Materials and Design 139 (2018) 96–103

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Fabrication of an ultralight flame-induced high conductivity hybrid sponge based on poly (vinyl alcohol)/silver nitrate composite

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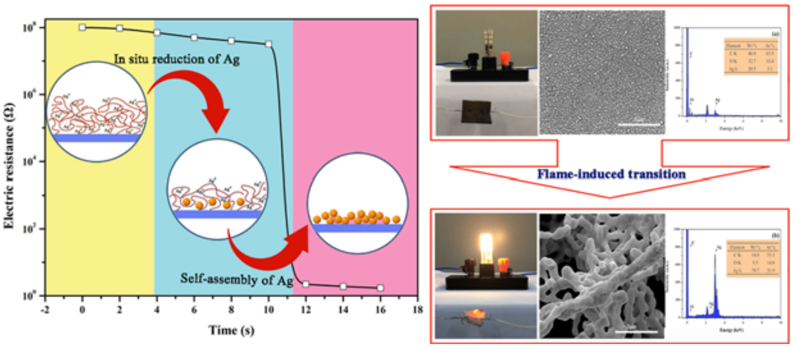
HIGHLIGHTS

- An ultralight monolith based on PVA/$AgNO_3$ composite embedded in ME sponge was prepared through a simple method.
- Electrical resistance of the ME/PVA/$AgNO_3$ hybrid sponge dropped by 8 orders of magnitude in 15 s when exposed to flame.
- As a result of the well-controlled growth of the Ag NPs, a 3D network based on silver clusters was constructed.
- This flame-induced high conductivity hybrid sponge could be used as a fire alarm device.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 August 2017
Received in revised form 28 October 2017
Accepted 31 October 2017
Available online xxxx

Keywords:
Silver nanoparticle
Poly (vinyl alcohol)
Melamine sponge
Flame-induced reduction

ABSTRACT

In this study, we presented a novel fire alarm device based on poly (vinyl alcohol) (PVA)/silver nitrate ($AgNO_3$) composite embedded in the structural template of melamine (ME) sponge. By using water as a benign solvent, the chelated PVA/$AgNO_3$ hybrid solution was absorbed into ME sponge, and then the ultralight ME monolith containing PVA/$AgNO_3$ was obtained after removing the solvent. When exposed to flame, monodispersive silver nanoparticles (Ag NPs) were synthesized by reducing $AgNO_3$ with PVA. The porous ME sponge acted as a structure-directing template during the in situ reduction process, leading to the controlled formation of a connected network for Ag NPs. Finally, the electrical resistance of the monolith suddenly dropped by 8 orders of magnitude in less than 15 s after flaming, which was due to the formation of a conductive path built by the neck formation of Ag NPs. This ultralight conductive monolith based on Ag NPs via flame-induced reduction of $AgNO_3$ could have broad applications in civil, military and aerospace fields.

1. Introduction

Metal nanoparticles (NPs) have received considerable attention over the past two decades due to their unusual properties. The unique and tunable optical properties endow metal NPs with great utility in novel optical technologies for biology and biomedicine [1–3]. Metal NPs have been widely used as catalysts in chemical transformations [4,5]. Massive conductive nanocomposite materials based on metal NPs have been developed and applied in food packing [6], electronic devices [7], sensors [8] and switches [9]. Among various metal NPs, silver nanoparticles (Ag NPs) [10–12] are most attractive to researchers because of their excellent chemical stability, electrical conductivity, antibacterial activity and diverse approaches for green synthesis.

The green synthetic methods of Ag NPs mainly include polysaccharide [13,14], Tollens [15,16], irradiation [17] and biological [18,19]

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https://doi.org/10.1016/j.matdes.2017.10.075
0264-1275/

approaches. In these methods, the selection of suitable capping and reducing agents is the key issue, which will produce a great impact on the size and morphology of Ag NPs generated. For instance, polysaccharides are mostly used as the green reducing agents for NPs synthesis, because the abundant hydroxyl groups enable them to reduce metal precursors. Besides, the stability is also considered to be a crucial property affecting the dispersion of metal NPs, thus various surfactants and polymers are commonly applied to stabilize metal colloids.

Poly (vinyl alcohol) (PVA), a typical water-soluble and environmentally friendly polymer, possesses good comprehensive properties [20–22]. Therefore, PVA has generally been considered as a good host material for metals and semiconductors, due to its good thermostability and chemical resistance [23,24]. Recently, a substantial amount of researches have been focused on the incorporation of PVA into the reduction of silver nitrate ($AgNO_3$) [25–27]. Pattabi et al. [28] studied the influence of PVA on the growth of Ag NPs. Results indicated that the carboxylate groups on PVA chains played a major role in the stabilization of the Ag NPs, and PVA with a lesser degree of hydrolysis was a better stabilizer than those with a higher degree of hydrolysis. Due to the strong metal–metal interactions, metal particles tend to form agglomerates during reduction process which will deteriorate its intrinsic properties. For example, the aggregation of Ag NPs diminishes their antimicrobial activity [29]. To overcome this drawback, PVA was frequently used as matrix or stabilizer to protect the Ag NPs from sintering. Taking advantages of the high surface area, high porosity and flexibility of polymeric nanofibers, Destaye et al. [30] immobilized the reduced Ag NPs onto electrospun PVA nanofibers. Furthermore, large numbers of hydroxyl groups in PVA chains formed interaction with Ag NPs to stabilize the latter's growth in the matrix at nanometric scale, thus obtaining a homogenous dispersion of Ag NPs by avoiding the agglomeration [31–33]. However, as reported by other researchers [34], the introduction of PVA also inhibited the growth rate of Ag NPs and decreased the resultant size of the particles. Such results could be explained in term of the decrease in reaction rate caused by the solubilization of PVA into the reaction site.

In fact, during the in situ reduction process for PVA/$AgNO_3$ system, PVA acted simultaneously as a polyol reducing agent for Ag ions [35, 36]. The conversion mechanism of silver cations into silver is reported by Zhang [37]. The metal chelation sites within PVA are primarily decomposed in the temperature regions of 39.7–72.6 °C and 182.7–199.6 °C, with silver ions reduced into metallic silver nanoparticles and hydroxyl groups of PVA oxidized into carbonyl groups. A similar mechanism was recently disclosed by Bai et al. [38] for thermal-induce reduction of PVA-silver nitrate system. A redox reaction between PVA and $AgNO_3$ occurred upon heating to 169–190 °C, where $AgNO_3$ was reduced to NO, N_2O and silver. Lin [39] systematically studied the in situ growth mechanism of Ag in the presence of PVA as both reducing agent and stabilizer during the annealing process. From a kinetic point of view, the hierarchical generation was confirmed during the self-assembling process of the silver species, followed by the formation of an interconnected network. Taking advantage of the interaction between silver salt and PVA, the Ag NPs were reduced and immobilized onto the PVA nanofibers [40–42], showing very strong antimicrobial activity and having a potential application in biomedical fields. Besides, after high-temperature calcination of the electrospun PVA/$AgNO_3$ fibers in an argon atmosphere, PVA matrix was completely eliminated and $AgNO_3$ was reduced to silver; Barakat et al. [43] successfully prepared the silver nanofibers. In this study, PVA/$AgNO_3$ composite was exposed to the ethanol flame to initiate the in situ reduction of Ag^+ ions by PVA, and the generating silver atoms started to aggregate and form a few oligomeric clusters, followed by the desired construction of a three-dimensional Ag monolith. The Ag products obtained through this method possess a high electrical conductivity and could be applied in many electronic devices.

Therefore, the objective of this paper was to fabricate a flame-induced conductive monolith based on PVA/$AgNO_3$ system, in which the chelated PVA/$AgNO_3$ composite was loaded onto the porous melamine (ME) sponge template. The electrical conductivity of this hybrid sponge was measured in real time during the combustion process, and the comparative analysis of the chemical composition before and after

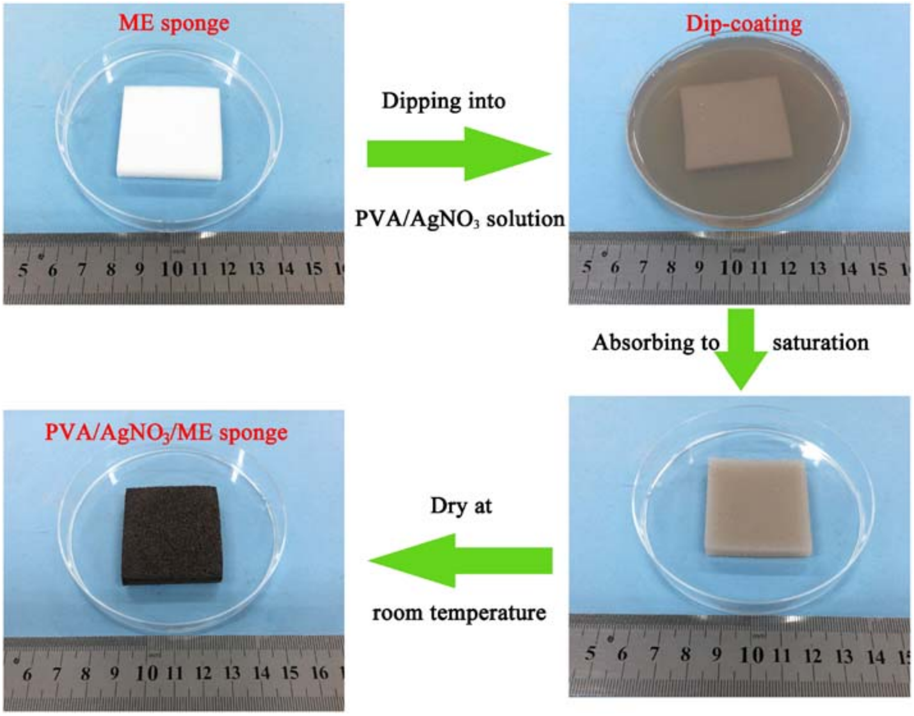

Fig. 1. Fabrication process of PVA/$AgNO_3$-wrapped ME sponge.