Composites Communications 9 (2018) 11–16

Contents lists available at ScienceDirect

Composites Communications

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

In situ prepared nanosized Pt-Ag/PDA/PVA-*co*-PE nanofibrous membrane for highly-efficient catalytic reduction of *p*-nitrophenol

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ARTICLE INFO

Keywords:
Nanofibrous membrane
Polydopamine
Pt-Ag
In-situ reduction
Catalyst
p-Nitrophenol

ABSTRACT

Combining highly-active noble metal nanoparticles and unique 3D nanofibrous structure is significant to enhance their intrinsic properties such as catalytic performance. Here, we prepared a poly (vinyl alcohol-*co*-ethylene) (PVA-*co*-PE) nanofibrous membrane (NFM) decorated by polydopamine (PDA) via a melt-phase-separated nanofiber-suspension coating followed by in-situ polymerization. The as-prepared PDA modified NFM worked as the in-situ reducing agent to capture silver ions and transfer them to Ag nanoparticles (NPs). Then Ag/PDA/NFM was further coated with Pt NPs by magnetron sputtering technique. The morphology and structure analysis showed that the Ag NPs in diameter from 10 to 200 nm and Pt nanoparticles coating has been successfully immobilized on PDA/NFM. The catalytic rate constant of Pt-Ag/PDA/NFM in the reduction reaction of *p*-nitrophenol (*p*-NP) was about 34.43×10^{-3} s^{-1} higher than that of Ag/PDA/NFM (30.20×10^{-3} s^{-1}) and Pt/PDA/NFM (0.188×10^{-3} s^{-1}), respectively, when magnetron sputtering time of Pt was 100 s. It can be attributed to the electronic effect in bimetallic catalyst and the enhancement effect of nanofibrous membrane with high specific surface area. Furthermore, Pt-Ag/PDA/NFM presented an excellent cyclic feature that still about 98% conversion of *p*-NP after 6 times implying its superiority in reduction degradation of *p*-nitrophenols.

1. Introduction

With the development of industry, industrial wastewater containing toxic and harmful chemical substances becomes more and more severe due to the degradation difficulty of the contaminants with complex structure [1,2]. Among these, *p*-nitrophenol (*p*-NP) is one of the typical pollutants [3]. Besides, the reduction product *p*-aminophenol (*p*-AP) of *p*-NP is an important intermediate for producing some kinds of antipyretic and analgesic drugs in the modern fine pharmaceutical industry [4,5]. Therefore, the conversion of *p*-nitrophenol into *p*-aminophenol is significant important. Till now, diverse methods including chemical catalytic reduction, photocatalytic degradation, microbial degradation, electrochemical treatment have been applied to this issue [6,7]. It has been recognized that employing catalyst with excellent catalytic performance is an effective approach for the reduction degradation of *p*-nitrophenol.

In recent years, the noble metal-based materials, especially the nano-sized particles with outstanding catalytic activity, have attracted considerable attention and frequently used in this reduction reaction [8,9]. Moreover, bimetallic nanoparticles with various structures present better catalytic performance than mono-metal nanoparticles [10–13]. Au@Ag nanoparticles decorated on graphene oxide have been reported with better catalytic capability than Au or Ag nanoparticles loaded on graphene oxide [14,15]. Nevertheless, it is still a great challenges to apply noble metal-based nano-materials in water directly owing to their rapid aggregation feature in water, which causes the deterioration of catalytic activities, as well as repetitive-use ability and secondary pollution issue [16]. Consequently, it is a good method to load the noble metal nanoparticles on the appropriate carrier materials, which makes nanoparticles more difficult to aggregate in water and easier to be recycled [17–19].

It is well known that the structure and properties of the supporter as well as the interface interaction between the nanoparticles and the support materials play a vital role in promoting its catalytic performance [20,21]. In virtue of this effect, diversified materials have been presented to load nanoparticles including polymeric microspheres [22], microporous membrane [23], polymeric hollow fiber membranes [24], nanofibrous membrane(NFM) [25], anodic aluminum oxide membrane

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https://doi.org/10.1016/j.coco.2018.04.004
Received 3 November 2017; Received in revised form 30 March 2018; Accepted 9 April 2018

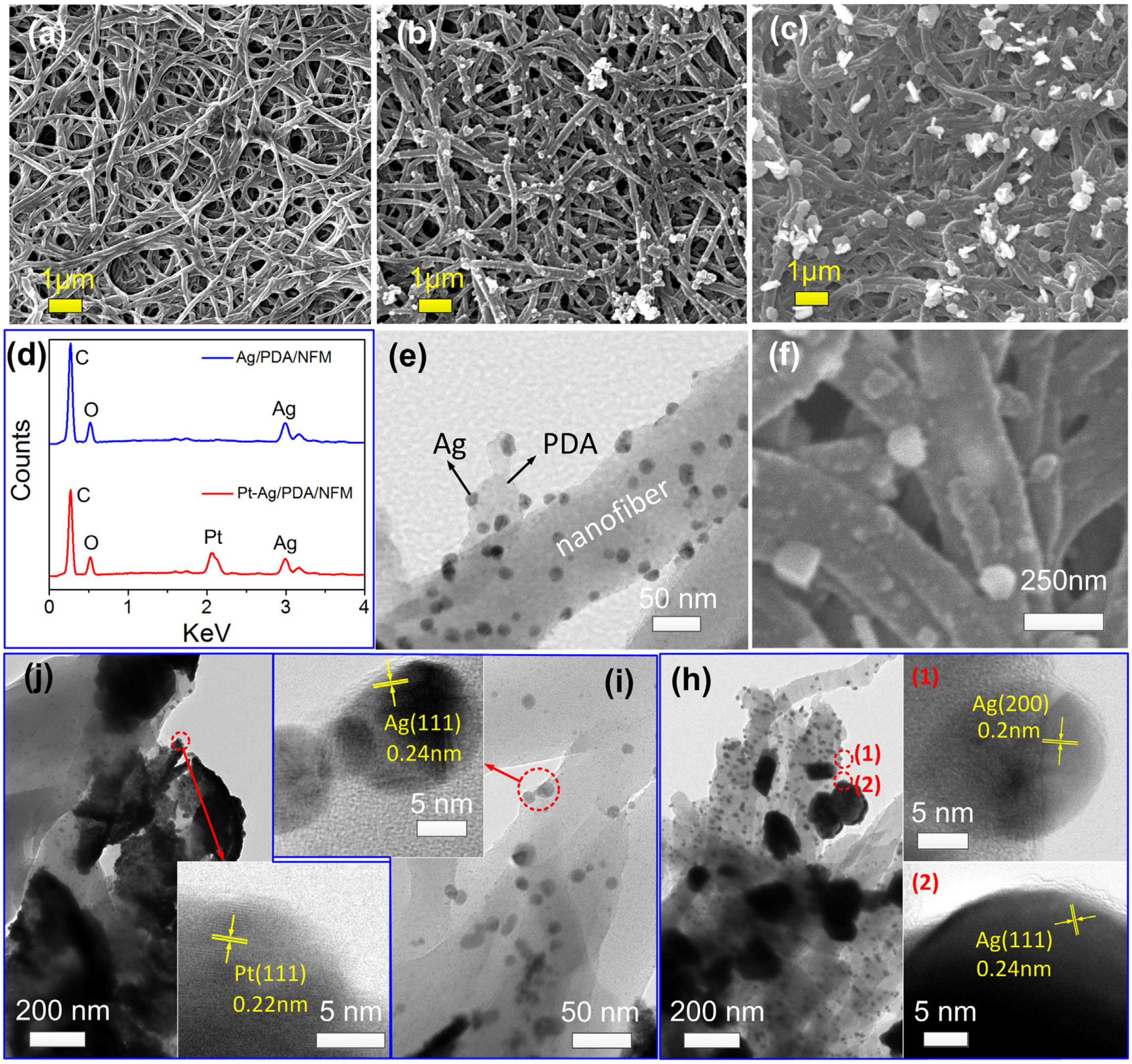

Fig. 1. SEM images of NFM(a), PDA/NFM(b), Ag/PDA/NFM(c)(f), (d) EDS spectrum of Ag/PDA/NFM and Pt-Ag/PDA/NFM, (e) TEM of single nanofiber coating with Ag NPs, (h)(i)(j)The HRTEM image of Ag/PDA/NFM and Pt-Ag/PDA/NFM.

[26], graphene oxide or graphene membrane [27,28], photolithographic Si micro wire arrays [29] and so on. In contrast, recently, nanofibers have been often utilized to immobilize the noble metal nanoparticles via chemical modification with the advantages of high specific surface areas, high porosity, as well as easier to be functionalized to support noble metal nanoparticles [30–33]. On the other hand, polydopamine (PDA) is one kind of marvelous polymers possessing plenty of catechol group and amine group [34]. The catechol groups are highly responsible to their robust and strong adhesion to all types of surfaces regardless of the substrate's chemistry [35,36]. Moreover, PDA also provides a great opportunity for post modification of various synthetic membranes applied in many fields ranging from chemistry, biology to industry [37]. It is also increasingly employed to capture many metal ions and immobilize them in pure metallic form via in-situ reduction procedure with catechol group [34]. Therefore, utilization of PDA is probably not only to enhance the interaction between nanofibers and improve the stability of membrane structure, but also to provide more active site for functional modification and anchoring nanoparticles effectively [38].

In our previous works, PVA-*co*-PE nanofiber had been prepared by melt extrusion phase separation method [39], then after being dispersed and coated on the non-woven fabric, the nanofibrous membrane was obtained [40], which had been successfully applied in various fields as diverse as filtration [41], adsorption [42], antibacterial [40], biosensor [43] and catalyst carrier [44]. Based on PVA-*co*-PE nanofibrous membrane (NFM), PDA worked as a bridge between surface of nanofibers and the groups capturing silver nanoparticles. In this study, the ability of in-situ reduction and immobilizing silver nanoparticles on modified PVA-*co*-PE nanofibrous membrane were investigated. the concentrations of silver ammonia solution and reaction time were changed to obtain different loading content of Ag NPs on PDA decorated PVA-*co*-PE NFM (PDA/NFM). Then Ag/PDA/NFM was further sputter coated by Pt NPs. Ultimately, the catalytic properties of Ag/PDA/NFM and Pt-Ag/PDA/NFM in the reduction reaction of *p*-nitrophenol were discussed.

2. Results and discussion

2.1. Morphology and structure

PVA-*co*-PE nanofibers with diameter in range of 100∼200 nm can be observed as shown in Fig. 1a. Nanofibers interweaved tightly with each other and formed a network indicating their flexible and crimped feature. The color of nanofibrous membrane changed from white to brown after the polymerization of dopamine, suggesting that polydopamine was deposited onto the membrane successfully (Fig. S2).