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Regular Article

Facile fabrication of a biomass-based film with interwoven fibrous network structure as heterogeneous catalysis platform

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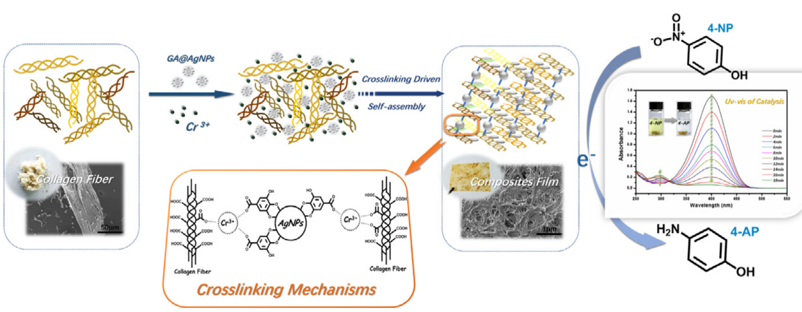
GRAPHICAL ABSTRACT



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ABSTRACT

The stable and efficient immobilization of silver nanoparticles (AgNPs) on/into processable biomass-based macro-support with porous networks is a promising and sustainable strategy to achieve both high catalytic activity and excellent reusability for heterogeneous catalysis. In this work, a collagenic composite film was facilely fabricated at room temperature, via the self-assembly of natural collagen fibers (CFs) and gallic acid modified silver nanoparticles (GA@AgNPs) induced by chromium (III) cross-linking in water. The morphology and microstructure of such GA@AgNPs-Cr-CFs composite film was investigated by Scanning Electron Microscope (SEM) and X-ray Photoelectron Spectroscopy (XPS), respectively. The results revealed that the cross-linking based on the coordinated complexation between chromium ions (Cr^{3+}) and carboxyl groups on CFs and GA@AgNPs played the critical role in the interwoven of collagen fibers, leading to a three dimensional (3D) interconnected porous network of the composite film with simultaneously incorporation and high payload of silver nanoparticles. Furthermore, this GA@AgNPs-Cr-CFs composite film exhibited excellent catalytic activity toward the reduction of 4-nitrophenol (4-NP), taking the advantage of its high specific surface area given by the interwoven fibrous network structure. More than that, such sustainable composite catalyst could be easily recovered and reused for ten cycles because of its high stability based on cross-linking. This catalytic platform constructed by natural fibers, noble metal nanoparticles and trivalent metal ions showed a sustainable avenue for heterogeneous catalytic system.

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1. Introduction

Over the past decade, silver nanoparticles (AgNPs) have attracted significant attention due to their unique optical, catalytic, electronic and antibacterial properties, which are considerably valued in various fields of science, ranging from chemistry to biotechnology [1–7]. One of the most popular application of silver nanoparticles is as catalyst, because of their high reactivity and selectivity [8]. The large surface area to volume ratio of AgNPs is the critical factor to their good catalytic performance [9]. However, due to the high surface energy, easy aggregation of silver nanoparticles always caused remarkable loss in catalytic activity, resulting in silver nanoparticles undesirable for large scale use in industrial application [10,11]. Nowadays, though AgNPs are usually stabilized by using surfactants or polymeric ligands to prevent aggregation, they were hardly to separate totally from the reaction solution and therefore could not be reused as catalysts [12,13]. Thus, many efforts have been devoted to immobilize AgNPs on/into solid matrix by formation of composite catalysts, which have attracted great interest because of their stability, reusability and good catalytic properties [14,15].

In the past, electrospinning has been widely employed to produce polymeric nanofibers with high surface area, which could be used as AgNPs supporting substrates for catalytic applications [16,17]. However, it was found that silver nanoparticles were easily embedded into polymer nanofibers rather than dispersed onto the surface of nanofibers, and the presence of the polymer layer surrounding the AgNPs usually limited the interaction between reactive species and the particle surface [18]. In addition, it is worth noting that organic solvents were commonly involved during the electrospinning process, which would also bring potential environmental and biological risks [19]. To address these drawbacks, natural biomass fibers instead of synthetic polymer fibers became more attractive as supporting substrates, due to their advantage of renewability, ease of preparation, hydrophobic/hydrophilic characters and ability of dispersing metal nanoparticles [20]. For example, silk fibroin and cellulose fibers have been investigated and utilized for supporting metal nanoparticles [21,22]. Unfortunately, these biomass-based composite catalysts often suffered from limitation of relatively low activity and catalytic durability in the application of heterogeneous catalysis [20]. That mainly because the hierarchical structures of above individual fiber could not afford high enough surface area. For metal nanocomposite to perform as ideal catalysts, they should possess some important characteristics, including high surface area of the substrate, easily accessible to various chemical reagents and uniform distribution of metal nanoparticles [23]. Therefore, macroscopic biotemplate with three-dimensional (3D) interconnected porous network structure has been demonstrated a green and promising strategy for immobilization of AgNPs to achieve both high catalytic activity and excellent reusability simultaneously [24]. Recently, Liang and co-workers reported immobilization of AgNPs on natural eggshell membrane (ESM) through procyanidin (Pro) and the AgNPs@Pro-ESM composites exhibited good catalytic activity and high reusability for the reduction of 4-NP due to the interwoven fibrous structure [25]. Despite the ESM shows great promise as biotemplate for immobilizing nanocatalysts, such protein-based material with interwoven fibrous 3D structure is very few in nature, difficult to be collected and also not processable. All these defects will restrict its large-scale application. Hence, we hypothesize here that an artificial membrane or film self-assembled by the interwoven of natural fibers may possess similar 3D interconnected porous network structure as that of ESM, which will be more advantaged and fascinating as novel support for immobilizing AgNPs. As another natural protein-based material, collagen fibers (CFs) that mainly comes from animal skins are one of the most abundant renewable biomass and very easily obtained, have been investigated as support for metal nanoparticles in heterogeneous catalysis by Shi's group, due to their triple helical structure which is flexible, hydrophilic and affiliative to metal nanoparticles [26,27]. However, so far, there is no literature report how to process artificial collagenic composite film with 3D interconnected porous networks by the interwoven of collagen fibers.

In leather manufacturing, chromium (III) irons (Cr^{3+}) have been used as the most popular tanning agents based on chemical cross-linking of the skin collagen by forming coordinated complexation with carboxyl groups on the collagen fibers [28]. Inspired by this chromium (III) cross-linking mechanism, Cr^{3+} irons may promise to be excellent linkage that synergistically construct fibrous network structure by inducing interwoven of collagen fibers with stable immobilization of metal nanoparticles on its surface [29,30]. On the basis of this idea, in the present work, gallic acid modified silver nanoparticles (GA@AgNPs) with high surface density of carboxyl groups and an average size of 8 nm were in situ synthesized according our previous work and selected as nobel metal nanocatalyst [31]. As shown in Scheme 1, the chromium cross-linking between CFs and GA@AgNPs could facilely drive the formation of a composite film with interwoven fibrous network structure and uniform incorporation of silver nanoparticles. Meanwhile, the catalytic performance of the composite film was investigated by employing the reduction of 4-NP into 4-aminophenol (4-AP). Take the advantage of high specific surface area of its 3D porous network structure, the composite film exhibited excellent catalytic activity and high reusability. To the best of our knowledge, this is the first report about sustainable catalytic platform constructed by natural fibers, noble metal nanoparticles and trivalent metal ions for heterogeneous catalytic.

2. Materials and experiments

2.1. Materials

Chromic chloride ($CrCl_3$, >99%) was purchased from Shudu Chemical Co. Ltd. (Chengdu, China). Gallic acid modified silver nanoparticles (GA@AgNPs) with concentration of 100 $\mu g\ mL^{-1}$ were prepared according to our previous work [31]. Silver standard solution with the silver concentration of 1000 μg/mL was purchased from Aladdin Technology Co. Ltd. (Shanghai, China). Sodium borohydride ($NaBH_4$, >96%), p-nitrophenol (4-NP) and other Chemical materials are purchased from Jinshan Chemical Reagents Corporation (Chengdu, China). All other chemicals were analytical reagents.

2.2. Preparation of collagen fibers (CFs)

Collagen fibers were prepared from cattle skin according to the procedures in previous work [32]. First, non-collagen components in the skin were removed by deliming, bating and pickling according to the pretreatment procedures of leather making. Then the skin was treated with 150% aqueous solution of acetic acid (16 g/L) for three times to remove mineral substances. After rinsed by water, the skin was dehydrated by absolute ethyl alcohol and dried in a vacuum for 24 h at room temperature. Collagen fiber powders were obtained by grinding the above cow skin and sieving (5–10 mesh).