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RESEARCH ARTICLE

High voltage preparation, characterization, and optical properties of silver dendrites in PVA matrix

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Abstract In this paper, we present a room-temperature synthesis of silver dendrites in a poly(vinyl alcohol) (PVA)-Ag composite system with the assistance of high voltage. In the silver dendrites, the nanounits are platelike, thus the surface plasmon absorption bands of silver dendrites are tuned from visible to ~800 nm, which is due to the template function of PVA and the assistance of high voltage. Scanning electron microscope (SEM), X-ray diffraction (XRD), and energy dispersive X-ray (EDX) data confirm that the structures are crystalline silver embedded in PVA. The absorption results indicate that the ratio of PVA and Ag do not influence the position but the intensity of the near-infrared (NIR) absorption. This material has potential use in the field of bio-application and infrared sensors.

Keywords silver dendrites, poly(vinyl alcohol) PVA, composite, high voltage, near-infrared (NIR) absorption

1 Introduction

Noble metal nanostructures have been widely exploited, motivated by its potential importance to a broad range of applications in designing new materials and devices in various fields, such as photography, catalysis, biological labeling, photonics, optoelectronics, and surface-enhanced Raman scattering (SERS) [1–3]. The intrinsic properties of a metal nanostructure can be tuned through changes in their size, shape, composition, structure, and morphology [4]. For the remarkable feature of surface plasmon resonance (SPR), changing the structure of the noble metal particles from a solid sphere to a shell formed on a silica nanoparticle [5] or to a hollow cage [6] can result in a shift of the optical extinction band from the visible to near-infrared region. Such structural and compositional tuning is quite useful in potential *in vivo* applications where tissue absorption in the near-infrared window (800–1200 nm) is minimal, and thus, favorable to optimal light penetration [7]. Because near-infrared (NIR) light is mainly adsorbed by the noble metal materials, it is thus efficiently converted to heat for cell and tissue destruction. To date, for this reason, much effort has been made in the design of rational methods for synthesizing higher ordered metal nanostructures, e.g., produce particle [8], one-dimensional [9], disk [10], belt [11], shell [12], dendrite [13] nanostructured metal materials, controlling the shapes and particle sizes of noble nanoparticles. Among them, silver dendrites have been studied extensively in recent years due to their special optical properties and promising applications in biomedicine, because the strong SPR absorption band can be tuned from visible to the NIR region by the special dendritic structure. Therefore, this class of material, if under moderately low exposures of extra corporeally applied NIR light, can be used to deliver a therapeutic dose of heat to kill the sick cells. In 1999, Yu et al. [13] reported the preparation of the Ag dendrites via ultraviolet irradiation photoreduction method. After that, researchers have synthesized Ag dendrites by an organic reducing agent such as tetrathiafulvalene [14] and ascorbic acid [15], ultrasonically assisted templated synthesis [16], plating [17], γ-irradiation route [18], and pulsed sonoelectrochemical methods [19]. However, the Ag dendrites prepared by these methods were not found to have the strong SPR band in the NIR region of 800–1200 nm, where the transparent window of biological tissues is located [20]. Thus, facile ways are expected to prepare silver dendrites which can present excellent NIR absorption and photothermal conversion property.

Here, we present an easy way to synthesize Ag dendrites with NIR photosensitive properties. In this method, silver/cross-linked poly(vinyl alcohol) (PVA) composite system is introduced. It is well known that PVA can reduce

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$AgNO_3$ to Ag at normal condition. However, this is a slow reaction and the products are silver nanoclusters or nanoparticles, which cannot show NIR absorption, because the crystalline silver without controlling growth are not ordered enough to present NIR photosensitive property. To solve this problem, we add a high voltage on this silver/PVA composite film with two aims: one is to accelerate the reaction, and the other is to control the growth. With the assistance of high voltage, silver dendrites with strong absorption in NIR can be synthesized in a few minutes at room temperature.

2 Experimental section

Figure 1 shows a schematic representation of the formation of embedded silver dendrites in a PVA matrix. In a typical procedure, a desirable analytically pure $AgNO_3$ was put into 10 mL of PVA (9 wt%) aqueous solution, which was then stirred for about 0.5 h to form a clear solution at room temperature. The ratio of PVA and $AgNO_3$ were tuned from 3:1 to 1:1. The hybrid material was carefully spin coated on a silicon substrate at a spin rate of 1000 rpm for 20 s, resulting in a thin film structure with uniform thickness. Then a cramp which linked to high direct current (DC) voltage (16 kV) served as a live end and was put on the center of the film. Silver dendrites appeared radiatively around the center as soon as the high voltage was on load as shown in the schematic diagram. The whole process was fast and in the normal condition. If the high voltage was added in the hybrid solution, then the 3-division Ag dendrites would appear.

The structure and phase purity of the nanoparticles were characterized by X-ray powder diffraction (XRD) using a Rigaku D/max-rA X-ray diffractometer with a Cu target radiation source. The size and morphology of the silver dendrites were examined using a Hitachi S-4800 field emission scanning electron microscope (FE-SEM) equipped with an energy dispersive X-ray (EDX) spectrometer. The absorption spectra were measured with a Shimadzu UV-3101PC ultraviolet visible (UV-VIS) NIR scanning spectrophotometer.

3 Results and discussion

Figure 2(a) shows the scanning electron microscope (SEM) image of the Ag dendrites prepared with the assistance of high voltage. The dendrites in the film spread from the center (high voltage), and composed a circle as the last schematic image in Fig. 1. The dendrite in Fig. 2(a) was a part of the radiative circle embedded in PVA. Figure 2(b) is the magnified images of Ag dendrites, from which it can be seen that ordered microstructured silver leafs align epitaxially all over the dendrites. The leafs on the bough have a flat hexagonal platelike shape with a sharpened or truncated top and a thickness of 400–500 nm.

Figure 3(a) shows the XRD patterns of the composite film. The Ag dendrites are well crystallized and all of the peaks can be readily indexed to the face-centered cubic (FCC) silver, which is in good agreement with the literature values (JCPDS No. 4-783).

In contrast to other diffraction peaks, the peak corresponding to the Ag(111) face (located at the Bragg diffraction peak at an angle 2θ of 38°) is sharp and tall, which means the good growth of the crystalline silver dendrites along the direction of 111 plane. The EDX spectra in Fig. 3(b) is used to detect the composition of the hybrid film. EDX data indicated both C and O peaks and characteristic Ag peaks of the obtained sample appear

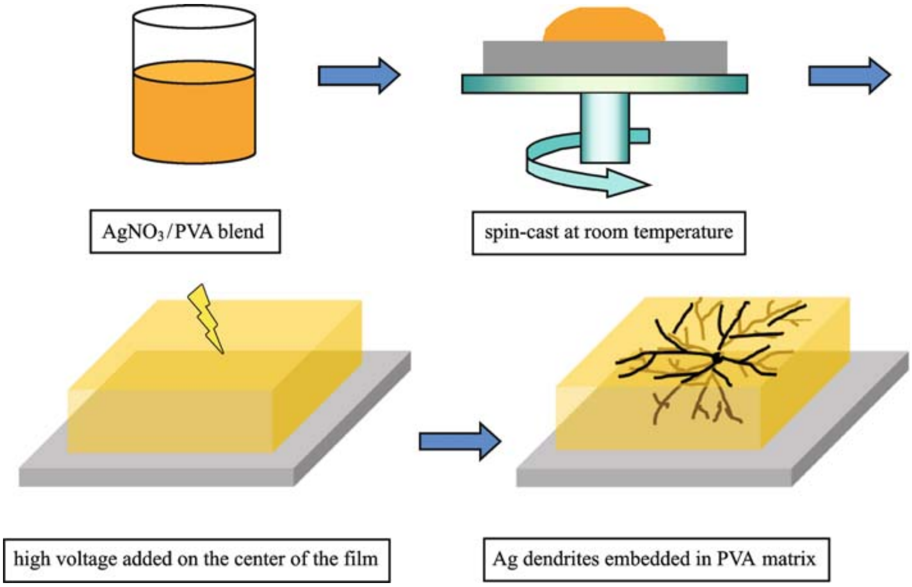


Fig. 1 Schematic representation of formation of a silver dendrites in PVA matrix

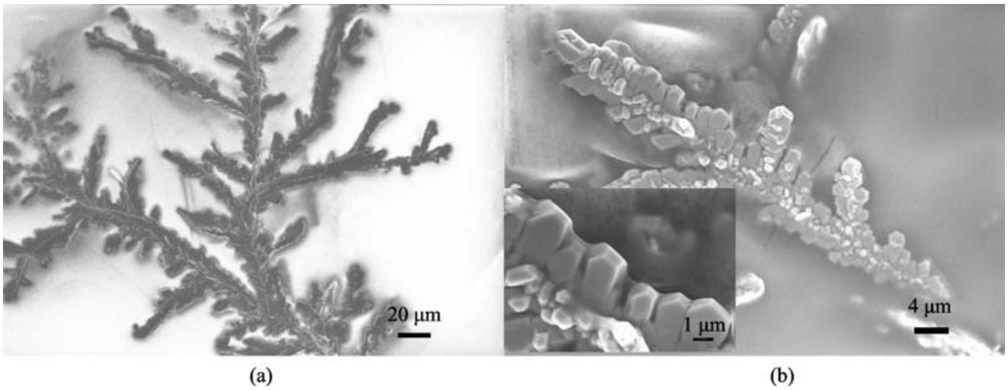


Fig. 2 SEM images of silver dendrites in PVA-Ag composite system. (a) Overview of dendrites; (b) magnified SEM images of dendritic structure, inset: image of silver leafs in dendrites

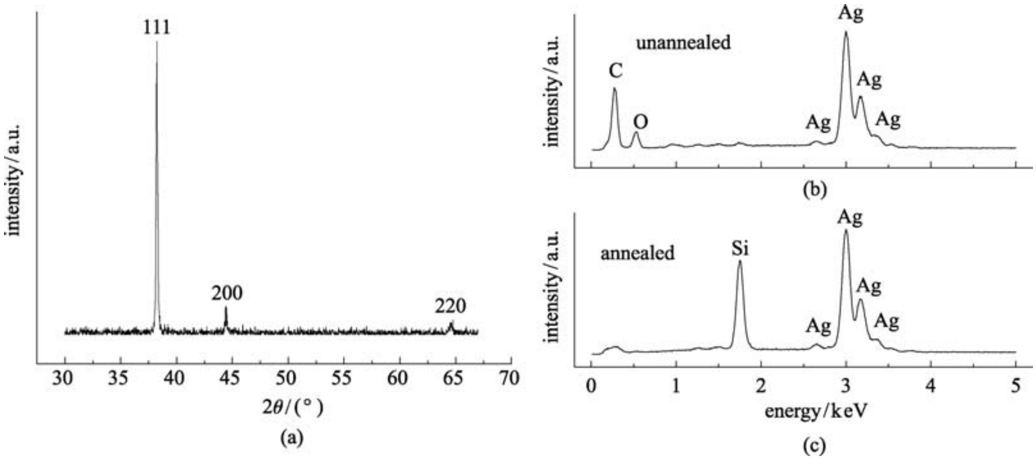


Fig. 3 XRD and EDX spectra of silver dendrites. (a) XRD patterns of silver dendrites; (b) EDX spectra of silver dendrites before annealing; (c) EDX spectra of silver dendrites after annealing

which correspond to PVA and Ag dendrites, respectively. It also proves the composite phase of PVA and silver. Figure 3(c) is the EDX pattern of the sample annealed at 500°C for 3 h. C and O peaks disappear and Si peak appears which means the polymer has been burned out and the silver is left on the Si substrate.

From the above detections, we can confirm that the composite material is formed from the reaction of the $AgNO_3$ and PVA. It is well known that PVA chains will turn to crosslink after treatment at high temperature (250°C). In this process, PVA can be oxidized by $AgNO_3$ into cross-linked PVA at room temperature by the assistance of high voltage. High voltage can provide the energy to make PVA into crosslink state like what happens at high temperature. Note that Ag ions play an important role as a catalyst for oxidation-reduction reactions. Under the high voltage, PVA chains form and Ag clusters appear along the polymer chain at the same time. As the reaction time goes on, the Ag clusters aggregate along the PVA chain and form the dendrites. A few minutes later, the dendrites grow up around the high voltage center. The rapid formation of the dendrites in this system is dependent on the two important roles: high voltage and PVA chain, which accelerate the reaction speed at room temperature (RT) and provide a template to form dendrites, respectively.

As to the formation mechanism hexagonal plate shaped leafs, we believe that the silver nanoparticles and polycrystalline aggregates attached to the boughs of dendrites align epitaxially to form the silver leafs during silver dendritic growth. However, from the view of thermodynamics, the silver dendrite, by virtue of its extended surface, has a considerably increased surface energy in contrast to the equilibrium shape, such as particles. Washio et al. [21] reported that the thermodynamically favorable shapes, for a FCC noble metal, are truncated nanocubes and multiple twinned particles. In this paper, for the high surface energy of platelike leaves, their formation requires kinetic control. Several groups [22–25] have synthesized silver nanomaterials with a flat platelike shape using different methods, including photo- or thermally induced transformation and chemical reduction.

Their results show that the condition of the silver platelike formation via kinetic control should compose two points: the high Ag ion concentration and the very slow reaction to ensure kinetic control. In contrast, if the reduction rate was too fast, the silver seeds with defects could evolve into other structures instead of nanoplates. As demonstrated in this paper, the silver ion concentration was high enough, but the reduction rate was accelerated by the assistance of high voltage, and the nanoplates grew up in a few minutes, which means kinetic control took effect. Two reasons may play a part: first, the formation comes from the function of PVA template and silver seeds can grow up along the PVA to form the platelike leafs even at high reduction rate; second, the reduction reaction happens in the PVA matrix not the liquid phase in which silver seeds can grow in any direction. So the defects cannot influence the formation of platelike leaves.

Figure 4 shows the absorption spectra of silver dendrites in composite films with the ratio of 3:1 to 1:1. As can be seen, the Ag dendrites all exhibit two SPR bands. The first one is at 450 nm and the other band shifts to 810 nm, which means that these samples can be used as infrared (IR) photosensitive material. We also found the same absorption spectra in the three-dimensional (3-D) silver dendrites. This property is due to the interaction of polarized light and the noble metal materials, which form the electronic coherent SPR oscillation. The electric field of incident light induces coherent collective oscillation of conduction band electrons with respect to the positively charged metallic core. This dipolar oscillation is resonant with the incoming light at a specific frequency that depends on particle size and shape. Noble metal materials, with morphology of shell, rod, plate, and so on, will show two bands: a strong longitudinal band in the near-infrared region corresponding to electron oscillation along the long axis and a weak transverse band in the visible region corresponding to electron oscillations along the short axis. In this work, the samples all show two absorption positions corresponding to transverse and longitudinal bands. It should be noted that as the ratio is 3:1, the strongest absorption is obtained at 810 nm. The absorption in both the visible and NIR region of the samples with the ratio of 2:1 and 1:1 decreases as the concentration of PVA decreases. The results indicate that the concentration of PVA just influence the intensity of the absorption but not the position. In this composite system, we believe that this red-shifted band comes from the micro-structured plates of the dendrites and the morphology does not change with the ratio. So we can confirm that the increase of concentration of the PVA just promotes the growth of the dendrites and does not change the intrinsic properties.

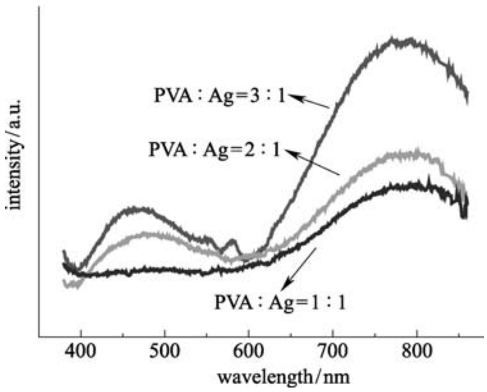


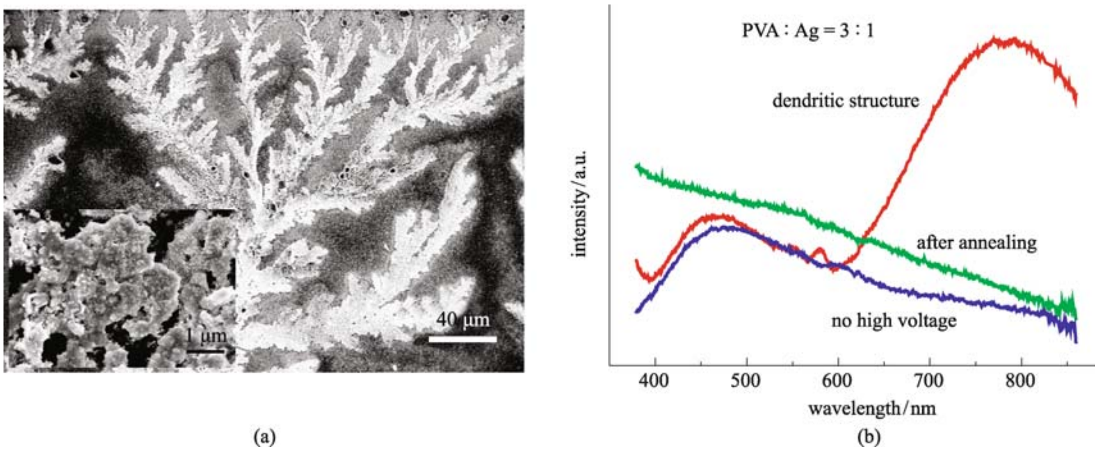
Fig. 4 UV-VIS-NIR absorption spectra of silver dendrites

As to the key roles of PVA and the assistance of high voltage, we get the proofs from two aspects. On the one hand, we detect the morphology and absorption property of the annealed film which is the only silver dendrites left on the substrate (confirmed by EDX measurement). The SEM images of the composite film with ratio of 3:1 annealing at 500°C for 3 h are shown in Fig. 5. No difference can be found from the overview of the dendrites (Fig. 5(a)) compared to the dendrites in composite system, but the magnified image (inset of Fig. 5(a)) shows that the microsructured slices are damaged as the PVA is burned out. Without the template of PVA, Ag dendritic structure collapses and further influences the NIR absorption function. We detected the change of the absorption spectra of the sample of 3:1. The red and blue lines in Fig. 5(b) correspond to the absorption spectra of before and after annealing dendritic sample, respectively. In contrast to the red line, the corresponding spectra of the annealed film (blue line) shows no absorption in the NIR region. This point can prove that PVA chains are the template of the silver dendrites which will lose the photosensitive property without the template. On the other hand, We detect the influence of the assistance of the high voltage in the process. The absorption spectrum of the composite film with ratio of 3:1 without the addition of high voltage, as seen in the green line in Fig. 5(b), only has one band at 450 nm. The results show that PVA can reduce the $AgNO_3$ into Ag, but the final products are nanoclusters or nanoparticles without absorption in NIR.

Because of the high voltage involved, the speed of the redox reaction was accelerated, and abundant PVA chains and the silver nanoclusters emerged at the same time and place, which guaranteed the formation of the Ag dendrites along the PVA chains. Different voltages (10–20 kV) of the silver dendrite formation were investigated. Though the silver dendrites synthesized with high voltage showed the relative faster grown speed, the samples within the voltage range all appeared in a few minutes and had the same absorption property.

4 Conclusion

In conclusion, Ag dendrites with excellent optical absorption covered the visible and NIR regions were synthesized



(a) (b)

Fig. 5 SEM images of composite film with ratio of 3∶1 annealing at 500°C for 3 h. (a) Image of silver dendrites annealed at 500°C for 3 h; (b) UV-VIS-NIR absorption spectra of silver dendrites with ratio of 3∶1 (red, blue and green lines correspond to silver dendrite before and after annealing, and without high voltage, respectively)

via a simple method in a PVA/Ag composite system. It is clear that PVA is responsible for both the formation of silver clusters and further growth of silver dendrites along with PVA chains; in turn, the silver act as an oxidizer to promote the formation of cross-linked PVA. High voltage played a key role in this work. Because of the high voltage involved, the acceleration of the redox reaction was guaranteed and the rapid formation of silver dendrites became possible. This inexpensive, simple, and fast method can be extended to morphology-controlled growth of other metals, such as gold, copper, etc., and application of this class of dendritic structures in biomedicine and IR sensor will be the subject of future study.

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