Applied Catalysis A, General 547 (2017) 205–213

Contents lists available at ScienceDirect

Applied Catalysis A, General

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

Research paper

Surfactant-assisted formation of silver titanates as active catalysts for methanol electro-oxidation

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ARTICLE INFO

Keywords:
Methanol oxidation
Ag/titanate
Surfactant template
Electrochemical properties
Photocurrent

ABSTRACT

Silver nanoparticles successfully incorporated in titanate nanosheets and synthesized hydrothermally via employing cetyltrimethylammonium bromide (CTAB) and triblock copolymer (pluronic F127) assisted templates were thoroughly characterized using transmission electron microscopy-selected area electron diffraction (TEM-SAED), X-ray diffraction, diffuse reflectance UV/visible absorption spectroscopy, N_2 sorptiometry, FTIR and Raman spectroscopy. The dispersed Ag nanoparticles of uniform size (2–3 nm) were found to contact intimately with titanate$_{F127}$ nanosheets to show superior crystallinity, wider layer distances and higher surface area and pore volume (S_{BET} = 51.1 m^2 g^{-1}, V_p = 0.081 cm^{3}g^{-1}) than Ag/titanate$_{CTAB}$ (7.2 m^2 g^{-1}, 0.02 cm^3 g^{-1}). This constructed Ag/titanate$_{F127}$ exhibits markedly improved electrocatalytic (1.4-fold) and photoelectrocatalytic (4.0-fold) activities and stabilities towards methanol oxidation than that of Ag/titanate$_{CTAB}$; as determined using cyclic voltammetry, linear sweep voltammetry and chronoamperometry. The enhanced activity of Ag/titanate$_{F127}$ was also attributed to electron transfer across the interface potential of the composite Ag-titanate$_{F127}$ as well as the delay of charge recombination that has been substantiated not only via exposed Ag but also through the non-decomposed carbon template. This enhanced electron transfer and electronic conductivity was established by impedance spectroscopy, and exhibits the maximum obtained photocurrent density (2.0 mA cm^{-2}) under visible light illumination ($\lambda > 420$ nm, 88 W). The results revealed that the template F127 had a significant effect not only on enhancing the titanate crystallinity and exhibiting a surface plasmon resonance band; unlike Ag/titanate$_{CTAB}$, but also in acquiring a high pore volume value and widened layers, which all work towards improving the Ag-titanate$_{F127}$ durability for methanol oxidation.

1. Introduction

Nowadays, researchers have developed efficient and practical sources of energy such as solar cells, lithium ion batteries, water splitting for H_2 generation and direct alcohol fuel cells [1–4]. Specifically, direct methanol fuel cells (DMFCs) have become increasingly attractive as energy sources for use in various mobile devices [5–7]. Consequently, more attention has been paid by researchers for developing efficient ways for converting and storing large amounts of energy. However, there are some drawbacks about the materials used in DMFCs which relate to the high catalyst cost, low kinetic efficiency and fast poisoning [8,9]. Accordingly, utilization of anodic electrodes other than Pt have attracted the attention of many researchers for methanol electro-oxidation such as nickel-based materials [10,11] as well as their alloys [12,13]. Other Pt substituent's such as palladium, rhodium, ruthenium, iridium and osmium were also employed, however their efficiencies did not improve much and sometimes they were lower than Pt based catalysts [14,15]. On the other hand, the choice of the support is very important in many issues, especially if it offers good interaction with the catalyst **to** govern not only the charge transfer [16] but also to control the catalyst loss. Good electrical conductivity and larger surface area maximizes also the fuel cell efficiency. Simultaneously, carbon supports such as Vulcan XC-72 that has been used as an appropriate support for Pt while performing DMFC has been replaced by other supports such as nanostructured carbon mesoporous carbon, carbon nanotubes, nanodiamond, carbon nanofibers and graphene [17–20]. The examination of non-carbonaceous based supports is very important in the context of carbon support corrosion and the resultant consequences, such as catalyst loss, which significantly affect the overall performance of the fuel cell. In this work, we discuss the performance, potential and issues connected with the use of titanates as non-carbon based supports, when supported Ag nanoparticles are applied as an

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http://dx.doi.org/10.1016/j.apcata.2017.08.031
Received 2 April 2017; Received in revised form 10 August 2017; Accepted 19 August 2017

anode catalyst in DMFC; as a substitute for the most common only used Pt. Fundamentally, the performance of such system is directly related to the material properties. Therefore, material technology plays a critical role in the development of electrochemical energy conversion and storage systems. Accordingly, titanium nanotubes of excellent chemical stability have shown unique advantages in the photocatalytic applications since their 1D structure offers direct paths for photo-generated electron transfer, and thus increases the efficiency of charge separation [21–23]. Furthermore, 1D structured catalysts possess larger active surface-to-volume ratios and thus assist the photocatalytic reaction within the electrolyte [24,25]. On the other hand, a comprehensive study concerning titanate supported Ag for DMFC was reported by Mohamed et al. [26] and in addition during forming composites with graphene and MWCNT. The superior electrical conductivity of Ag/titanate as well as the low resistivity and the larger surface area have shown improved electrochemical methanol oxidation [26]. Besides, the exhibited strong metal support interaction and the consequences thereof, including the facile electron transfer and particles size decrement promoted the oxidation of methanol. This has stimulated us to use another strategy for the synthesis of Ag/titanates. Accordingly, we have used cetyltrimethylammonium bromide and pluronic F127 surfactants to appropriately organize titanate networks in relation to stabilization and potential functionalization of Ag nanoparticles. Structure, surface, optical and morphological characterization were well determined using XRD, TEM-SAED, N_2 sorptiometry, UV–vis diffuse reflectance, Raman and FTIR spectrometry. These materials were then evaluated as DMFCs to try correlating the structure-activity relationship for maximum optimization and utilization.

2. Experimental

2.1. Synthesis of titanate$_{CTAB}$ and titanate$_{F127}$ and their Ag supported ones

Into 20 ml titanium isopropoxide, 0.036 g of cetyltrimethylammonium bromide (CTAB) dissolved in 100 ml NaOH (10 M) was added drop-wisely to form a gelatinous solution, which left under stirring for 4 h. This gelatinous solution was then left at room temperature for 4 h, then hydrothermally autoclaved at 373 K for 72 h. Afterward, it was filtered and washed with a water-ethanol mixture, followed by drying at 373 K and calcining at 673 K for 6 h. A portion of uncalcined titanate$_{CTAB}$ was used to prepare 3%Ag-titanate$_{CTAB}$ via suspending the former in a mixture of ethanol-water then leaving it stirring for 2 h followed by sonication at 313 K for 1.0 h. Exposing of the latter mixture into an UV Hg lamp (λ = 256, power = 100 W) for 25 min to confirm complete reduction of Ag ions into Ag nanoparticles was accomplished. Then, the sample was dried at 373 K overnight and finally calcined at 673 K for 4 h. This sample is denoted as 3%Ag-titanate$_{CTAB}$.

Similarly, Pluronic F_{127} ($HO(CH_2CH_2O)_{100}(CH_2CH(CH_3)O)_{70}(CH_2CH_2O)_{100}H$), which was dissolved in ethanol-water mixture together with titanium iso-propoxide, was used as a template similar to CTAB. The resulting clear solution was mixed thoroughly for 2 h and then aged for 5 h at ambient temperature. Then, 30 ml 10 M NaOH was added step wisely till complete precipitation. That precipitate was transferred into a Teflon lined autoclave to be treated hydrothermally at 373 K for 72 h. Subsequently to hydrothermal treatment, the products were recovered by centrifugation and then washed 3 times with deionized water. The solids were isolated by filtration and washing with deionized water, and then dried overnight at 333 K. They were further calcined in air at 673 K for 6 h to remove the copolymer template. This sample was denoted as titanate$_{F127}$. A portion of the uncalcined titanate$_{127}$ was suspended in water and a solution of $AgNO_3$ was added in a slow way to prepare 3 wt% Ag/titanate$_{127}$ followed by sonication at 315 K for 1.0 h. Then, this mixture was exposed into the Hg UV lamp; similarly to the CTAB assisted sample, to reduce Ag ions. Subsequently, the sampled was dried at 373 K overnight and finally calcined at 673 K for 4 h. This sample is denoted as 3%Ag-titanate$_{F127.}$

2.2. Catalyst characterization

The X-ray diffraction patterns were carried out using a Philips 321/00 instrument operating with Ni-filtered Cu Ka radiation (l = 1.541 Å) at 36 kV and 16 mA. The surface texturing properties namely S_{BET} surface area, total pore volume (V_p) and mean pore radius (r) were determined from N_2 adsorption isotherms measured at 77 K using a volumetric apparatus. Raman spectra were measured by means of U-1000 laser Raman spectrometer using the 488 nm line of an ArC laser as the excitation beam. The FT-IR spectra were monitored via a single beam Thermo Scientific Nicolet iS10 instrument in the 4000–400 cm^{-1} region. The UV–vis diffuse reflectance spectra (DRS) of synthesized materials were obtained with a UV–vis spectrophotometer (JASCO Corp., V-570) with an integrating sphere attachment in the margin 200–800 nm. TEM micrographs and selected area electron diffraction (SAED) images were measured using a FEI model Tecnai G20 (Super twin) with double tilt 1010 operating at an accelerating voltage of 200 KV.

2.3. Electrochemical and photoelectrochemical methanol oxidation

Voltammetric measurements were carried out in a standard three electrode electrochemical cell at room temperature (25 °C) with an autolab PGSTAT204 attached with Nova 1.11 software for data processing. The titanate$_{F127}$, Ag/titanates$_{F127}$, titanates$_{CTAB}$ and Ag/titanates$_{CTAB}$ electrodes were used as working electrodes at an area equal 1.0 cm^2. These electrodes were systematically prepared via mixing with the carbon black and PVDF with ratios of 85:10:5 respectively, and then loaded onto the FTO conducting glass. The deposited electrodes were transferred to the electrochemical cell with or without acidified (0.5 M H_2SO_4) CH_3OH of 0.6 M concentration. A thin platinum electrode was used as a counter electrode whereas the saturated Hg/Hg_2SO_4 (MSE) electrode was served as a reference electrode, where all potentials were referred to the MSE. The cyclic measurement sweep between −0.8 V and 1.3 V with scan rate of 10 mV s^{-1} was adopted unless otherwise stated. Linear sweep voltammetry (LSV) was conducted at the scan rate of 10 mV s^{-1} in the acidic aqueous solution. The amperometric I–t curves were recorded in the acidic aqueous solution at 0.2 V for 1000 s. A visible light (of wavelength > 420 nm) 88 W Hg lamp was used as a light source and the photocurrent measurement was determined via using LSV. Electrochemical impedance spectroscopy (EIS) measurements performed on the same apparatus (autolab PGSTAT204) were performed with amplitudes of 10 mV in the frequency range 100 kHz-0.1 Hz. The justification of the impedance spectra was determined in view of the Kramers-Kronig transformation.

3. Results and discussion

3.1. Bulk structure and morphology characteristics

The XRD pattern obtained as a result of autoclaving titanium isopropoxide with triblock copolymer F127 and NaOH (10 M) at 100 °C followed by annealing at 400 °C (titanate$_{F127}$) indicates polymorphs structure consisting mainly of $Na_2Ti_3O_7$; with reflections located at $2\theta = 9.8°(111)$, 16.9°(101), 30.9°(003), 31.8°(202), 38.2°(013), 45.5°(104) and 48.0°(020). Additionally, a minor amount of the rutile phase; with reflections at $2\theta = 27.5°(101)$ and 56.2°(002) were also shown together with titanium metal evidenced by small reflections at $2\theta = 35°$ and 40.5°, the origin of which requires further investigation. Incorporating Ag within the above system and calcining at 400 °C (Ag-titanate$_{F127}$) exhibits the existence of the same peaks, with some modification and most importantly enhancement of the peak around $2\theta = 10°$ proposing the inclusion of Ag nano-crystallize into the titanate structure. The peaks related to titanium metal suffer a marked decrease