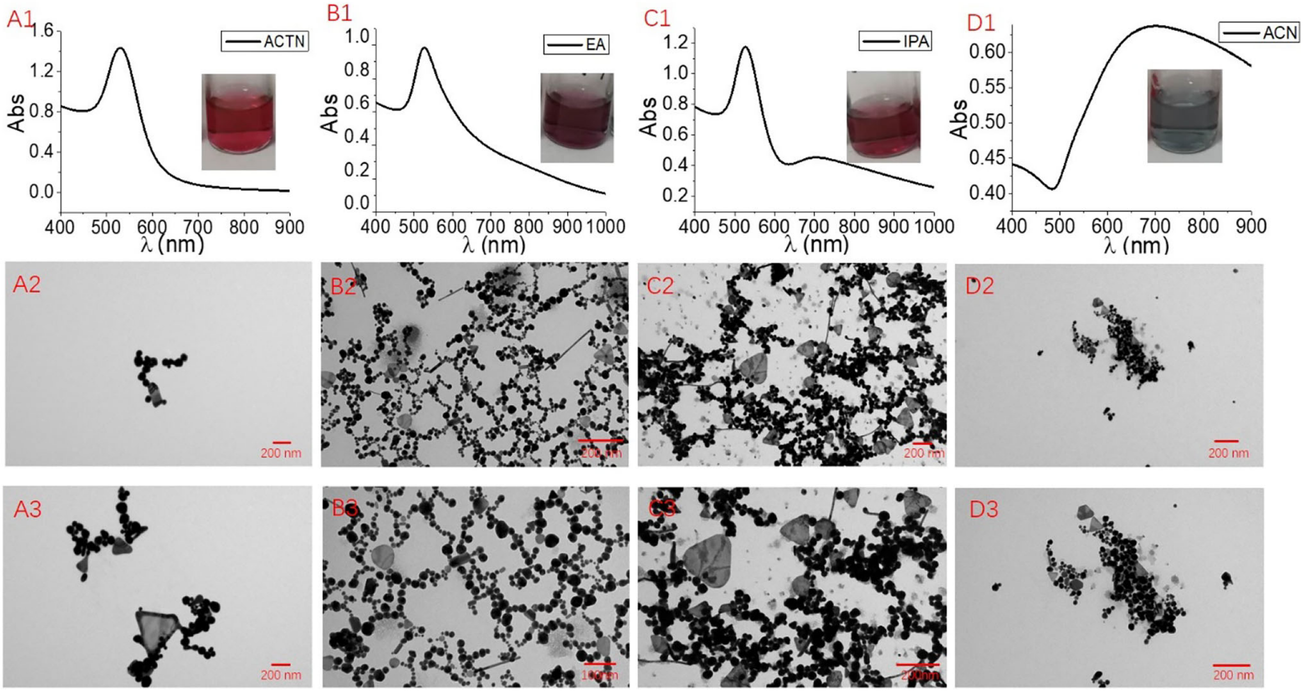

Fig. 3 (Color online) The UV absorption spectra and TEM characterization of gold nanostructures. The UV absorption spectra of acetone, ethanol, isopropanol and acetonitrile were A1–D1, respectively. A2–D3 are the corresponding TEM images

4 Conclusion

UV irradiation is a facile photochemical method for synthesis of gold nanostructures. In order to control both sizes and shapes, most studies introduced different solvents or protective agents in the synthesis system. Our study focused on the mere solvent effects on gold nanostructures synthesis. Apparently, both ketone and alcohol solvents tend to form gold nanospheres. Solvents like ACN and THF can induce the formation of nanostructures with other shapes (like rods or triangles), and the AuNPs have more tendency to aggregate. So they cannot be used as protective agents, otherwise the products are unstable in solution. Therefore, adding protective agents could be a good choice when synthesizing nanostructures in these solvents. The solvent effects on AuNP synthesis are significant, and we hope this article can help to choose right solvents for AuNP synthesis using UV irradiation.

References

1. R.A. Sperling, P. Rivera gil, F. Zhang et al., Biological applications of gold nanoparticles. Chem. Soc. Rev. **9**, 1896–1908 (2008). https://doi.org/10.1039/B712170a
2. F. Zhang, E. Lees, F. Amin et al., Polymer-coated nanoparticles: a universal tool for biolabelling experiments. Small **22**, 3113–3127 (2011). https://doi.org/10.1002/smll.201100608
3. M.L. Marin, K.L. McGilvray, J.C. Scaiano, Photochemical Strategies for the Synthesis of Gold Nanoparticles from Au(III) and Au(I) Using Photoinduced Free Radical Generation. J. Am. Chem. Soc. **49**, 16572–16584 (2008). https://doi.org/10.1021/ja803490n
4. S. Eustis, H.-Y. Hsu, M.A. El-Sayed, Gold nanoparticle formation from photochemical reduction of Au^{3+} by continuous excitation in colloidal solutions. A proposed molecular mechanism. J. Phys. Chem. B **11**, 4811–4815 (2005). https://doi.org/10.1021/jp0441588
5. K.L. McGilvray, C. Fasciani, C.J. Bueno-Alejo et al., Photochemical strategies for the seed-mediated growth of gold and gold–silver nanoparticles. Langmuir **46**, 16148–16155 (2012). https://doi.org/10.1021/la302814v
6. C. Zhao, S. Qu, J. Qiu et al., Photoinduced formation of colloidal Au by a near-infrared femtosecond laser. J. Mater. Res. **7**, 1710–1714 (2011). https://doi.org/10.1557/JMR.2003.0235
7. K. Kurihara, J. Kizling, P. Stenius et al., Laser and pulse radiolytically induced colloidal gold formation in water and in water-in-oil microemulsions. J. Am. Chem. Soc. **9**, 2574–2579 (1983). https://doi.org/10.1021/ja00347a011
8. K. Malone, S. Weaver, D. Taylor et al., Formation kinetics of small gold crystallites in photoresponsive polymer gels. J. Phys. Chem. B **30**, 7422–7431 (2002). https://doi.org/10.1021/jp020176i
9. J.M. Zhu, Y.H. Shen, A.J. Xie et al., Photoinduced synthesis of anisotropic gold nanoparticles in room-temperature ionic liquid. J. Phys. Chem. C **21**, 7629–7633 (2007). https://doi.org/10.1021/jp0711850
10. H. Qian, Y. Zhu, R. Jin, Size-focusing synthesis, optical and electrochemical properties of monodisperse Au38(SC2H4Ph)24 nanoclusters. ACS Nano **11**, 3795–3803 (2009). https://doi.org/10.1021/nn901137h
11. S. Helmi, C. Ziegler, D.J. Kauert et al., Shape-controlled synthesis of gold nanostructures using DNA origami molds. Nano Lett. **11**, 6693–6698 (2014). https://doi.org/10.1021/nl503441v