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ORIGINAL ARTICLE

Facile synthesis of bimetallic nanoparticles by femtosecond laser irradiation method

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Bimetallic;
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Abstract Bimetallic Pt–Au and Fe–Pt nanoparticles are successfully fabricated by high-intensity laser irradiation of aqueous solution without any chemical reducing agent. The mechanism of the formation of bimetallic nanoalloys by laser irradiation of the solution without using any reducing agent was mainly attributed to the optically induced decomposition of water molecule. When an intense femtosecond laser field is focused in an aqueous solution containing metal ions, the free electrons will be produced by the dissociation of water molecules, these free electrons and hydrogen radicals contained in the plasma might be caught by H^+ or OH^- ions to form the bubbles of H_2 and O_2 gases or they can be trapped by metal ions, resulting in the formation of metal atoms during the femtosecond laser irradiation process. The average size of the bimetallic nanoparticles increases with irradiation time. This technique is simple and 'green' process without using any chemicals except for metal salt and dispersing agent.

1. Introduction

Nanoparticles have attracted great attention because their physical and chemical properties often deviate from their bulk materials when the particle size decreases to a specific regime (Chen et al., 1998). Binary alloy nanoparticles (NPs) have been intensively studied especially in the research field of catalysis because of their bifunctional catalytic properties (Stamenkovic et al., 2002, 2007; Paulus et al., 2002). Currently, gold–platinum (Pt–Au) bimetallic alloys have attracted much attention for electrocatalysis in a fuel cell. The Pt–Au nanoalloys are expected to provide synergistic catalytic activities such as suppression of adsorbed poisonous species like carbon monoxide (CO) on Pt atoms, and the change in electronic band structure to modify the strength of the surface adsorption (Hernández-Fernández et al., 2008; Wang et al., 2008; Selvarani et al., 2009; Derrick et al., 2007). The decrease of activation energy promoting oxidative desorption and suppressing the adsorption of CO was considered as a factor that leads to a sufficiently high adsorptivity to support catalytic oxidation in alkaline electrolytes. High quality magnetic nanoparticles have attracted increasing attention because of their potential technological applications in high-density data storage. In order to enhance the thermal stability of the magnetic recording medium, the magnetic material used should exhibit high magneto-crystalline anisotropy and high coercivity. FePt nanoparticles can be used in ultrahigh density magnetic

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recording because they are magnetically hard, chemically stable and possess high magneto-crystalline anisotropy (Song et al., 2006).

In tradition, most bimetallic alloy nanoparticles can be prepared by wet-chemical methods such as chemical reduction or physical process such as microwave synthesis (Tekaia-Elhsissen et al., 1999; Chau, 2007). For example, bimetallic particles can be synthesized by reduction or disproportionation of inorganic compounds in liquid polyols (Viau et al., 1996). However, some problems need to be addressed in these synthesis processes. (1) Most chemical methods are not so environmentally friendly since they often use a lot of organic solvent (e.g. DMF) and need reducing agents. (2) An organic capping agent is usually needed to cap the bimetallic nanoparticle during wet-chemical synthesis to control the particle growth. Fabrication of metal alloy by the femtosecond laser irradiation can provide a "Green synthesis" solution, in which no organic solvent or chemical reducing agent is needed. In general, when an intense femtosecond laser field is focused in an aqueous solution containing metal ions, the free electrons will be produced by the dissociation of water molecules, forming energetic radicals such as H and OH (Nikogosyan and Angels, 1980; Chin and Lagaće, 1996). These free electrons and hydrogen radicals contained in the plasma might be caught by H^+ or OH^- ions to form the bubbles of H_2 and O_2 gases as confirmed by gas chromatography test in the previous works (Zhao et al., 2003a,b) or they can be trapped by metal ions, resulting in the formation of metal atoms during the femtosecond laser irradiation process. It is expected that an intense optical field will strongly interact with molecules and produce highly charged ions resulting in significant optical decomposition of molecules and succeeding formation of different molecules or particles, the femtosecond laser irradiation of a liquid is a potential novel method of material processing. In this work, synthesis of bimetallic metal nanoparticles such as Pt–Au and Fe–Pt by using femtosecond laser irradiation of aqueous solution was demonstrated. The intense optical field created by femtosecond laser pulse induced the production of highly charged ions and molecules due to the optical decomposition of metal precursor molecules. The effect of dispersing agent and irradiation time for the formation of bimetallic nanoparticles was also studied.

2. Experimental

The Pt–Au metal precursor aqueous solution was prepared by dissolving chloroauric (III) acid tetrahydrate ($HAuCl_4.4H_2O$, Aldrich) and chloroplatinic (IV) acid hexahydrate ($H_2PtCl_6.6H_2O$, Aldrich, >99.9%) in deionized water. The Fe–Pt precursor aqueous solution was prepared by dissolving iron (III) chloride ($FeCl_3$, Aldrich) and chloroplatinic (IV) acid hexahydrate ($H_2PtCl_6.6H_2O$, Aldrich, >99.9%) in deionized water. Polyvinylpyrrolidone (PVP, Aldrich) with concentration of 1.0×10^{-2} wt.% was added to the solution as dispersing agent. All the preparations of the metal precursor solution and laser irradiation experiment were carried out in a darkened room because of the photosensitive property of the gold and platinum precursor molecules. The concentration of each bimetallic precursor solution was set to 5.0×10^{-4} M. All the solutions were transparent, and no apparent difference was observed. As a target of laser irradiation, 3 ml of each aqueous solution was dispensed in a $10 \times 10 \times 45$ mm quartz glass cuvette that is optically transparent at the wavelength of incident laser light. Femtosecond laser beam was generated from a chirped-pulse amplified Ti:sapphire laser system (Newport Corporation, Spectra-Physics) with the wavelength of 780 nm. The pulse energy was 3 mJ with the pulse width of 100 fs. The repetition rate was controlled at 30 and 1000 Hz respectively. The laser beam was introduced to the cuvette nor-

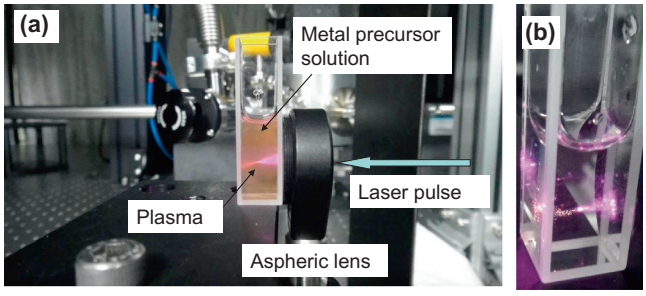

Figure 1 (a) Optical image of experimental set-up for femtosecond laser fabrication of nanoparticles, (b) magnified optical image of femtosecond laser irradiation of aqueous solution.

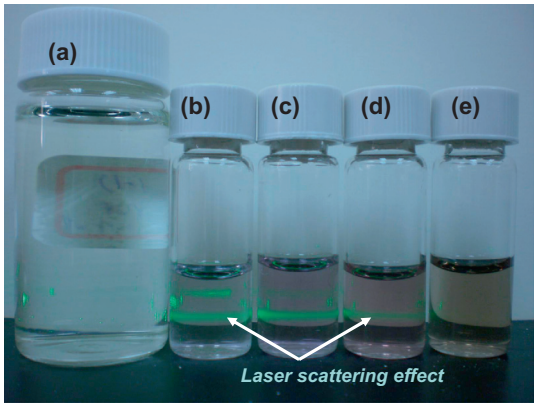

Figure 2 Optical image showing the light scattering properties of metal precursor solution irradiated for (a) 0, (b) 3, (c) 5, (d) 10 and (e) 20 min.

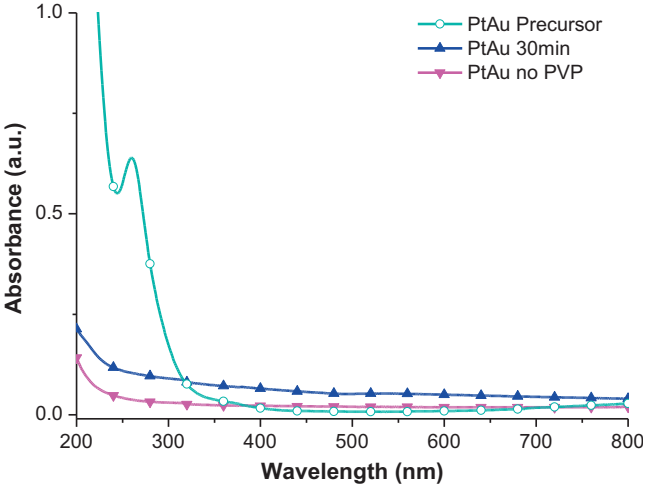

Figure 3 UV absorption spectra of the Pt–Au sample before and after laser irradiation.

mal to its surface and tightly focused in the solution by an aspheric lens with the focal length of 8 mm and the numerical aperture of 0.5. The experimental set-up was shown in Fig. 1.

The effect of irradiation time on the structural property of bimetallic Pt–Au nanoparticles was studied. The precursor solution was irradiated with a high intensity laser from 3 to 20 min. Optical properties of the solution before and after laser irradiation were characterized by a UV–vis spectrophotometer (PerkinElmer Lambda 750). Transmission electron microscopes (TEM: JEOL, JEM-2010F) were employed to take electron micrographs of the products after irradiation. The samples for TEM observation were prepared by placing a few drops of the solution on a carbon-coated copper grid (Ted Pella Inc.) immediately after the irradiation and dried in air at room temperature. The compositional distributions of individual bimetallic nanoparticles were examined by X-ray energy dispersive spectroscopy (EDS) in a JEOL 2010F TEM at room temperature using a beam voltage of 200 kV.

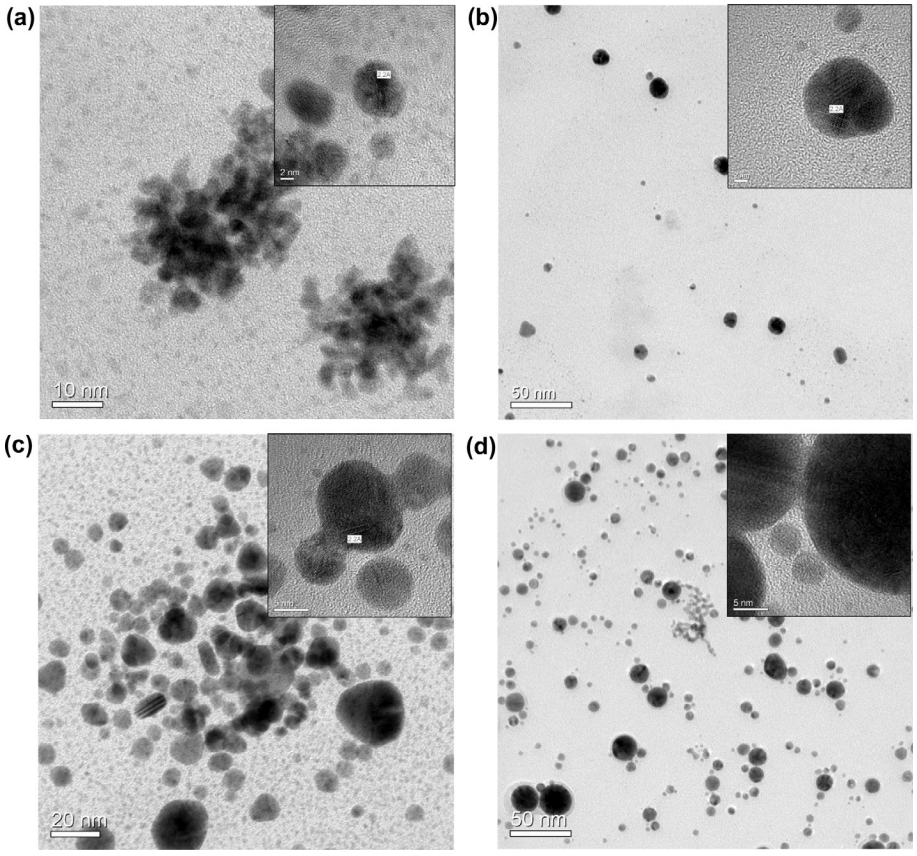

Figure 4 TEM images of bimetallic Pt–Au nanoparticles formed by irradiating the precursor solution for (a) 3, (b) 5, (c) 10 and (d) 20 min (Inset: HRTEM images).

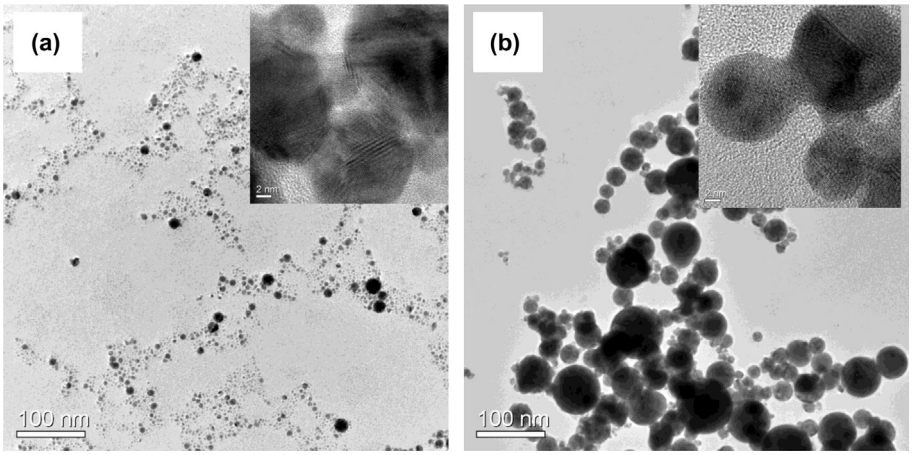

Figure 5 TEM image of bimetallic Pt–Au nanoparticles after irradiation of (a) 15 min. (Inset: HRTEM image), (b) 30 min. (Inset: HRTEM image).

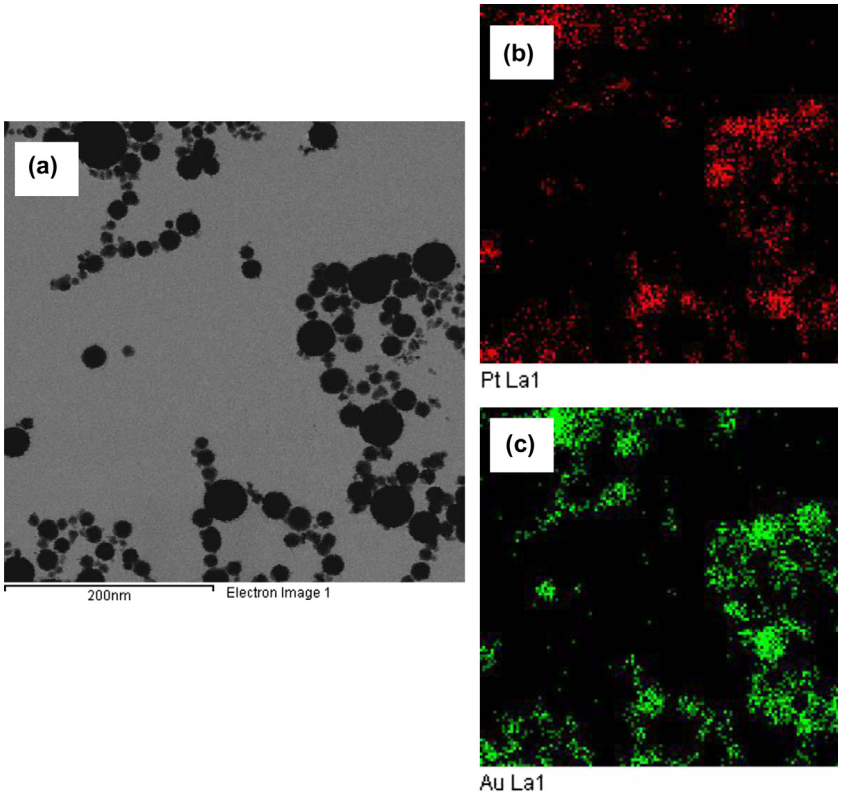

Figure 6 TEM image and Energy-dispersive X-ray (EDS) mapping of bimetallic Pt–Au nanoparticles formed by irradiating the precursor solution without PVP for 15 min.

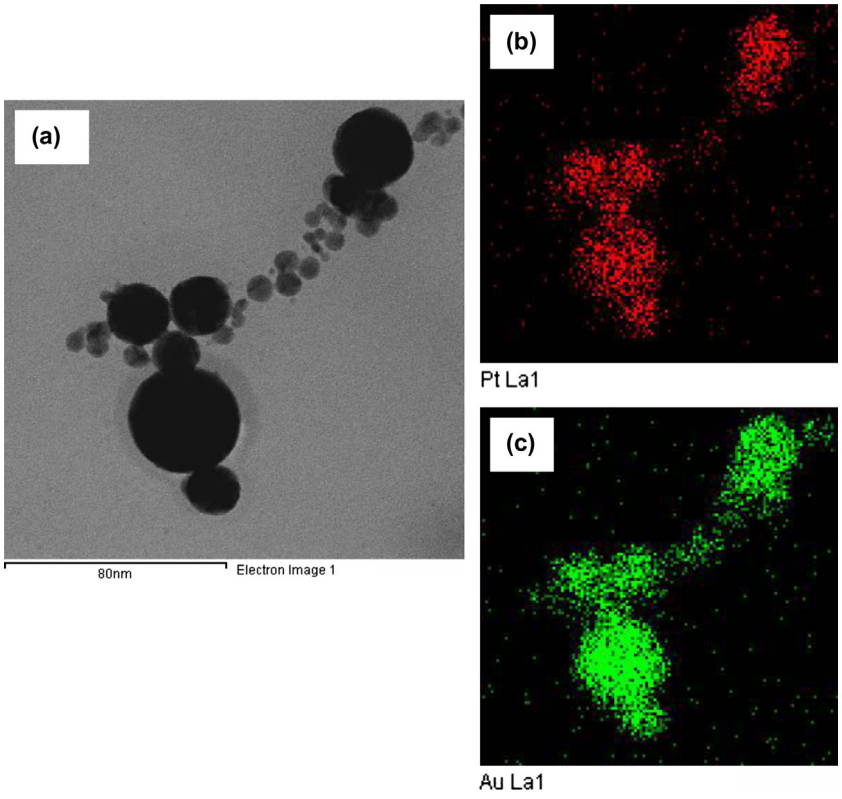

Figure 7 TEM image and Energy-dispersive X-ray (EDS) mapping of bimetallic Pt–Au nanoparticles formed by irradiating the precursor solution without PVP for 30 min.

3. Results and discussion

Bimetallic nanoparticles can be synthesized through femtosecond laser irradiation of aqueous solution. During a typical synthesis, very tiny flashes of sparks and gas bubbles were observed around the focal point during laser irradiation as shown in Fig. 1(b). These gasses were identified as oxygen and hydrogen by chromatographic analysis (GC-8A, Shimadzu Co.). It is expected that the gases were produced by the decomposition of water molecules through the laser induced break down facilitated by a high intensity laser field. The preparation of Pt–Au alloy nanoparticles is still a challenge because of the different reduction kinetics of Au and Pt ions. Phase segregation was observed in preparation of Pt–Au bimetallic nanoparticles via coreduction method (Mihut et al., 2002). The larger atomic radius of gold may result in lattice strain to contribute to the segregation of Au to the nanoparticle surface. As the optical field generated in the focal point of the femtosecond laser is very close to the Coulomb electric field in a hydrogen atom, the high intensity optical field induced the decomposition of Pt and Au precursor molecules. Polyvinylpyrrolidone was added to prevent the aggregation of the primary particles. The long polyvinyl chains of PVP molecules interact with the surface of nanoparticles and provide steric protection. It is expected that the addition of PVP can enhance the dispersibility and also prevent aggregation of nanoparticles. PVP was added to the Pt–Au and Fe–Pt precursor solution with the concentration of 1.0×10^{-2} wt.%.

Fig. 2 shows the light scattering properties of metal precursor solution irradiated for (a) 0, (b) 3, (c) 5, (d) 10 and (e) 20 min respectively. The laser scattering effect occurring in the sample clearly demonstrates that nanoparticles were formed in the solution after femtosecond laser irradiation. It can be seen that the color of the solution gradually changes from pale yellow to pale reddish-brown with increasing the laser irradiation time.

Fig. 3 shows the UV absorption spectra of the Pt–Au sample before and after laser irradiation. There is an absorption peak around 262 nm caused by $[PtCl_6]^{2-}$ ions in the Pt–Au precursor solution. However, the peak disappears after laser irradiation for 30 min irrespective of PVP addition, indicating that the precursor molecules were completely decomposed and reacted to form the bimetallic nanoparticles. In addition, absorption peaks around at 520 nm caused by the SPR of typ-

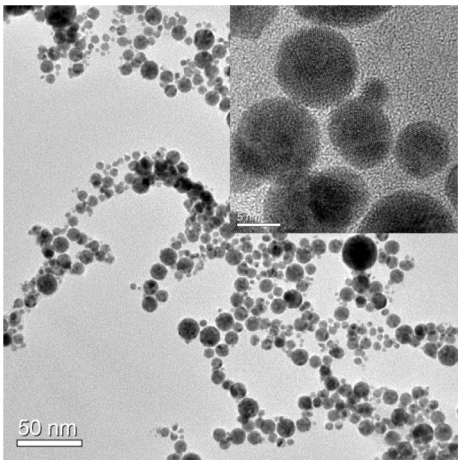

Figure 8 TEM image of Pt-Au nanoparticles after irradiating the precursor solution with PVP for 30 min. (Inset: HRTEM image).

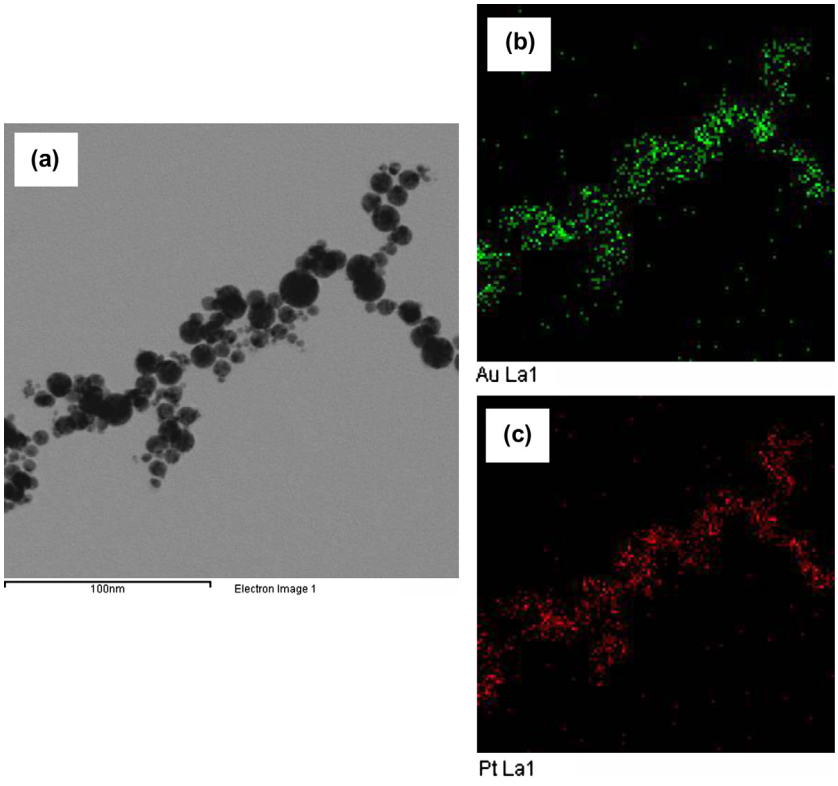

Figure 9 Energy-dispersive X-ray (EDS) mapping of bimetallic Pt–Au nanoparticles formed by irradiating the precursor solution with PVP for 30 min.

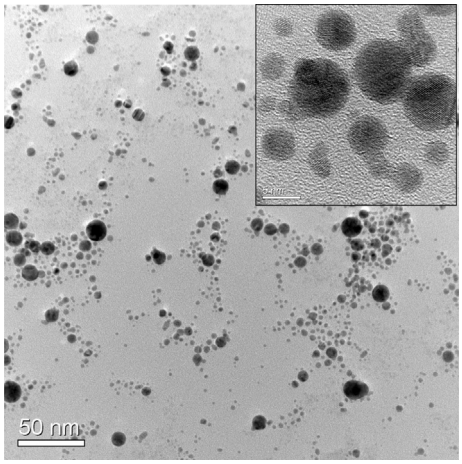

Figure 10 TEM image of bimetallic Pt–Au nanoparticle sample prepared by irradiating the precursor solution with femtosecond laser of 1000 Hz for 10 min.

ical gold nanoparticles were not seen in the spectra of the products with or without PVP addition, indicating the samples are indeed bimetallic alloy and were not formed by pure Au and pure Pt nanoparticles independently. Fig. 4(a–d) shows the TEM images of bimetallic Pt–Au nanoparticles formed by irradiating the precursor solution for 3, 5, 10 and 20 min respectively. It can be seen that aggregation of particles still occurs in the sample with short laser irradiation time (i.e., 3 min). According to the TEM analysis, it can be seen that the average size of the Pt–Au alloy nanoparticles increases with laser irradiation time. Particles with size larger than 20 nm were seen when the irradiation time was increased to 10 min. The shape of the nanoparticles also becomes more spherical after prolonged laser irradiation. Fig. 5(a and b) shows the TEM images of Pt–Au bimetallic nanoparticles formed by irradiating the precursor solution for 15 and 30 min respectively, both without adding PVP in the precursor solution. It can be seen that the average size of the bimetallic nanoparticles increases with laser irradiation time. The nanoparticles grow significantly after irradiating the Pt–Au precursor solution for 30 min. It is expected that the small metallic particles will be sintered together easily to form larger ones after prolonged femtosecond laser irradiation. Fig. 6 and 7 shows the Energy-dispersive X-ray (EDS) mapping of bimetallic Pt–Au nanoparticles formed by irradiating the precursor solution for 15 and 30 min respectively, both without PVP addition. A comparison of these images clearly reveals that the Pt and Au atoms distributed uniformly within individual nanoparticles. Fig. 8 shows the TEM image of Pt–Au nanoparticles prepared by irradiating the precursor solution with PVP for 30 min. By comparing the TEM images of Fig. 5(b) and Fig. 8, the average particle was drastically reduced with PVP addition. The addition of PVP significantly improved the dispersibility of the particles and the controllability of their mean particle size, compared with the sample without PVP. Although the interaction between each unit of PVP and metal nanoparticles is very weak, the collective interaction occurs simultaneously at a whole PVP molecular frame with a lot of active groups, significantly reducing the particle growth rate. Fig. 9 shows the Energy-dispersive X-ray (EDS) mapping of

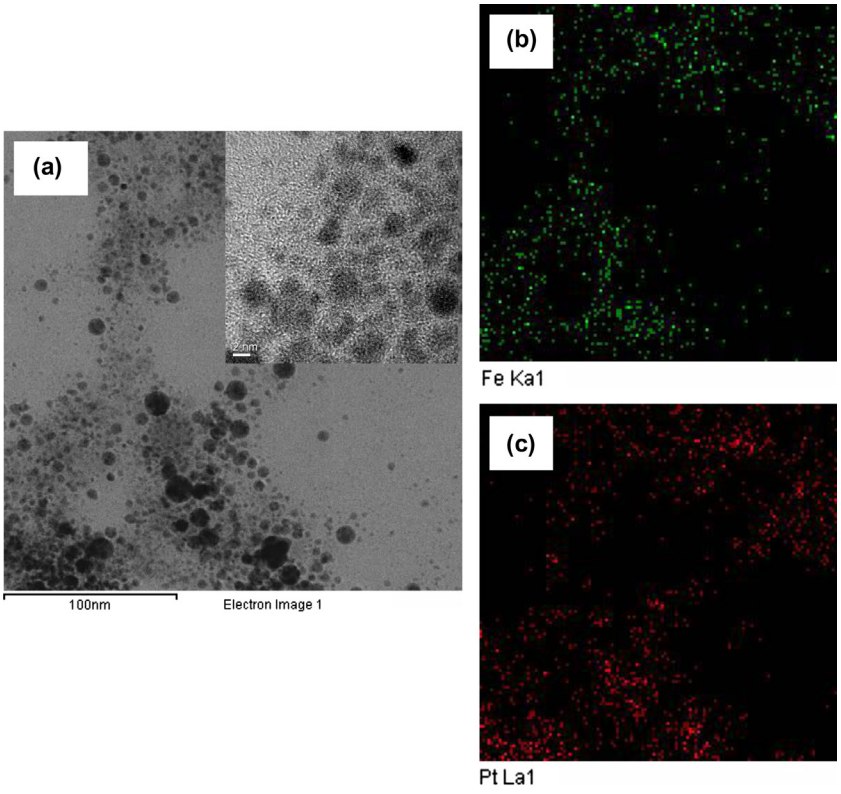

Figure 11 TEM image and Energy-dispersive X-ray (EDS) mapping of Fe–Pt nanoparticles after irradiating the precursor solution with PVP for 30 min. (Inset: HRTEM image).

bimetallic Pt–Au nanoparticles formed by irradiating the precursor solution with PVP for 30 min. A comparison of these images clearly reveals that the Pt and Au atoms are distributed uniformly within individual nanoparticles. In order to study the effect of laser repetition rate on structural property of nanoparticles, we also increased the repetition rate of laser to 1000 Hz. Fig. 10 shows the TEM image of Pt–Au bimetallic nanoparticle sample prepared by irradiating the precursor solution with femtosecond laser of 1000 Hz for 10 min. By comparing Figs. 4(c), 10, the nanoparticles prepared by higher repetition rate of laser have more spherical structure and smaller size in diameter. The reason may be attributed to the fact that more nuclei can be formed in a shorter time by using higher repetition rate of laser.

Other type of bimetallic nanoparticles such as Fe–Pt fabricated by femtosecond laser irradiation was also demonstrated. Fig. 11 shows the TEM images of Fe–Pt nanoparticles after irradiating the precursor solution with PVP for 30 min. It can be seen that in addition to irregular-shaped large particles with a diameter of several tens of nanometers, many nanometer-sized fine particles with a relatively wide size distribution were found.

The mechanism of the formation of bimetallic nanoalloys by laser irradiation of the solution without using any reducing agent was mainly attributed to the optically induced decomposition of water molecule. The solvated electrons and hydrogen radicals were formed in the aqueous solution like a kind of photochemical reaction. Generation of oxygen and hydrogen gasses around the focal spot during laser irradiation strongly indicates that hydrogen and hydroxyl radicals were simultaneously produced in the solution. Among them, solvated electrons and hydrogen radicals can act as a strong reducing agent in the solution. During the femtosecond laser synthesis of bimetallic Pt–Au nanoparticles, metal ions such as Pt and Au in the solution were easily reduced to zero-valance atoms forming 'core' of the particles. Further collisions with molecules result in subsequent growth of the nuclei and codeposition of Pt and Au atoms on the nuclei to form the larger ones. It was suggested that the reaction, formation and growth of particles mainly occur at the focal point of the femtosecond laser in the solution. The high temperature and pressure gradient created at the focal point of femtosecond laser are expected to enhance the formation of bimetallic nanoparticles. The formed particles will be carried away from the focal point by the tiny gas bubbles circulating through the solution.

4. Conclusion

Bimetallic Pt–Au and Fe–Pt nanoparticles are successfully fabricated only by high-intensity laser irradiation of aqueous solution without any chemical reducing agent. The average size of the bimetallic nanoparticles increases with irradiation time. The addition of PVP significantly improved the dispersibility of the particles and the controllability of their mean particle size, compared with the sample without PVP. It should be noticed that the technique is quite simple and 'green' process without using any chemicals except for metal salt and dispersing agent. Other nanoalloys can also be potentially fabricated in aqueous solution using the femtosecond laser irradiation method.

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