

A Facile and Efficient “One-Step” Synthesis of Au⁰ with Tunable Size

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Abstract

We demonstrated for the first time that nonionic surfactants such as T-80 not only act as stabilizing or protecting agents, but also can act as reducing agents for a facile “one-pot” synthesis of gold nanoparticles in an aqueous medium with tunable size at ambient conditions.

Introduction

Metallic nanoparticles are quite attractive because of their physicochemical characteristics such as catalytic activity, optical, electronic, and magnetic properties (1-7). In particular, because of their applications in catalysis (8,9), chemical sensing (10), biological reporters (11,12), and photonics (13), the preparation methods of gold nanoparticles (Au⁰) and their characterizations have been widely investigated (14-16) for a long time. There are many established methods for Au⁰ syntheses, including conventional chemical reduction (15-20), heat-treatment (21), microwave irradiation (22), sonochemical (23), photolytical (24,25), seeding growth approach (26-30), and so on. For most applications and fundamental studies (15,31-33), the control of the size (26-30), shape, and dispersity is desirable along with a simple, convenient and widely applicable synthetic method. A survey of the synthetic reports (15-17) clearly indicates that nanoparticle properties, such as stability and particle size (26-30), strongly rely on the experimental methodology and the employed conditions. Two primary perceptions can be distinguished in the solution synthesis of Au⁰. The first, involves the reduction of AuCl₄⁻ ions in aqueous media, employing any one of the reducing agents such as sodium borohydride, hydrazine, hydroxylamine, and sodium naphthalenide in the presence or absence of additional stabilizing ligands. The second involves the synthesis in organic solvents. The most popular method is the two-phase synthesis reported by Brust et al. (34), which involves the transfer of AuCl₄⁻ ions into toluene with the use of tetraalkylammonium bromide and subsequent reduction with sodium borohydride in the presence of thiols. Recently, efforts have been made to develop one-phase syntheses in which the reduction of metal takes place homogeneously in a selected organic solvent (18,19). However, the control over particle size and dispersity in a particular synthetic protocol is rather poor. The disadvantage of all of these methods is the impurities that are introduced by the use of toxic reductants. Further, to the best of our knowledge, no investigation has been proved that the non-ionic surfactant such as Tween 80 (T-80) alone could viable to synthesis Au⁰ in an aqueous



Figure 1

Photographs showing samples of the reaction solutions with colour changes during the formation of Au⁰ in aqueous solution at room temperature

medium at room temperature. Most syntheses reported (15-17) so far used either conventional reducing agents (15-20) and/or a kind of external energy sources (21-25) so as to followed multistep procedures (15-17,35) to produce Au⁰. To provide tailored nanoparticle samples for a wide range of applications, any synthetic method must be convenient and general, in addition to providing nanoparticles with well-defined structures.

Here, we report a facile one-step synthesis, of Au⁰ with controlled size by using only T-80 in aqueous medium. Different from previous syntheses where either reducing agents and/or energy sources were used for particle formation, the current synthesis did not use these additional sources. We have made the discovery that nonionic surfactants in the presence of a gold salt in an aqueous medium are able to yield well-dispersed Au⁰. Interestingly, the reaction proceeds even at 4°C and also in the absence of light. Furthermore, we could control the particle size of the Au⁰ by simply altering the

reaction conditions. Consequently, we demonstrated that the use of a reductant for the syntheses of Au⁰ is not required, and reducing agents and/or external energies can be avoided. This procedure could be widely applicable, and the desired particle size can be prepared by simply changing the reaction conditions. This approach opens up new horizons in nanotechnology, materials science, and biomedical research.

Experimental

Method

In a typical experiment, 0.4 mM of KAuCl₄ was added to 10 mL of 1 wt% aqueous solution of T-80 and kept in a dark place at room temperature. The solution turned from yellow to colorless, then to pink color, and finally to red after 6 h, indicating the formation of Au⁰. Experiments with different concentrations of gold salt and T-80 were used to produce

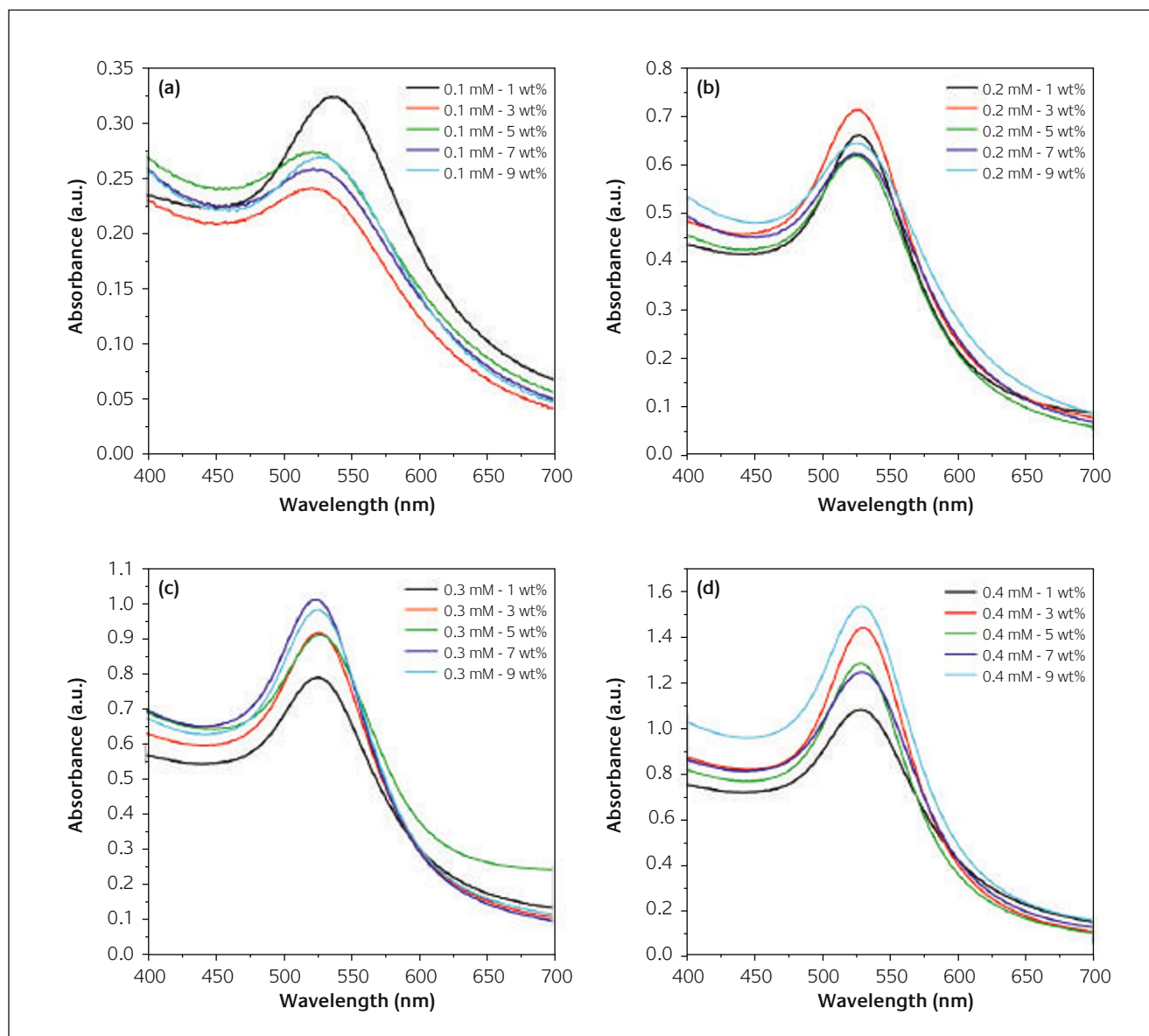


Figure 2

UV-vis spectra of Au⁰ prepared using 0.1 mM (a), 0.2 mM (b), 0.3 mM (c), and 0.4 mM (d) concentrations of gold salt with 1, 3, 5, 7, and 9 wt% of T-80, respectively

different sizes of Au⁰, which has been mentioned in the text appropriately for clear understanding.

Instruments

The UV-visible absorption spectra were recorded on a Varian Cary 500 spectrophotometer. The morphology and the crystalline size were studied with a Philips T20ST transmission electron microscope (TEM). TEM specimens were prepared by placing a few drops of sample solution on a copper mesh covered with a carbon film. The X-ray diffraction (XRD) pattern were measured on a Rigaku Diffractometer with a copper radiation ($\lambda = 0.15406$ nm) at 40 kV and 40 mA.

Results

The size of the particles is tuned by controlling the molar ratio of T-80 to metal precursor and heating conditions. In a typical experiment, 0.1 mM of gold salt was added to the aqueous T-80 surfactant solution (10 wt%) at room temperature. After 6 h, the color of the solution changed slowly from colorless to pink and then to red (Figure 1). A transmission electron microscope (TEM) sample was prepared after 11 h standing. The particle sizes were calculated and are summarized in the Table 1. The average size of the Au⁰ particles was 3.02 ± 0.52 nm, as determined from a statistical study with 105 nanoparticles. When the concentration of gold salt was increased to 0.4 mM, we observed that the size of Au⁰ increased to 4.87 ± 1.73 nm, calculated from 129 nanoparticles. Interestingly, the size of Au⁰ also increased to 5.86 ± 1.86 nm, when we decreased the concentration of T-80 (to 1 wt%). We also carried out several experiments to investigate the size variation of Au⁰ by changing the concentration of the gold salt and surfactant and the characteristic surface plasmon band of Au⁰ obtained at different concentrations shown in Figure 2.

The reactions were typically carried out at room temperature, although higher temperatures were also studied. It is worth to mention that, the particle size of the Au⁰ could also be controlled by using different temperature conditions. The TEM images and the related histograms describing the dispersity in size distribution of the Au⁰ synthesized by using 0.4 mM gold salt and 1 wt% T-80 at different temperatures are presented in Figure 3. As shown in

Figure 3, the average size of 1.48 ± 0.02 (a), 3.30 ± 0.07 (b), 10.32 ± 0.65 (c), and 25.55 ± 1.45 nm Au⁰ were synthesized at 4°C, 25°C, 45°C, and 65°C, respectively. The as-prepared nanoparticles show minimal polydispersity, are well dispersed in the solution medium and non-agglomerated. It is evident that, as the temperature increased, the diameter and the yield of the Au⁰ increased. This consequence can be explained by the higher reactivity of T-80 with a higher temperature. Interestingly, as the temperature increased the reaction time for the formation of Au⁰ decreased. The correlation between reaction temperature, time, and particle size is shown in Figure 4, which markedly shows that the average size of Au⁰ is directly proportional to temperature and inversely proportional to time. The difference in size variation as a function of temperature suggests that the growth mechanism is kinetically controlled. The detailed schematic demonstration of the size controlled one-step synthetic protocol by using different temperatures is shown in Figure 5a.

The kinetic of formation of the Au⁰ (by using 0.4 mM gold salt and 1 wt% T-80 at room temperature) was followed by UV-vis spectroscopy, and the spectra obtained in Figure 6. A decrease in the intensity of the characteristic surface plasmon band in UV-vis spectroscopy for the AuCl₄⁻ ion at $\lambda_{\max} = 323$ nm was observed, featuring a concomitant growth of new bands in the range of $\lambda_{\max} 530$ -540 nm. These are related to the characteristic surface plasmon band of gold nanoparticles (15), corroborating the formation of Au⁰. After 6 h, the band at 323 nm completely disappeared. This band evolved with time, finally reaching a constant absorbance after 6 h and only a slight increase in the absorption occurred thereafter, and both the final absorbance value and the peak position remained constant even after storage for several weeks. To evidently display the reaction dynamics of the formation of Au⁰ with time, the dependence of the Au-nanoparticle absorption intensity around 535 nm with time is also shown in Figure 6. As seen from the curve (Figure 6, inset), the reaction was almost terminated after 6 h. The UV-vis absorption profile (Figure 5b) is also dependent on the size of the Au⁰ (15). The absorption spectrum for the 1-2 nm sized Au⁰ shows a moderately developed plasmon peak, which may indicate that the particle size distribution is probably broad. However, the TEM and its histogram show that the as-prepared particles have a minimal polydispersity and are well dispersed in the solution medium. Most noteworthy is the observation that the Au⁰ according to this procedure were found to be

Table 1

Average size and shape of Au⁰ from varying concentration of gold salt and T-80

Gold salt conc. (mM)	T-80 conc. (wt %)	Average diameter (nm)	λ_{\max} (nm)	Shape distribution (%)
0.1	10	3.02 ± 0.52	523	100 spherical
0.4	10	4.87 ± 1.73	525	100 spherical
0.1	1	5.86 ± 1.86	537	100 spherical

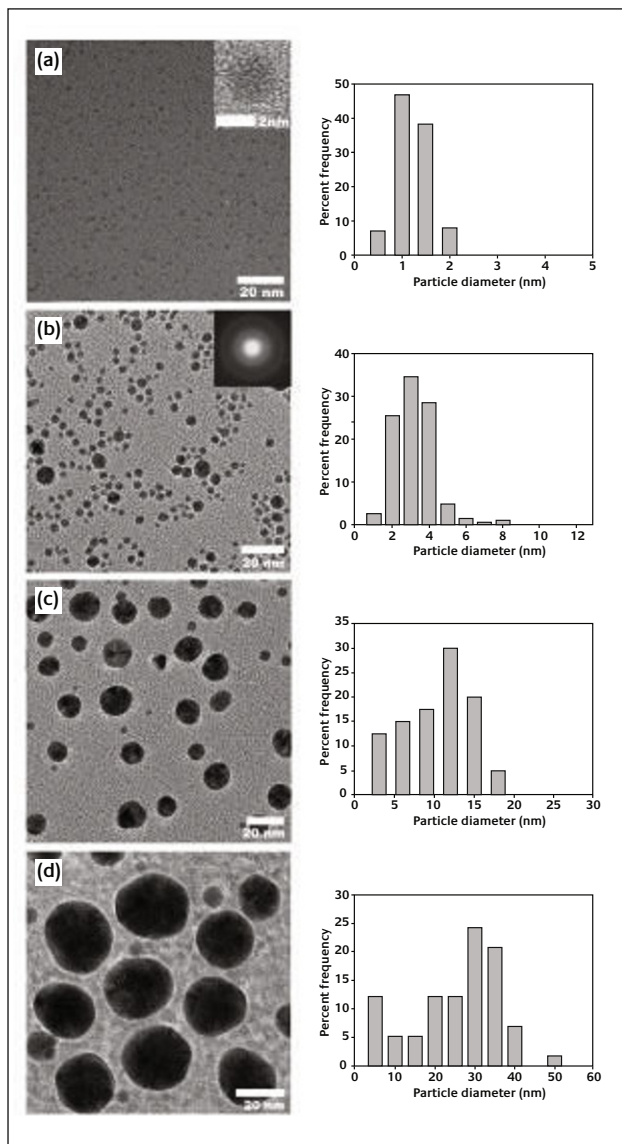


Figure 3

TEM images and related histograms of monodisperse Au⁰ synthesized using different temperature: (a) 4°C, (b) 25°C, (c) 45°C, and (d) 65°C. The inset shows the HRTEM image of single nanoparticle (a) and the selected-area diffraction pattern of Au⁰ (b), revealed the crystalline nature of the Au⁰

highly stable and did not show any signs of aggregation, even after storage for several months. The T-80-stabilized Au⁰ could be isolated and were found to be redispersible in water. Therefore, this approach is very simple and inexpensive, enabling the one-step synthesis of well-dispersed and stable Au⁰ with the desired size even without any sophisticated equipment or facilities, just requiring the basic starting materials (gold salt and surfactant).

The HRTEM image showing the lattice fringes of the nanoparticles exhibits the crystalline nature of the nanoparticles (Figure 3a, inset). A selected-area electron diffraction (SAED) pattern, shown in the inset of Figure 3b, clearly reveals that the Au⁰ features a face-centred cubic (fcc) structure (18). The XRD pattern (Figure 7) of the Au⁰ synthesized (0.4 mM gold salt, 1 wt% T-80) at room

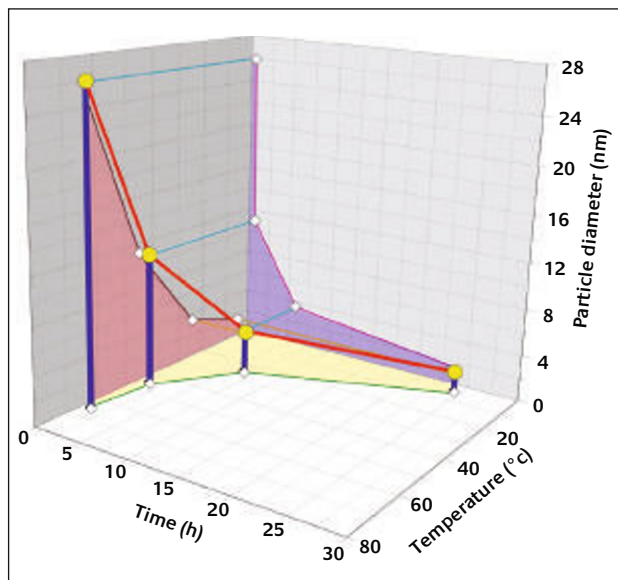


Figure 4

3D-plot showing the temperature and time effects relative to the Au⁰ diameter

temperature, revealed typical reflexes of fcc gold, which are in good agreement with the results obtained from the TEM SAED pattern. The lattice parameter obtained of 4.072(1) Å coincides with the literature value of 4.078 Å (JCPDS No. 04-0784).

Other studies used different protective agents and organic solvents to produce Au⁰ from gold salts, however, always in the presence of reducing agents (15-20) and/or external energies (21-25). Typically, chemical or photo induced reduction mechanisms are invoked to describe such processes. Such mechanisms are fundamentally different from the surfactant-induced mechanism proposed here that could involve the repeat unit C-C-O of T-80 in the reaction with the Au⁰. The hydrophilic groups in T-80 (polyethers) also known as poly(oxyethylene) groups, which are polymers of ethylene oxide. The structure and molecular model of T-80 are shown in Figure 8a with a 3D visualisation of the T-80-wrapped Au⁰ (Figure 8b). To elucidate that further, we extended our technique for the synthesis of Au⁰ to other surfactants, taking into consideration the versatility of different surfactants for molecular organization (36). Therefore, we employed also ionic surfactants such as sodium dodecylsulfate and cetyltrimethylammonium bromide. In contrast, these surfactants did not produce any Au⁰ under the same conditions, even after a one-month period. The reason is that they do not have ethoxy groups (C-C-O) as well as they form stable complexes (via the sulfate or bromide ion) with the gold ion that further hinders the particle nucleation processes. T-80 proved to be by far more efficient and first screening studies on other nonionic surfactants were found to corroborate these findings. Therefore, we believe that in this case the main factor determining the formation of Au⁰, is the existence of long and/or branched, polar chains, such as poly(oxyethylene) (C-

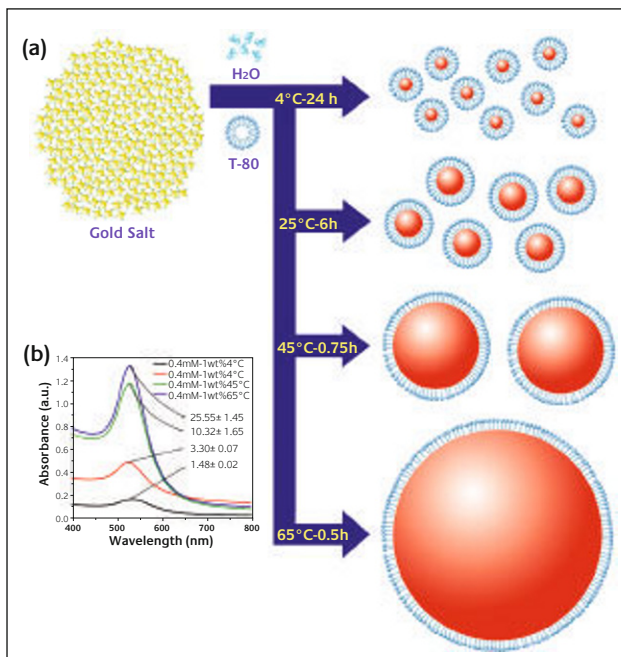


Figure 5
 (a) Schematic illustration of the size-controlled synthesis of monodisperse Au⁰ by using T-80 at different temperature conditions and (b) the corresponding UV-vis spectra

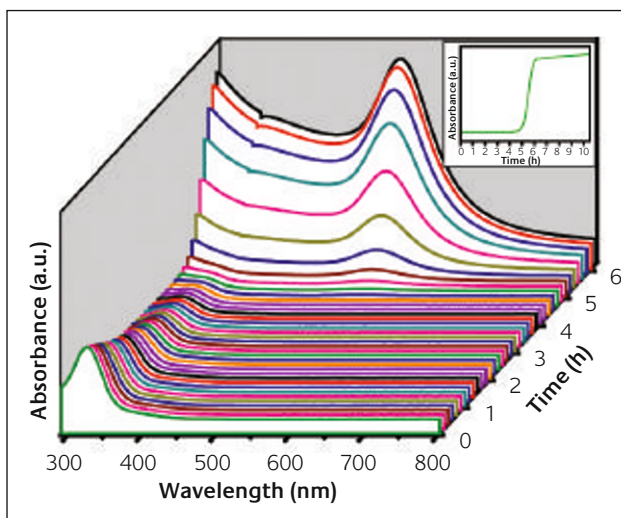


Figure 6
 Time-dependent UV-vis spectra showing the conversion of gold salts to Au⁰ after adding T-80 in aqueous solution at room temperature. Inset shows the corresponding extinction profiles around 535 nm as a function of time

C-O) chains. In order to prove this, the experiments were carried out with PEG alone. It is observed that, the Au⁰ obtained are very large, not uniform in shape, size, dimension and showed greater agglomeration as evidenced from its TEM image (Figure 9a). This further corroborates that the poly(oxyethylene) (C-C-O) chains of T-80 play a vital role in the formation of Au⁰. Further, Barnickel et al. (37) projected that the oxo groups from the polyether can form hydroperoxides with oxygen from the air, reducing AuCl₄⁻ to Au⁰. Hence, T-80 has more ethoxy groups per molecule (20

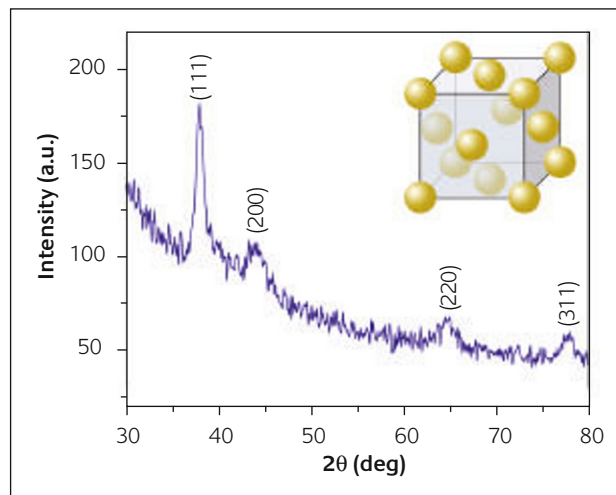


Figure 7
 Powder X-ray diffraction (XRD) pattern of the as-prepared Au⁰, confirming the formation of pure fcc gold

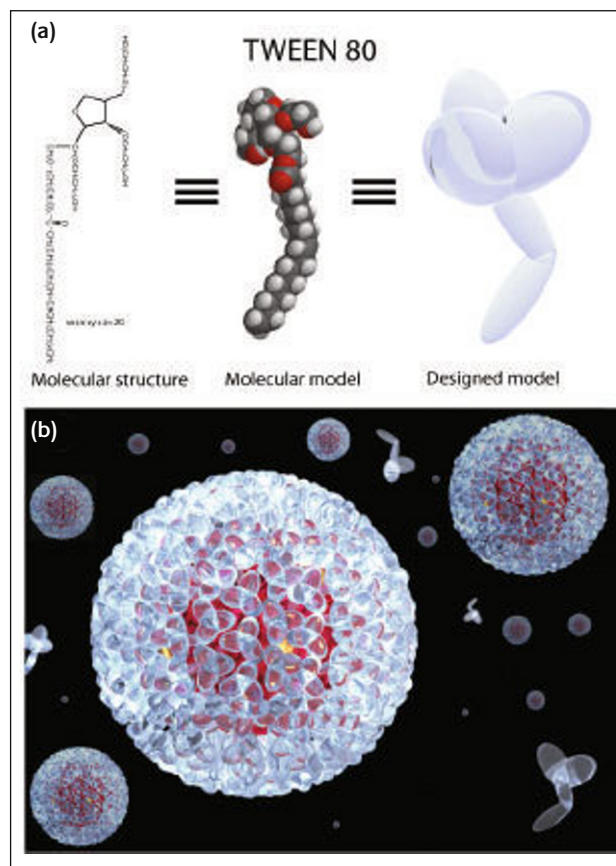


Figure 8
 (a) Structure and molecular model of T-80 and (b) a 3D visualization of the T-80-wrapped Au⁰

groups) than their surfactant (7 ethoxy groups) and the number of reducing equivalents should be of the same order at least. Therefore, the T-80 reduces gold ions to the neutral state via oxidation of oxyethylene groups into hydroperoxides, at the same time the surfactant molecules consequently adsorb onto the surface of the Au⁰, encouraging stabilization. In order to elucidate the role of

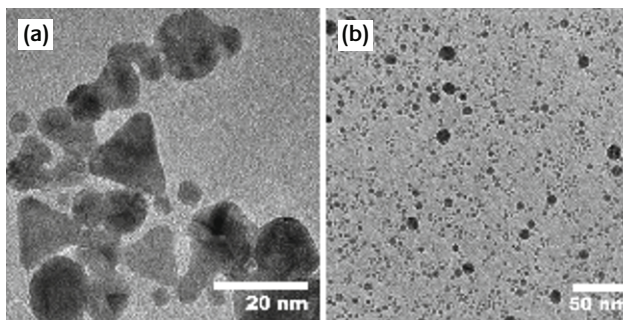


Figure 9
TEM images of Au⁰ synthesized from (a) PEG and (b) T-80 in aqueous solution at room temperature

atmospheric oxygen in the formation of hydroperoxides by oxidation of the oxyethylene groups, which are able to reduce the gold ions to neutral state, the experiment was carried out under anaerobic conditions (nitrogen atmosphere). It was observed that no significant difference between the reactions proceeded under aerobic and an anaerobic condition. While the C-C-O moieties of T-80 may contribute to the overall reduction mechanism, it is important to consider that T-80 and PEG are hydroxy-terminated. It is likely that the terminal OH groups are also responsible for the Au³⁺ reduction. However, the detailed mechanisms of the formation process are not yet fully understood. Nevertheless, we anticipate that the T-80 acts both as the reducing and stabilizing agent, and due to its dual character, it was possible to synthesize well-dispersed Au⁰ (Figure 9b) in aqueous solution at room temperature. The efficiency is shown by performing the reaction at a temperature of 4°C, without utilizing any other agents or external energy. Further investigations on the mechanism of Au⁰ formation by T-80 will be needed to address this issue in detail.

The facile one-step synthetic procedure developed in the present study offer several very important advantageous features over the conventional methods for the synthesis of Au⁰: First, this route permits well dispersed Au⁰ to be obtained in aqueous solution at room temperature, without employing any reductant agents and external energy. Therefore, this approach is very simple and inexpensive, enabling the synthesis of Au⁰ with the desired size even without any sophisticated equipment or facilities, just requiring the basic starting materials. Second, the desired particle size can be prepared via one-step by simply changing the reaction conditions. Third, the synthetic process is environmentally friendly and economical, as it uses exclusively non-toxic and inexpensive materials, namely surfactant and water. Thus, it is thought viable to be readily integrated into a variety of systems, especially those that are relevant to biomedical applications. Fourth, this synthetic strategy has the potential to be a generalized process that can be extended readily to the synthesis of different kinds of metal nanoparticles. Studies in this direction are underway.

Conclusions

In conclusion, we proved that nonionic surfactants such as T-80 not only act as stabilizing or protecting agents, but also can act as reducing agents for the size controlled synthesis of Au⁰ at room temperature in aqueous medium. Further, we demonstrated that the current facile one-step synthetic protocol is highly valuable to prepare well-dispersed and stable Au⁰ with required particle size. Considering the ubiquitous occurrence of surfactants in everyday life, e.g., in shower gels, toothpaste, cleaning agents, washing powders, dishwashing liquids, etc., the impact of these results could be tremendous. Consequently, the general formation of metal nanoparticles with a high toxicity potential under very mild conditions cannot be excluded.

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