Convenient synthesis of stable silver quantum dots with enhanced photoluminescence emission by laser fragmentation*

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A new strategy for the facile synthesis of very stable and mono-dispersed silver (Ag) quantum dots (QDs) is developed by laser fragmentation of bulk Ag in water using polysorbate 80 as a dispersing and stabilizing agent. The surfactant plays an important role in the formation of size-controlled Ag nano-structures. The Ag QDs have excellent photo-stability of $\sim$ 500 h and enhanced photoluminescence (PL) at 510 nm. This has significant implications for selective and ultrasensitive PL probes. Based on laser fragmentation in the biocompatible surfactant solution, our results have opened up a novel paradigm to obtain stable metal QDs directly from bulk targets. This is a breakthrough in the toxicity problems that arise from standard chemical fabrication.

Keywords: size-controlled Ag nano-structures, pulsed laser fragmentation

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1. Introduction

Silver (Ag) nano-materials with exceptionally small nanocrystal sizes of a few nanometers including quantum dots (QDs) have received increasing attention as super-active catalysts, faster responsive sensors, biological imaging, as well as selective and ultrasensitive fluorescent probes.[1–8] This is due to their unique optical properties associated with the excitation of plasmons. Compared with large Ag nano-objects, the Ag QDs are of fine structure with a high surface area, high carrier transport-mobility, superior thermal/chemical stability, and better surface grafting properties.[4–9] Moreover, the enhanced electromagnetic field near Ag QDs can be employed in surface-enhanced Raman spectroscopy, which has opened up the possibilities of using these biocompatible Ag QDs for in vivo anatomical imaging and early stage tumor diagnosis with deep tissue penetration.[1–3] Increasing evidence has shown that the excellent properties of Ag QDs are strongly dependent on the mono-dispersed Ag QDs with exceptional stability of the colloidal solution. Meanwhile, these specific applications are often complicated because of potential toxicity issues arising from the inevitable purification procedures of nano-particles via standard chemical fabrication based on the reduction of a precursor salt with a reducing agent. The development of new methods of conveniently synthesizing stable and mono-dispersed Ag QDs is important.

Laser fabrication in liquid is a new green approach to the synthesis of novel meta-stable phases of materials.[10–16] It is an attractive technique with a high non-equilibrium processing character. It offers a breakthrough in toxicity challenges. Stable Ag nano-particles and Ag_2O/Ag nano-colloids have been reported by using laser ablation in different surfactant solutions.[15–17] Yan *et al.* fabricated a mixture of Ag_2O/Ag nano-cubes, pyramids, triangular plates pentagonal rods, and bars with sizes ranging from 400 nm to 1000 nm by laser ablation of Ag in polysorbate 80, 40, and 20 aqueous solutions.[16] Stable Ag nano-colloids with diameters from $\sim$ 10 nm to $\sim$ 30 nm have been generated by laser ablation in isopropanol, ethylene glycol, and biopolymers such as chitosan.[17] By using dodecanethiol solution in heptanes, Ag nano-particles with the diameters of 5 nm–30 nm were produced by laser ablation.[15] It should be noted that these reports mainly focused on the synthesis of Ag nano-particles with large sizes or the fabrication of smaller Ag nano-colloids via some potentially toxic surfactants such as dodecanethiol, isopropanol, heptanes, etc. The schemes, which are environmentally friendly or have negligible toxicity, make stable and small Ag QDs remain incomplete.

Herein, we design a simple, versatile, and rapid route to controllably synthesize stable and mono-dispersed Ag QDs directly from a bulk Ag target based on laser fragmentation in liquid solution containing distilled water and polysorbate 80. The polysorbate 80 is a dispersing and stabilizing agent and is a nonionic surfactant or biocompatible emulsifier. It is often used as an emulsifier in foods or a solubilizer in mouthwash or an effective drug delivery vehicle in the brain, etc.[16] Moreover, the liquid can be adjusted to obtain desirable nanostructures because the polysorbate 80 concentration plays a critical role in the synthesis of nano-scale Ag nano-particles during laser ablation of a Ag target.

We use polysorbate 80 concentrations ranging from 0%

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to 25% v/v, and the mean diameters of the Ag nano-particles substantially decrease from about 65.5 nm to 2.2 nm resulting in the photoluminescence (PL) spectra of Ag nano-clusters at 510 nm that is drastically enhanced from about 3438 a.u. to ∼40618 a.u. (The unit a.u. is short for atomic unit.) Moreover, the strong PL emission of Ag QDs shows excellent photostability after keeping them in liquid for 500 h. Meanwhile, a detailed discussion of the relevant mechanism is addressed. The aim of this work is to extend a new method of synthesizing the highly photoluminescent and stable Ag QDs. We then use this approach to generate other metal complex nano-structures by laser fragmentation.

2. Experimental setup

This scheme used pulsed laser ablation of a solid target in liquid. It is similar to that described in previous studies.[10–12,14–17] In a typical experiment, a well-polished pure (99.99%) Ag target was placed on the bottom of a rotating glass dish with a speed of ∼ 100 rpm that was filled with polysorbate 80 and distilled water to 3 mL ($V_{\text{polysorbate}}$: V_{water} = 0% v/v–25% v/v). A Q-switched Nd-YAG (yttrium aluminum garnet) laser (Quanta Ray, Spectra Physics) beam operating at a wavelength of 1064 nm with a pulse duration of 10 ns and 5 Hz repetition rate was focused onto the Ag target surface. The laser beam was focused on the target by a quartz lens with 50-mm focal length, and the average spot size of the laser beam at the target was measured to be about 300 μm. During the laser irradiation, the liquid was protected by N_2 gas at a flow rate of 10 sccm to avoid the formation of surface oxidation Ag nano-particles in the liquid. The laser beam intensity was about 6.5 GW/cm^2, and the ablation lasted 1.5 h. After laser fragmentation, the Ag nano-particles were repeatedly centrifuged at 18000 rpm for 20 min in an ultracentrifuge, and the precipitates were carefully washed in ethanol three times. The sediments were dropped on a copper mesh and dried in an oven at room temperature for observation by transmission electron microscopy (JEOL-JEM-2100F). In addition, the crystallographic investigations of the Ag nano-particles were analyzed by x-ray diffraction (XRD) patterns (Rigaku RINT-2500VHF) using Cu Kα radiation (λ = 0.15406 nm). Morphological investigations and chemical composition measurements were performed by field emission scanning electron microscope (SEM, Hitachi S-4800) equipped with energy-dispersive x-ray spectroscopy (EDS). The absorption spectra of the Ag colloidal suspensions were measured with a UV–Vis–IR spectrometer (Cary 50). A 325-nm CW semiconductor laser (18 mW) was used as an excitation source with a spot size of ∼ 170 μm. The PL spectra of the Ag colloidal suspensions were dispersed by a monochromator (Jobin-Yven iHR320) with a 300/mm grating, and detected by a thermo-electrically cooled CCD detector (Synapse).

3. Results and discussion

After cumulative pulse laser ablation of pure Ag metal in distilled water with the polysorbate 80 concentration of 0% v/v, low magnification and high resolution images of the

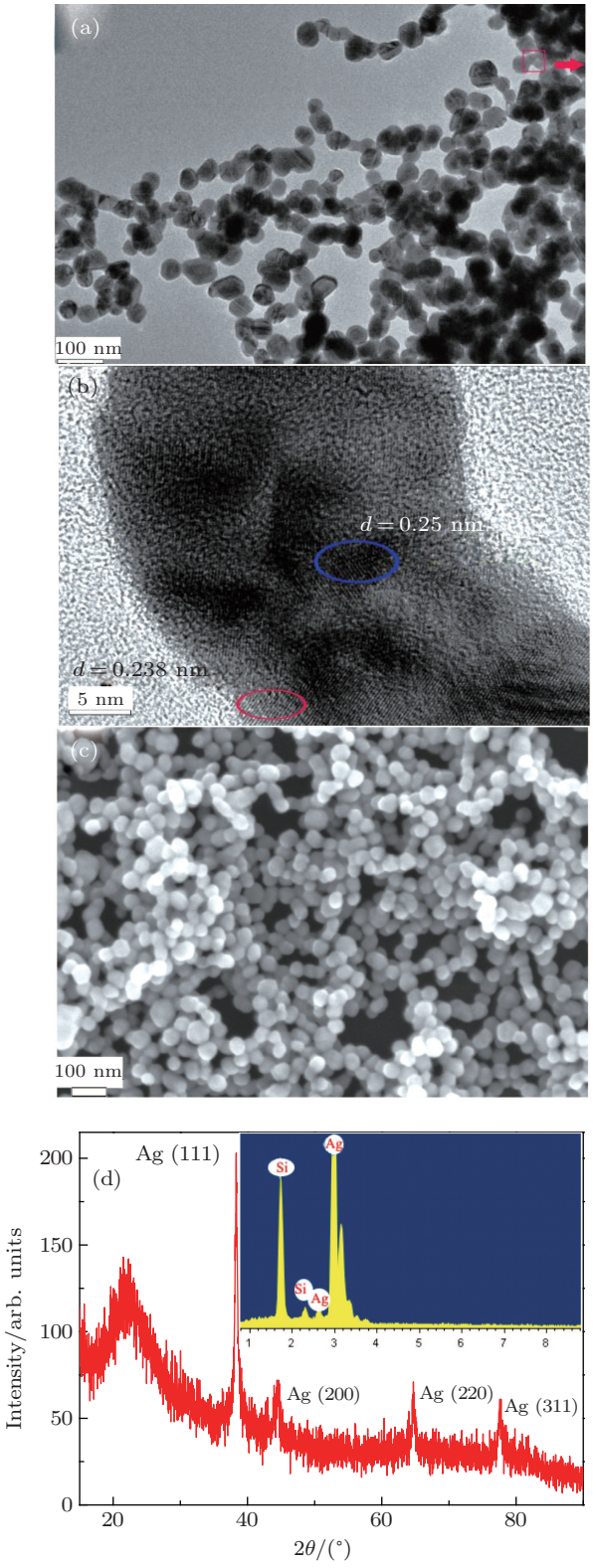


Fig. 1. (color online) (a) and (b) The representative low-magnification and enlarged TEM images of the nano-particles by laser ablation of pure Ag metal in distilled water, respectively; (c) the SEM morphology of the products fabricated in distilled water; (d) XRD pattern of the nano-particles and inset showing the result of the EDS.

nano-particles are collected with transmission electron microscopy (TEM; Figs. 1(a) and 1(b), respectively) and scanning electron microscopy (SEM; Fig. 1(c)). The morphologies in Figs. 1(a) and 1(c) clearly show that numerous quasi-spherical nano-materials with diameters varying from about 60 nm to 80 nm are interconnected and accreted with each other. They form short curvilinear groups with a necklace-like structure. The HRTEM image in Fig. 1(b) provides a typical structural detail of the cross points of two nano-particles. The region marked by red lines in Fig. 1(b) with a d-spacing of 0.238 nm is indexed as the (111) plane in the Ag structure. On the other hand, the area marked by blue lines in Fig. 1(b) with a periodicity corresponding to a d-spacing of 0.25 nm could be indexed with reference to the Ag (422) plane structure. This is formed by stacking fault defects via cumulative pulse laser sintering. The relatively strong peaks of the XRD pattern depicted in Fig. 1(d) only contain diffraction peaks from Ag nano-structures. This is consistent with the chemical composition result (the Ag element and Si signal from the Si substrate) of EDS as seen in the inset of Fig. 1(d).

The above results in Fig. 1 clearly confirm that multiple pulses of laser ablation of the Ag target in distilled water will result in the formation of interconnected Ag nano-spheres. In the following section, we will describe the possible growth of Ag nano-particles. Without any surfactant in the liquid, the extreme conditions characterized by the highly non-equilibrium

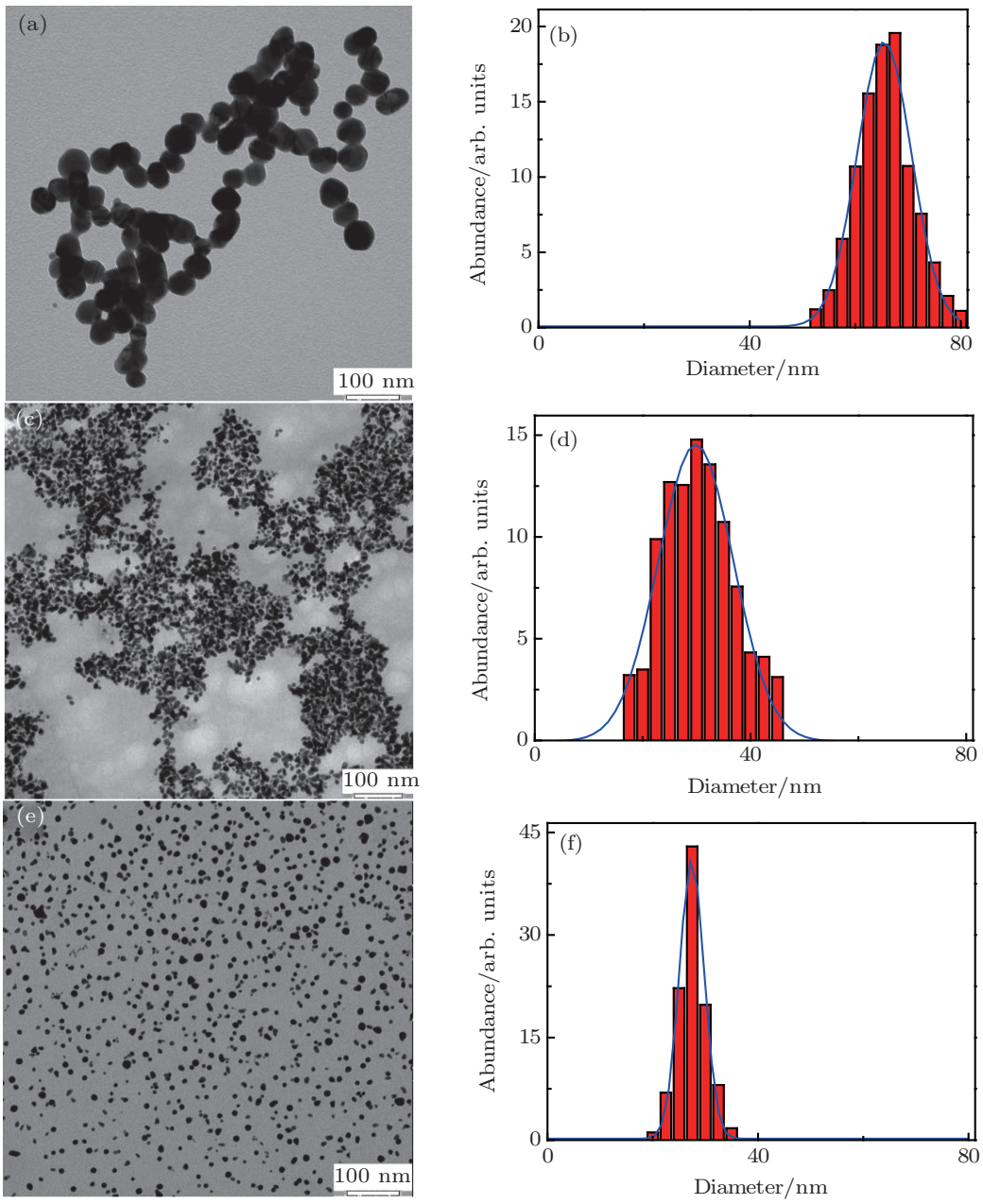


Fig. 2. (color online) TEM images and the corresponding size distribution histograms of typical Ag nano-particles fabricated in the aqueous solutions of polysorbate 80 with different concentrations: (a) and (b) 5% v/v, (c) and (d) 10% v/v, (e) and (f) 15% v/v, respectively.

feature include high temperature and pressure. This will enable laser sintering of the assembled particles to play an important role in the pulse ablation process. The Ag nano-particles interconnect with each other via magnetic-dipole interaction in distilled water and then accrete together by the highly localized melting in the following subsequent laser ablation—this has been reported previously.[12,13] With the liquid solution containing polysorbate 80, the nonionic surfactant acts as a dispersing and stabilizing agent. It plays a critical role in the formation of mono-dispersed Ag nanostructures. In this way, the Ag nano-crystals are not hinge jointed, but are fabricated individually. Laser fragmentation of the separated Ag nano-crystals will dominate the subsequent laser irradiation process. This results in the fabrication of numerous ultra-small Ag nano-structures. Following this mechanism, a higher concentration of polysorbate 80 in the liquid solution should lead to more dispersed Ag nano-particles. This will then lead to the formation of stable and mono-dispersed Ag QDs.

To verify this laser fragmentation process, we increase the concentration of polysorbate 80 via water to 5%, 10%, and 15% v/v, respectively. The typical TEM images and the corresponding particle size distribution histograms of the final particles are illustrated in Figs. 2(a)–2(f), respectively. Each size distribution is obtained by measuring the diameters of more than 1200 particles in sight on the TEM images. In the aqueous solution of 5% polysorbate 80, the Ag nano-particles remain close to each other (Fig. 2(a)). They are likely to be fabricated individually and are not hinge jointed. The mean size of the Ag nano-particles is about 65.5 nm (Fig. 2(b)). At 10% and 15% polysorbate 80, more water-dispersed Ag nanomaterials can be clearly seen in Figs. 2(c) and 2(e), respectively. As shown in Fig. 2(e), the separated Ag nano-particles characterized by narrow size dispersion (less than 10-nm full width at half maximum in the inset) are fabricated individually and are monodisperse. The mean sizes of the Ag nanomaterials decreased to 29.8 nm and 25.4 nm in Figs. 2(d) and 2(f), respectively. Increasing the polysorbate 80 concentrations to 20% v/v and 25% v/v result in ultra-small Ag nanostructures (Figs. 3(a) and 3(c)), respectively. In addition to the well-dispersed Ag nano-structures, the mean size drastically drops from 4.5 nm to 2.2 nm as the polysorbate 80 concentration increases to 20% v/v and 25% v/v respectively. The mean diameter with an error bar of 5% as a function of polysorbate 80 concentration is displayed in Fig. 3(e). The mean diameter decreases nonlinearly with an increase of polysorbate 80 concentration, and the size reduction can be described as a Boltzmann function. The detailed functional form and the fit parameters are summarized (Fig. 3(e)). It should be noted that the activated liquid with much higher polysorbate 80 concentration ($>$ 25% v/v) will enable the laser excitation of the surfactant. This will then result in complicated chemical reactions between the Ag ions and the activated liquid. This is unfavorable for the synthesis of pure Ag QDs. In brief, the polysorbate 80 controls the size of the product even down to 2-nm mono-dispersed Ag QDs.

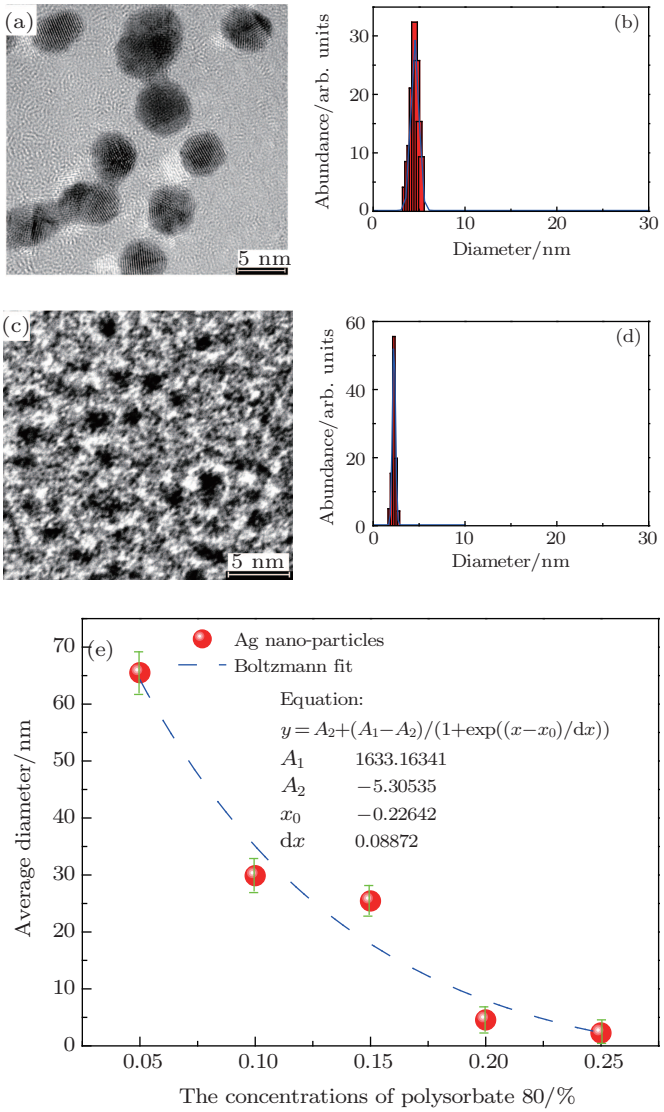


Fig. 3. (color online) TEM images and the corresponding size distribution histograms of representative Ag nano-particles fabricated in the aqueous solutions of polysorbate 80 with different concentrations: (a) and (b) 20% v/v, and (c) and (d) 25% v/v, respectively. (e) The curve of the mean diameter of Ag nano-particles versus the polysorbate 80 concentration ($V_{\text{polysorbate}} : V_{\text{water}} = 5\%$ v/v–25% v/v). The inset shows the detailed functional form and the fit parameters.

Finally, the unique optical properties of size-controlled Ag nano-particles are illustrated by the absorption and PL spectra (Fig. 4). After pulses of laser fragmentation of the Ag target in liquid solution with polysorbate 80 concentrations of 5%, 10%, 20%, and 25% v/v, respectively, the Ag nano-spheres are separately dried in a vacuum oven at 30 °C for 1 h. The powder weight is carefully measured by an electronic analytical balance with an accuracy of 0.1 mg. Based on the result of the mean diameter in Fig. 3(e), the approximate volume ratios of the Ag nano-spheres fabricated in liquid solutions with polysorbate 80 concentrations of 5%, 10%,

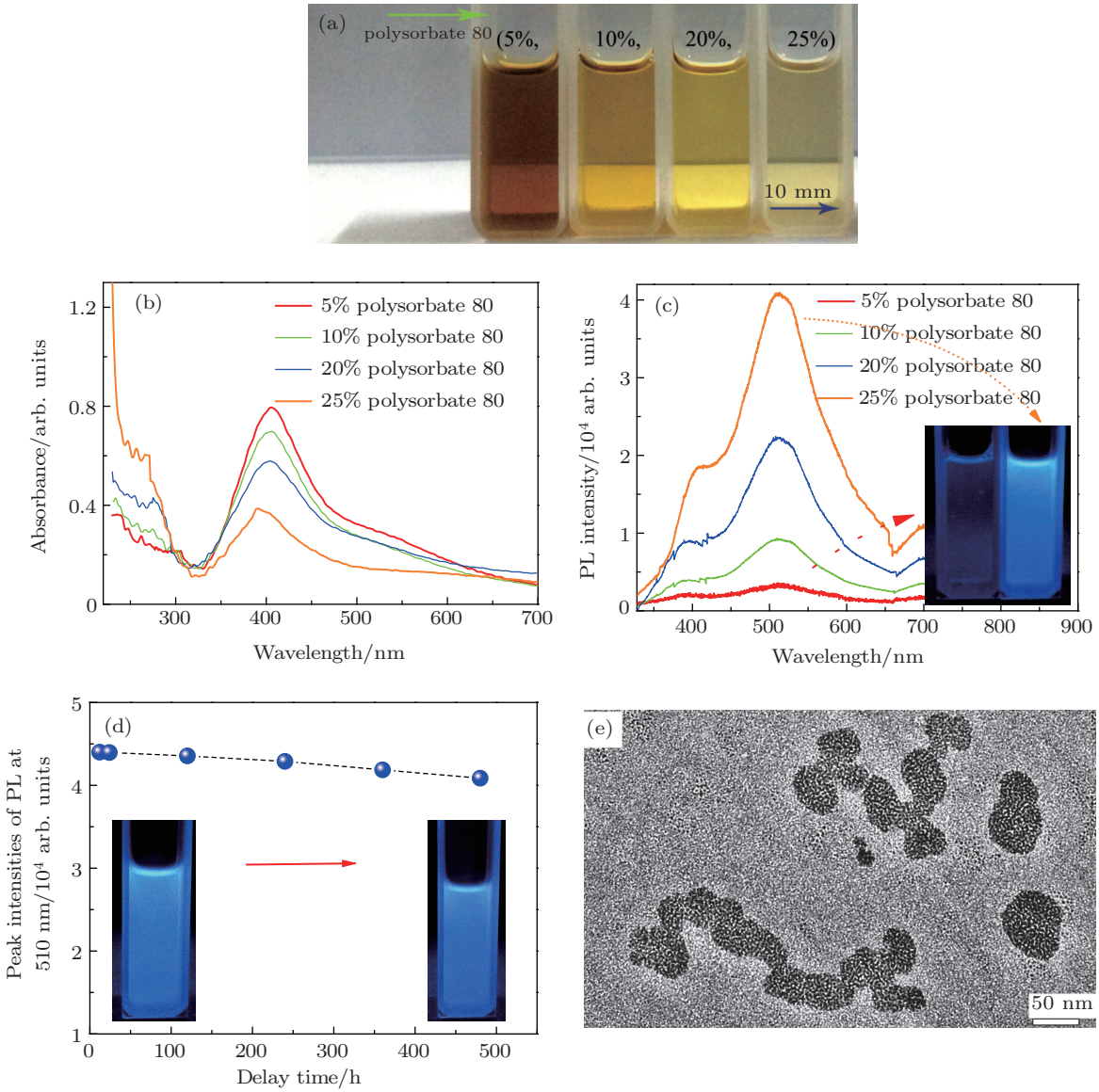


Fig. 4. (color online) (a) Direct photographs of Ag colloidal suspensions fabricated by pulsed laser irradiation of the Ag target in liquid solutions containing polysorbate 80 ($V_{\text{polysorbate}} : V_{\text{water}} = 5\%$ v/v–25% v/v). (b) and (c) The UV-visible absorption and photoluminescence (PL) spectra of the as-prepared Ag colloidal suspensions, respectively. The insets in panel (c) show the photographs of large-sized Ag colloidal suspension and Ag QDs solution under irradiation by a 254-nm UV lamp, respectively. (d) The peak intensities of the PL spectrum of Ag QDs at about 510 nm versus the time delay at room temperature. The insets show the photographs of Ag QDs under irradiations by a 254-nm UV lamp for a delay time at 12 h and about 400 h, respectively. (e) The typical TEM images of Ag QDs after keeping them in liquid for 500 h.

20%, and 25% is about 1, 8, 2500, and 26000. Four beakers are filled with 200-mL distilled water and 1-mg, 8-mg, 2.5-g, and 26-g Ag nano-materials, respectively. In this way, there are no significant differences in the total quantity of Ag nano-spheres among the four solutions. The direct photographs of 2-mL Ag colloidal suspensions are shown in Fig. 4(a). The increasing polysorbate 80 concentration leads to a significant change in the solution color from red-brown to light yellow. This is due to the ultra-small size and mono-dispersed structures of Ag QDs. Moreover, the UV-visible optical absorption spectra of Ag nano-particle solutions in Fig. 4(b) clearly show the relative intensities of the absorption spectra at 407 nm and below 300 nm. This region decreases and improves as the size becomes smaller (from about 60 nm to 2 nm). Interestingly, more visibly enhanced PL emissions excited by a 325-nm CW semiconductor laser centered at about 510 nm are clearly illustrated in Fig. 4(c) when the polysorbate 80 concentration varies from 5% v/v to 25% v/v. Owing to the exceptionally small nanocrystal sizes, the PL spectrum of the mono-dispersed Ag QDs solution in Fig. 4(c) shows a peak intensity at about 510 nm. It is greatly improved to about 40618 a.u, which is almost a factor of 12 higher than the peak intensity of the Ag nano-structure with 5% polysorbate 80. Meanwhile, the insets in Fig. 4(c) show direct photographs of relatively weak and strong PL emissions from Ag nano-spheres with a larger size ($\sim$ 60 nm) and Ag QDs solutions under irradiation at 254-nm UV light, respectively. The PL emission of pure polysorbate 80 in distilled water (25% v/v) irradiated with a pulsed laser beam for 1.5 h is investigated. It shows a very weak PL spectrum from 400 nm–650 nm. Therefore, the pho-

todecomposition of polysorbate 80 can be ignored. It is reasonable to deduce that the strong PL emission in Fig. 4(c) originates from the Ag QDs structure. Owing to the quantum confinement and edge effects, the excitation of the surface plasmon polaritons within Ag QDs can create a strong local optical field and result in high PL. Moreover, the mono-dispersed Ag QDs are also characterized by remarkable photo-stability at room temperature in addition to enhanced fluorescence emission in the visible region. The peak intensity of the PL spectrum at 510 nm versus the delay time with respect to the laser fragmentation is displayed in Fig. 4(d). The stable emission property of these Ag QDs could still be sustained for hundreds of hours. The measured peak intensities are nearly constant even up to 500 h. The corresponding photographs (the insets in Fig. 4(d)) confirm the similar emissions at 12 h and 480 h after fabrication. There is no substantial increase in Ag QD size after keeping them in liquid for 500 h. In addition to the effect of the polysorbate 80, the stability of the Ag QDs structure is due to the ultra rapid cooling and freezing of the superheated Ag nano-crystals. This is a function of pulse. In the longer time region ($>$ 11 days), the visible emission will gradually decrease because of inevitable recombination process in Ag QDs. This can be confirmed by the TEM, which shows worm-like Ag nano-clusters (Fig. 4(e)). Further studies will investigate dispersion and stabilization of other noble-metal QDs fabricated by green, simplistic, and versatile strategies. This would be applicable to biological imaging, fluorescent probes, etc.

4. Conclusions

In this work, size-controlled Ag nano-structures are carefully devised through multiple pulse laser fragmentation of a Ag metal target in a liquid medium containing nonionic surfactant polysorbate 80 as a dispersing and stabilizing agent. The well mono-dispersed Ag QDs with a mean size of approximately 2 nm can be obtained by simply increasing the surfactant concentration in distilled water to 25% v/v. In addition to the enhanced PL emission in the visible region, the remarkable photo-stability of these water-dispersed Ag QDs remains for about 500 h after synthesis. The product has negligible toxicity by using cell proliferation. This is because there are no toxic elements used during fabrication. This work confirms the possibility of using these Ag QDs for in vivo anatomical and early stage tumor diagnosis if the PL emission can be shifted to the infrared region.

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