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Room temperature surfactant-assisted one-step solid-state synthesis of Ag_2CO_3 quasi-one-dimensional nanostructures

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ABSTRACT

A novel and simple room temperature one-step, solid-state route has been described to synthesize Ag_2CO_3 quasi-one-dimensional nanostructures in the presence of a suitable nonionic surfactant, polyethylene glycol (PEG) 400. The as-prepared Ag_2CO_3 nanostructures were characterized by powder X-ray diffraction (XRD) and transmission electron microscopy (TEM). The role of nonionic surfactant PEG 400 in the formation of Ag_2CO_3 quasi-one-dimensional nanostructures has been discussed. The results indicated that the surfactant PEG 400 played a key role for the formation of Ag_2CO_3 quasi-one-dimensional nanostructures. A possible growth mechanism of Ag_2CO_3 quasi-one-dimensional nanostructures has been discussed in detail based on the experimental results and analysis.

1. Introduction

The silver-oxygen system has been studied considerably owing to the importance of this system in the silver-catalyzed epoxidation of ethylene to ethylene oxide [1–3]. In addition, recent studies have demonstrated that nanoscale silver carbonate (Ag_2CO_3) particles are promising antimicrobial agents against diverse bacterial strains [4]. For instance, the previous research has indicated that Ag_2CO_3 nanoparticles stabilised over alumina nanoneedles exhibit potent antibacterial properties [4]. However, to the best of our knowledge, there are a few reports on the synthesis of Ag_2CO_3 nanostructures. It therefore is essential to develop new synthetic method for controllable synthesis of Ag_2CO_3 nanostructures due to their potential applications in medical devices and medical treatment.

Since the quantum-confinement effects of one-dimensional (1D) nanoscale materials are very important for the research of fundamental physical properties [5–10], design of new synthetic routes for one-dimensional (1D) nanoscale materials is a long-pursued goal of chemists and materials scientists. Many methods have been developed to synthesize 1D nanoscale materials up to date. Among these methods, vapor–liquid–solid (VLS) [11], vapor–solid (VS) [12] and solution-based methods are mainly used to synthesize 1D nanoscale materials, such as nanowires [13,14], nanobelts [15], nanorods [16], nanotubes [17,18], and nanoneedles [19]. However, vapor–liquid–solid and vapor–solid methods of the synthesis of 1D nanoscale materials usually require high synthetic temperature and catalysts. While for solution-based methods, an appropriate choice of synthetic solvent is sometimes crucial to the successful synthesis of 1D nanostructures, and therefore a complicated process is usually required. In addition, although hard-template-directed methods can be successfully employed to prepare 1D nanoscale materials with uniform and controllable dimensions, a sophisticated process to fabricate templates and a tedious process to remove the templates from the products are required for these methods. Our recent research jobs have demonstrated that room temperature one-step, solid-state process can be used to prepare nanoscale materials [20–23]. For example, in our previous work, we have demonstrated that semiconducting PbS nanoparticles with an average diameter of about 10 nm could be synthesized via a simple room temperature one-step, solid-state reaction in the presence of a suitable surfactant $C_{18}H_{37}O(CH_2CH_2O)_{10}H$ (abbreviated as $C_{18}EO_{10}$) [20]. Here we report on the synthesis of Ag_2CO_3 quasi-one-dimensional nanostructures via a simple one-step, solid-state route in the presence of a nonionic surfactant, polyethylene glycol (PEG) 400. The route requires neither complex apparatus and reagents nor sophisticated techniques and templates. The experiments can be carried out at room temperature.

2. Experimental

All of the chemical reagents used in the experiments were analytical grade. The procedure employed for preparing Ag_2CO_3 quasi-one-dimensional nanostructures is as follows. In a typical synthesis, 5.84 g of $AgNO_3$ and 6.15 g of $Na_2CO_3 \cdot 10H_2O$ were ground for 5 min each before mixing with 6 ml (6.87 g) of PEG 400. After grinding for 30 min, the products were washed several times with distilled water, and subsequently washed three times with ethyl alcohol (EtOH) to remove PEG 400, $NaNO_3$ and unreacted chemicals. Finally, the products were dried in an oven at 60 °C for 3 h.

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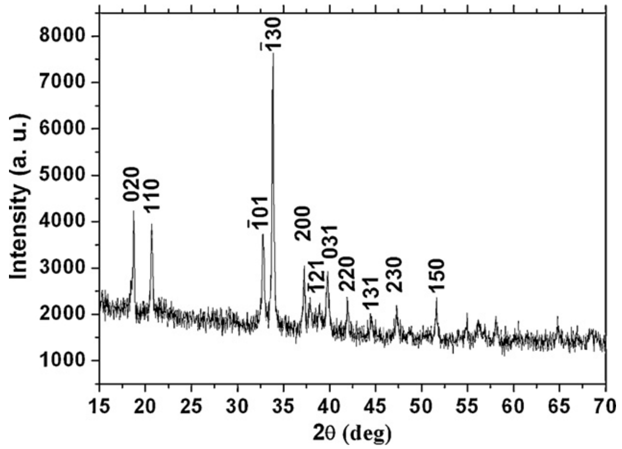

Fig. 1. XRD pattern of the as-prepared Ag_2CO_3 quasi-one-dimensional nanostructures.

The powder XRD analysis was performed using a Rigaku (Japan) Dmax X-ray diffractometer with graphite monochromatized Cu Kα radiation (λ = 0.154178 nm), employing a scanning rate of 0.02° s^{-1} in the 2θ range from 10 to 90°. Transmission electron microscopy (TEM) images were taken with a HITACHI H-700 transmission electron microscope, using an accelerating voltage of 200 kV.

3. Results and discussion

3.1. Characterization of sample

Fig. 1 shows the XRD pattern of the as-prepared Ag_2CO_3 quasi-one-dimensional nanostructures. All the diffraction peaks can be readily indexed to monoclinic phase Ag_2CO_3 with lattice constants of $a = 4.851$, $b = 9.544$ and $c = 3.253$ Å (JCPDS No. 26-0339). Several main diffraction peaks have been indexed according to JCPDS card as shown in Fig. 1. No peaks from impurities such as silver oxides are detected in XRD pattern. Thus the XRD result indicates that the as-prepared Ag_2CO_3 quasi-one-dimensional nanostructures via our present method are composed of pure monoclinic Ag_2CO_3 phase.

Fig. 2 shows the TEM images of the Ag_2CO_3 quasi-one-dimensional nanostructures with different magnifications. Low-magnification TEM image as shown in Fig. 2a indicates that the as-prepared product is composed of quasi-one-dimensional structures with length of up to 2 μm. Interestingly, high-magnification TEM image (Fig. 2b) clearly indicates that these quasi-one-dimensional structures are composed of nanoparticles through aggregating together. From TEM image in Fig. 2b one also can find that some Ag_2CO_3 quasi-one-dimensional nanostructures were broken into nanoparticles during preparing sample. A careful examination indicates that the nanoparticles have an average diameter of about 15 nm.

Comparative experiments have been performed to understand the role of surfactant PEG in the formation of Ag_2CO_3 quasi-one-dimensional nanostructures and the growth mechanism of Ag_2CO_3 quasi-one-dimensional nanostructures. When the experiment was conducted in the presence of EtOH, instead of PEG, whilst keeping other experimental conditions constant, only Ag_2CO_3 nanoparticles with an average diameter of approximately 12 nm were obtained as shown Fig. 3a. In order to further understand the role of nonionized surfactant PEG, we preformed the experiments using PEG with lower as well as high molecular weight than PEG 400 as surfactants. Fig. 3b shows the typical TEM image of the as-prepared Ag_2CO_3 nanostructures by using PEG 200 (Mw: 200) as surfactant. One can find that the as-prepared product mainly consists of nanostructures which is composed of nanoparticles. The nanoparticles aggregate to form large nanoparticles. However, one also can find that there are a few short one-dimensional nanostructures as indicated by arrows in Fig. 3b. Fig. 3c shows a typical TEM image the Ag_2CO_3 prepared in the presence of the surfactant, PEG 400 (Mw: 400), the images clearly indicates that the Ag_2CO_3 quasi-one-dimensional nanostructures were obtained. When the experiment was conducted by using large molecular weight PEG 600 (Mw: 600) as surfactant, the as-prepared product is mainly composed of one-dimensional nanostructures with lengths of up to 8 μm as presented in Fig. 3d, indicating that the length of as-prepared Ag_2CO_3 quasi-one-dimensional nanostructures increases with increasing of molecular weight of surfactant PEG. Thus, comparative experiments clearly indicate that the surfactant PEG 400 plays a vital role for the formation of Ag_2CO_3 quasi-one-dimensional nanostructures.

3.2. Role of surfactant PEG

It is well known that PEG, as a sort of nonionized surfactant, has molecular formula of $H–(O–CH_2–CH_2)_n–OH$. The monomer of PEG was apt to exist with chain structures in water and there existed a large quantity of activated oxygens in PEG molecular chains, resulting in strong interactions between PEG molecules and metal ions to form metal ions–PEG 1D chain structures. Therefore, in the case of our experiment, Ag^{1+}–PEG 1D chain structures can be formed when PEG and Ag^+ are mixed together in water [24,25]. Thus, we postulated that these Ag^+–PEG 1D chain structures could serve as templates to direct the formation of Ag_2CO_3 quasi-one-dimensional nanostructures. The above analysis indicates that the surfactant PEG may serve as a soft template to direct the formation of Ag_2CO_3 quasi-one-dimensional nanostructures.

3.3. Growth mechanism of Ag_2CO_3 quasi-one-dimensional nanostructures

Based on the above experimental results and analysis, a possible growth mechanism of Ag_2CO_3 quasi-one-dimensional

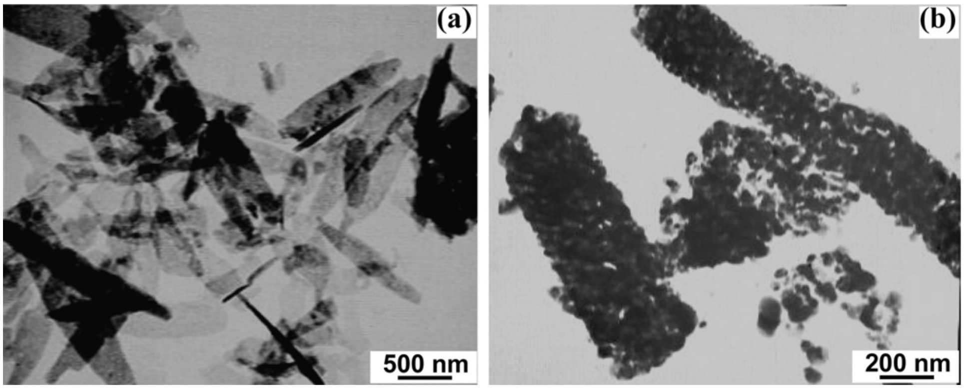

Fig. 2. TEM images the as-prepared Ag_2CO_3 quasi-one-dimensional nanostructures with different magnifications. (a) ×20,000 and (b) ×50,000.

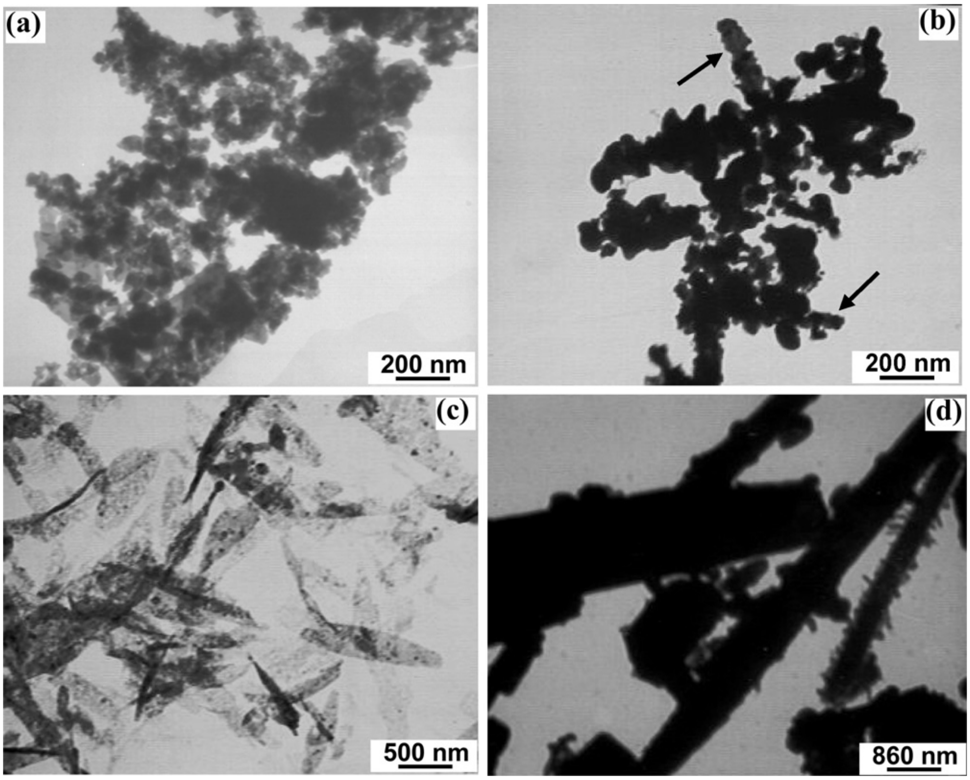

Fig. 3. (a) TEM image of Ag_2CO_3 nanoparticles prepared in the presence of EtOH. (b) TEM image of the as-prepared Ag_2CO_3 nanostructures by using the surfactant PEG 200 as surfactant. (c) TEM image of Ag_2CO_3 quasi-one-dimensional nanostructures prepared in the presence of PEG 400. (d) TEM image of the Ag_2CO_3 nanostructures prepared in the presence of PEG 600, showing long one-dimensional nanostructures.

nanostructures is proposed. The Ag_2CO_3 quasi-one-dimensional nanostructures are formed via following one-step, solid-state reaction:

$$2AgNO_{3(s)} + Na_2CO_3{\cdot}10H_2O_{(s)} \rightarrow Ag_2CO_{3(s)} + 2NaNO_3 + 10H_2O\,(T = 298\,K) \quad (1)$$

In contrast to the aqueous solution process, where the chemical reaction is carried out in aqueous solution conditions, Ag_2CO_3 quasi-one-dimensional nanostructures are formed by applying a solid-state process at ambient temperature in the presence of nonionic surfactant PEG 400, instead of in aqueous solution conditions. In this condition, the consolution curve of PEG 400-H_2O from their reaction scheme is similar to those of a high molecular weight polymer in confined water space having an upward curvature and possibly very asymmetric. According to the Flory–Higgins theory, the relevant interactions for the phase transition in small confined space are those involving the hydrophilic chains of PEG 400 and water. This would suggest to treat the system as a polymer having a molecular weight coincident with the weight of hydrophilic part of the PEG 400. So, the larger asymmetry and the much smaller critical micelle concentration (CMC) of their system with regard to PEG 400 would reflect that PEG exposes more ethylenoxide monomers to the surface than in aqueous solutions. These ethylenoxide monomers interact with water molecules of $Na_2CO_3{\cdot}10H_2O$ to form a chain structure [26]. As analysis above, there are large quantities of activated oxygens in these PEG molecular chains. Thus the strong interactions between PEG molecules and metal ions can be taken place to form Ag^+–PEG 1D chain structures when PEG and Ag^+ are mixed together. Then, Ag_2CO_3 particles may grow along the Ag^+–PEG 1D chain structures, leading to the formation of Ag_2CO_3 prototypical one-dimensional nanostructures. Finally, these prototypical one-dimensional nanostructures grow into quasi-one-dimensional nanostructures through self-aggregating of the newly formed Ag_2CO_3 nanoparticles with reaction going on. The growth mechanism of Ag_2CO_3 quasi-one-dimensional nanostructures is similar to the formation process of CuO quasi-one-dimensional nanostruc-

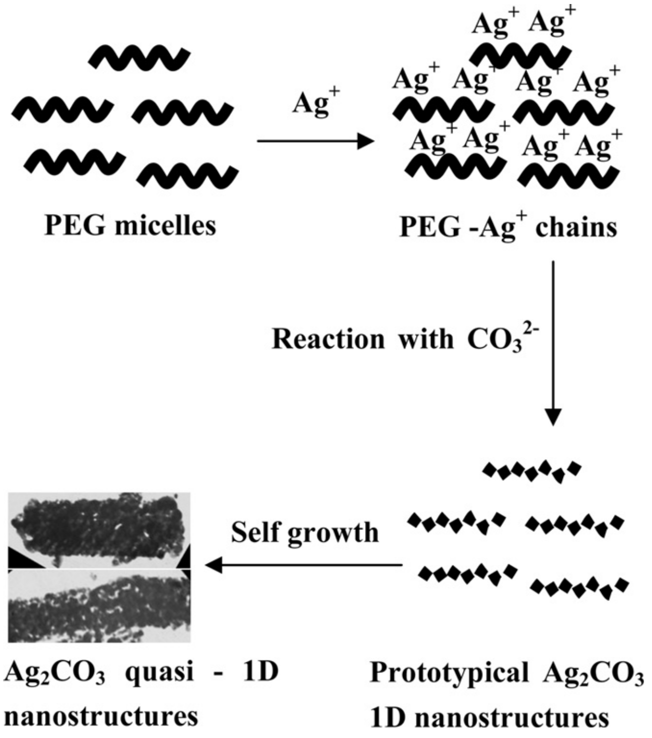

Fig. 4. Schematic representation of the growth mechanism of Ag_2CO_3 quasi-one-dimensional nanostructures.

tures [25]. On the other hand, the length of chain structure formed by PEG in water increases with increasing the molecular weight of PEG, thus using PEG with molecular weights of 200, 400, and 600, the Ag_2CO_3 one-dimensional nanostructures with different length are obtained. The formation process of Ag_2CO_3 quasi-one-dimensional nanostructures is schematically illustrated in Fig. 4.

4. Conclusions

In summary, Ag_2CO_3 quasi-one-dimensional nanostructures can be successfully synthesized by employing a one-step, solid-state process in the presence of the nonionic surfactant PEG 400 at ambient temperature. The as-prepared Ag_2CO_3 quasi-one-dimensional nanostructures were characterized by XRD and TEM. The experimental results indicated that the surfactant PEG 400 played a critical role for the formation of Ag_2CO_3 quasi-one-dimensional nanostructures. The possible growth mechanism of Ag_2CO_3 quasi-one-dimensional nanostructures has been discussed in detail. This easy and unique route for the synthesis of Ag_2CO_3 quasi-one-dimensional nanostructures in the presence of a suitable surfactant may be extended to synthesize unique nanostructures of other materials.

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