



Aminosilicate sol-gel supported zinc oxide-silver nanocomposite material for photoelectrocatalytic oxidation of methanol



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ABSTRACT

A (3-aminopropyl) triethoxysilane supported zinc oxide-silver nanocomposite material [APS/(ZnO-Ag)_{NCM}] was prepared by a simple chemical reduction method and their optical, structural, morphology, elemental and surface properties were studied by UV-DRS, PL, XRD, SEM, TEM, EDX and XPS analysis. The photoelectrocatalytic activity of APS/(ZnO-Ag)_{NCM} modified electrode was investigated towards methanol oxidation. The modification of ZnO nanomaterial with silver nanoparticle resulted in improvement of interfacial charge transfer and minimized the electron-hole charge recombination process. This process significantly enhanced the photoelectrocatalytic activity and performance due to synergic effect of silver. The aminosilicate sol-gel support improved the deposition of silver metal on ZnO surface and it promotes efficient charge transfer in photoelectrocatalysis. The APS/(ZnO-Ag) modified electrode showed four-fold enhancement in photocurrent generation toward photoelectrocatalytic oxidation of methanol compared with ZnO. This aminosilicate sol-gel stabilized APS/(ZnO-Ag)_{NCM} is an efficient photoelectrode for the photoelectrochemical applications.

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1. Introduction

Zinc oxide nanostructure is a key functional material which exhibits interesting optical, electronic and photonic properties [1,2]. Hence, it has been received much attention in the field of photocatalysis, photoelectrocatalysis, dye-sensitized solar cells, sensors, field effect transistors and ultraviolet (UV) light emitters [3–11]. However the drawbacks are also associated with the bare ZnO because of its quite wide band-gap (3.37 eV) semiconductor material. It makes utilization of ultraviolet (UV) region only and it hereby undergoes rapid electron-hole charge recombination which leads to the poor photocatalytic performance [12]. An addition of foreign elements with zinc oxide may extend its photoabsorption range into visible region and prevent electron-hole charge recombination process [13–15]. This seems to be a promising alternative way to overcome this limitation. Several attempts are made either by metal or non-metal doping or deposition and semiconductor coupling with parent material [16–19]. The metal deposition on ZnO surface, which possesses efficient photocatalytic activity under

visible region, has received much attention in the field of photocatalysis and photoelectrocatalysis. The metal nanoparticles acts as an electron sink for photo-induced charge carriers, thus improves the interfacial charge transfer and thereby minimize the charge recombination processes [20–24]. On account of, the aminosilicate sol-gel support is improved metal deposition on semiconductor surface, promotes efficient charge transfer in photocatalysis and photoelectrocatalysis [25,26].

Direct methanol fuel cells (DMFC) are efficient power source for many electronic devices due to its mass energy can be easily functionalized to electronic devices [27,28]. Recently, photoelectrocatalytic oxidation of methanol attracted much more attention in DMFC research. In order to increase the photoelectrocatalytic performance by the addition of noble metal with semiconductor material [29–31], several researchers have investigated using the semiconductor and semiconductor/metal nanocomposite materials for photoelectrocatalytic oxidation of methanol, which includes TiO₂ [32], TiO₂-Au [29], TiO₂-Ag [30], TiO₂/Pt-Ru [31], EDAS/(TiO₂-Au)_{nps} [26], TiO₂/POM-Au [33] and APS/(P25-PTA-Au)_{NCM} [34].

In our present study, we have synthesized ZnO NPs, (ZnO-Ag)_{NCM} and APS/(ZnO-Ag)_{NCM} modified electrode used for

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photoelectrocatalytic oxidation of methanol. The photoelectrocatalytic performance of APS/(ZnO-Ag)_{NCM} modified electrode showed higher efficiency when compared to the ZnO and (ZnO-Ag)_{NCM}. The APS/(ZnO-Ag)_{NCM} modified electrode showed better photoelectrocatalytic activity towards methanol oxidation due to the presence of Ag nanoparticles on the ZnO surface. This APS/(ZnO-Ag)_{NCM} photoelectrode could be a promising material for the future photoelectrochemical and photovoltaic applications.

To the best of our knowledge this is the first report of photoelectrocatalytic oxidation of methanol using ZnO-Ag nanocomposite supported with aminosilicate material. The previous analyzed reports are available for photoelectrochemical oxidation of methanol using titanium dioxide with high cost gold based composite materials [26,29,34] and no other reports are found for ZnO based composite with silver for photoelectrochemical oxidation of methanol. In our study for the first time we have attempted to replace TiO₂-Au with ZnO-Ag for methanol oxidation.

2. Experimental

2.1. Materials

Zinc acetate dihydrate, sodium borohydride, silver nitrate and methanol were obtained in analytical grade of Merck product, (3-aminopropyl) triethoxysilane (APS) was purchased from Sigma-Aldrich. The indium doped tin oxide (ITO) coated conducting glass plates with a surface resistance of 4–8 Ω sq⁻¹ (CG-411N-1507) was received from Delta Technologies Ltd, USA.

2.2. Preparation of ZnO nanoparticles

The ZnO nanoparticles were prepared by simple solid-state pyrolysis method. In a typical preparation method, 5 g of zinc acetate dihydrate was taken in the silica crucible and then placed in a muffle furnace and calcinated at 600 °C for 2 h. Finally, the white colour ZnO nanoparticles were obtained and it was naturally cooled to room temperature and then stored in dark.

2.3. Synthesis of APS/ZnO-Ag nanocomposite material

0.5 g of prepared ZnO NPs dispersed in 50 mL of distilled water, followed by addition of 100 μL of APS with reaction mixture and was stirred for 30 min to get a homogeneous mixture of APS/ZnO. Then 0.125 g of AgNO₃ was gradually added to the above reaction mixture and stirring was continued for 30 min. The freshly prepared ice cold sodium borohydride solution was added drop-wise into reaction mixture until brownish yellow colour obtained and the reaction mixture was vigorously stirred for another 60 min. Then the obtained APS/(ZnO-Ag)_{NCM} were collected by centrifugation (8000 rpm for 15 min) and washed with distilled water and ethanol. The centrifugation and washing was repeated for four times to remove the loosely bound Ag NPs and impurities. The synthesized nanocomposite material was dried in hot air oven at 110 °C for 1 h to remove the moisture completely. The sol-gel supported aminosilicate functionalized ZnO-Ag nanocomposite material was successfully synthesized by facile chemical reduction method. Similarly (ZnO-Ag)_{NCM} was synthesized as mentioned in the above procedure with the absence of APS.

2.4. Material characterization

The diffuse reflectance spectra (DRS) of prepared nanocomposite materials were measured using Shimadzu UV-2550 UV-Vis spectrophotometer with ISR-2200 diffuse reflectance

accessory. Photoluminescence (PL) spectra were detected with a JASCO-FP-6500 spectrofluorimeter using xenon laser with the excitation light source at 350 nm. The crystalline structure was characterized by X-ray diffraction (XRD) analysis on a Bruker Advance at with Cu Kα radiation (λ = 1.54178 Å). The morphology and composition of samples were studied by VEGA3 TESCAN scanning electron microscopy (SEM) at 30.0 kV with Bruker energy dispersive X-ray analysis (EDX) accessory and JEOL 2010 transmission electron microscope (HR-TEM) with an accelerating voltage of 200 kV. The surface components and chemical states of the material was investigated by ThermoScientific Multilab 2000 X-ray photoelectron spectroscopy employing with Al Kα X-rays (1486.6 eV).

2.5. Photoelectrochemical experiment

The APS/(ZnO-Ag)_{NCM} modified electrode was fabricated by 5 mg of APS/(ZnO-Ag)_{NCM} dispersed into 1 mL of ethanol sonicated for 30 min and stirred for about 24 h to get a homogeneous solution. It was coated on a conducting side of ITO glass plates and was allowed to dry at room temperature for solvent evaporation and then placed at 80 °C in hot air oven for 1 h. The photoelectrochemical measurements were conducted by the conventional three electrode system containing a APS/(ZnO-Ag)_{NCM} modified electrode as working electrode, platinum electrode as a counter electrode and Ag/AgCl as a reference electrode with 0.1 M Na₂SO₄ used as the supporting electrolyte. All the photoelectrochemical experiments were carried out in room temperature and the nitrogen gas was purged into electrolyte solution before starting the experiment. A 450 W xenon lamp was used as light source and photocurrent measurement was carried out using computerized CHI-760D electrochemical workstation (CH Instruments, Inc., USA).

3. Results and discussion

3.1. APS supported ZnO-Ag nanocomposite

ZnO-Ag hybrid nanocomposite is a composition of semiconductor-metal nanoparticles. The two steps synthesis method was usually followed for preparation of semiconductor-metal nanocomposite materials. At first, the semiconductor material is prepared followed by which the metal precursor is added, it is then reduced by using suitable reducing agent [35,36]. Moreover this type of process some time produced self-nucleated and isolated metal nanoparticles formation. To avoid this problem to prepare amino silicate supported ZnO-Ag nanocomposite material an inorganic silicate polymer material incorporated with semiconductor-metal fabrication which improves the stability, photocatalytic and photoelectrocatalytic activity of hybrid nanocomposite materials was added [25,26,34]. Typically, APS ((3-aminopropyl) triethoxysilane) is an inorganic silicate material is supported with ZnO-Ag is shown in Scheme 1. In this process zinc oxide surface was covered with amino silicate material (APS) then Ag was deposited. An ZnO surface have exist large amount of hydroxyl groups, it attacks and displaces the ethoxy (CH₃CH₂O-) groups on the APS surface thus forming a covalent bond with silicate (Si-O-Si-) group to form an APS/ZnO. As well as silver salt attached on APS surface and was reduced by sodium borohydride. Then the covalent bond formed at the interface between the Ag NPs and silicate surface followed by decreasing the possibility of the formation of self-nucleated Ag NPs and improving stability of ZnO-Ag nanocomposite material.

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