Thin Solid Films 519 (2011) 5609–5615

Contents lists available at ScienceDirect

Thin Solid Films

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

$AuCl_4^-$ ions-assisted fabrication of bimetallic {Poly(ethylenimine)-Ag/Au} multilayer polyelectrolyte film and application in electrocatalysis

Shi-Kuo Li [a], Li Zhang [a,b], Fang-Zhi Huang [a], Xue-Rong Yu [a,c], An-Jian Xie [a,*], Yu-Hua Shen [a,*], Yang Wang [a]

[a] School of Chemistry and Chemical Engineering, Anhui University, Hefei 230039, China
[b] Anhui Key Laboratory of Spin Electron and Nanomaterials (Cultivating Base), Suzhou University, SuZhou 234000, China
[c] Anhui center for disease control and prevention, Hefei 230061, China

ARTICLE INFO

Article history:
Received 3 May 2010
Received in revised form 14 March 2011
Accepted 15 March 2011
Available online 31 March 2011

Keywords:
Bimetallic {PEI-Ag/Au} multilayer film
Electrocatalytic oxidation
Ascorbic acid

ABSTRACT

Bimetallic {Poly(ethylenimine) (PEI)-Ag/Au} multilayer film was *in situ* simultaneously fabricated by alternating immersions of a substrate in PEI-Ag^+ and $AuCl_4^-$ solutions followed by chemical reduction with $NaBH_4$ solution. In the process, the $AuCl_4^-$ ions not only play an important role of a reaction reagent, but also served as an assembly reagent. Au, Ag nanoparticles (NPs) were observed with a spherical morphology and well-dispersed in the composite multilayer film, and the size of Au NPs in the bimetallic {PEI-Ag/Au} multilayer film was smaller than that of the single Au NPs formed in {PEI/Au} multilayer films. It was also very interesting to observe that this bimetallic {PEI-Ag/Au} multilayer film exhibited more efficient electrocatalytic activity for the oxidation of ascorbic acid than the multilayer film containing only single Au or Ag NPs. These results indicated that this bimetallic composite multilayer film may be potentially applied in electrochemical biosensors.

1. Introduction

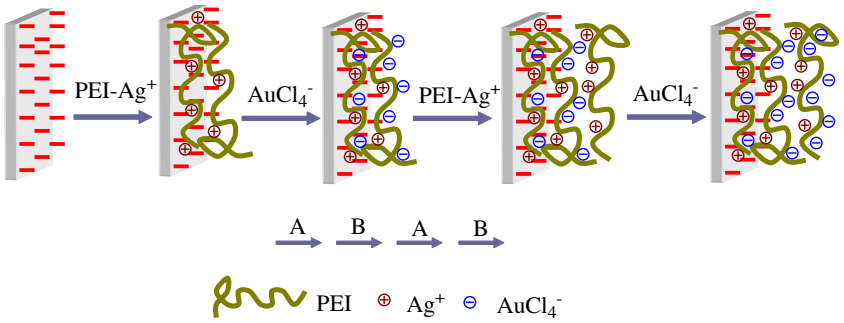
Noble metal nanoparticles (NPs) exhibit many unique electronic, optical, and catalytic properties that are different from those of the corresponding bulk metals, which have been widely applied in the areas of catalysis, nonlinear optical devices, electron microscopy markers, and the emerging area of plasmonics [1–4]. The intrinsic properties of NPs are determined by its size, shape, composition, crystallinity, and especially the dielectric environment [5–7]. Consequently, the development of fabrication of binary NPs by a facile procedure has recently become a very important topic.

Au and Ag NPs, as the significant members of the noble metal NPs, own some fascinating properties. Several methods have been previously developed to fabricate the composite film containing single Au or Ag NPs by using polymer templates [8], Langmuir–Blodgett (LB) technique [9,10], and layer-by-layer (LBL) self-assembly methods [11,12]. LBL technique has been regarded as the most convenient way to fabricate inorganic NPs. The film thickness, homogeneous and stable structures on a variety of surfaces can be controlled at a molecular level. Some binary inorganic colloids/polyelectrolyte composite films have been constructed by this method [13]. Bruening et al. [14,15] prepared the Poly(ethylenimine) (PEI)-Ag/Poly(acrylic acid) (PAA) multilayer films as antibacterial membranes for wound treatment by alternatively depositing PEI-Ag^+ complex and PAA on the surface, which was subsequently reduced by $NaBH_4$. Rubner et al. [16] fabricated PAA/poly(allylamine hydrochloride) (PAH) multilayer polyelectrolyte film and *in situ* synthesized Au NPs in the nanoreactors of the film. Frank Caruso et al. [17,18] assembled composite thin films containing individual Au or Ag NPs on the spherical submicrometer-sized polystyrene and silica particles by employing PAH and PAA-Ag^+ or Au^{3+} complex ions. We recently reported that *in situ* one-step synthesis of Ag NPs in PEI multilayer films based on a Keggin structure compound under UV-irradiation, and found that the films exhibit good electrocatalytic activity for the oxidation of uric acid [19]. Therefore, it can be briefly concluded that the multilayer thin film is usually constructed by the polyelectrolyte with pairs of opposite charges based on the electrostatic interactions. However, inorganic molecules or ions have been seldom reported for assembling composite thin film.

In this manuscript, we fabricate the bimetallic {PEI-Ag/Au} multilayer film through alternative adsorption of PEI-Ag^+ complexes and $AuCl_4^-$ ions followed by reduction with $NaBH_4$ solution. The small $AuCl_4^-$ ions in this report play the roles of an assembly reagent and a reaction agent. This bimetallic composite multilayer film shows higher electrocatalytic activity for the oxidation of ascorbic acid than the film only containing the individual Au NPs. Using inorganic ions

* Corresponding authors. Tel.: +86 551 5108702; fax: +86 551 5107342.
E-mail addresses: anjx@163.com (A.-J. Xie), s_yuhua@163.com (Y.-H. Shen).

0040-6090/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2011.03.034



Scheme 1. Schematic representation of fabrication of bimetallic $\{PEI\text{-}Ag^{+}/AuCl_4^{-}\}_n$ multilayer films via alternating deposition of PEI-Ag^{+} complex and $AuCl_4^{-}$ ions layer-by-layer.

and oppositely charged polyelectrolyte for fabricating multilayer films, and *in situ* simultaneously assembled the bimetallic multilayer film have few been reported. This study provides a feasible protocol for the fabrication of bimetallic multilayer films, and the resulting film could be potentially applied to the field of electrochemical biosensors.

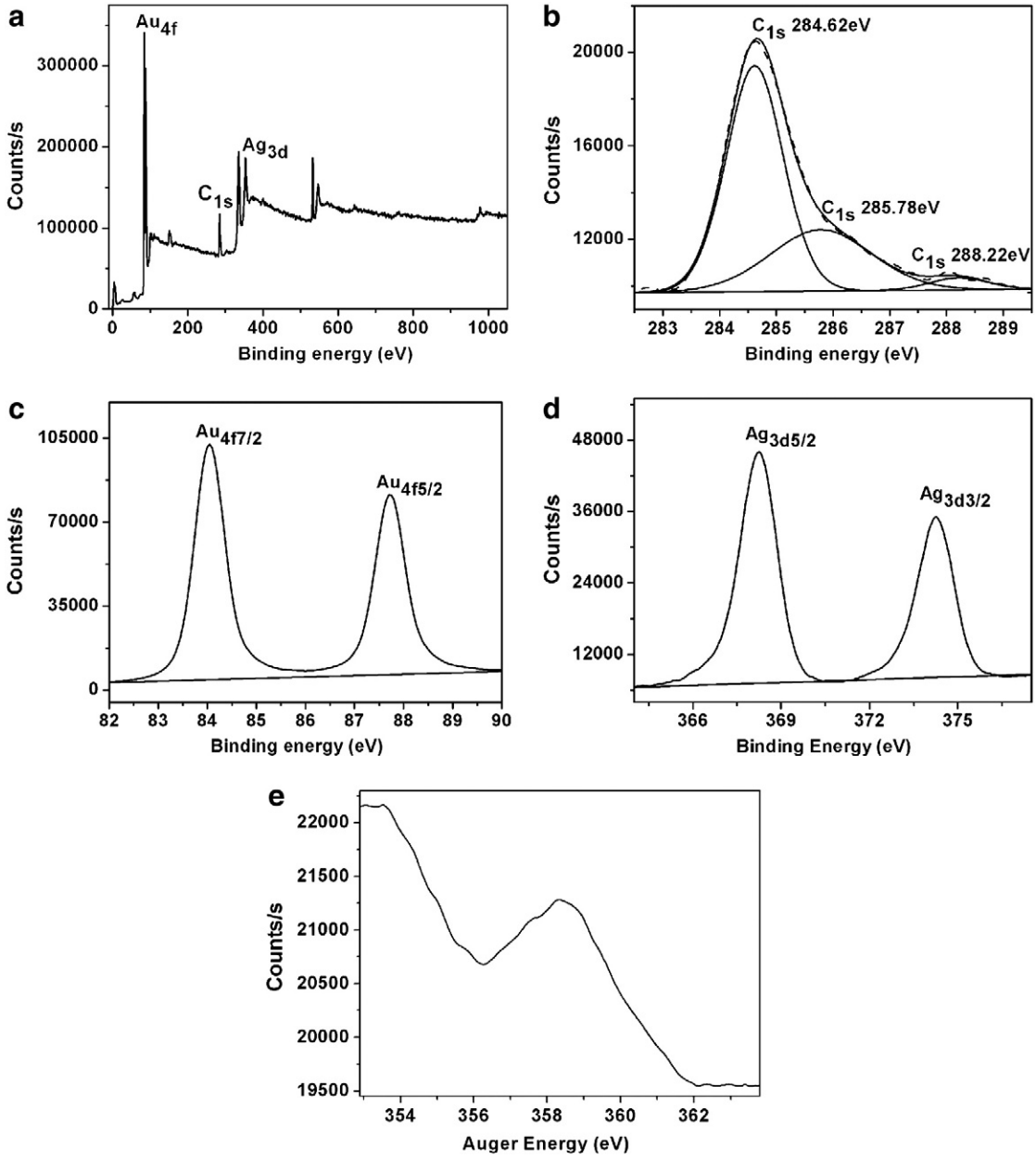


Fig. 1. XPS of bimetallic $\{PEI\text{-}Ag/Au\}_{25}$ composite multilayer films fabricated on silicon substrate (a) XPS survey, (b) C_{1s}, (c) Au_{4f}, (d) Ag_{3d} and (e) Auger energy spectrum, respectively.