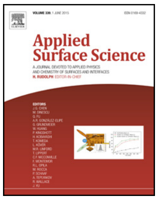
Applied Surface Science 339 (2015) 22–27

Contents lists available at ScienceDirect

Applied Surface Science

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



Charge transfer behavior of graphene-titania photoanode in CO_2 photoelectrocatalysis process

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ARTICLE INFO

Article history:
Received 30 October 2014
Received in revised form 8 February 2015
Accepted 23 February 2015
Available online 1 March 2015

Keywords:
Charge transfer
Recombination rate
CO_2 conversion
Photoelectrocatalysis

ABSTRACT

In the present study, a graphene-titania composite photoelectrode was synthesized, characterized and examined for the photoelectrocatalytic (PEC) response. The charge transfer process on the semiconductor/electrolyte interface was investigated via electrochemical impedance spectroscopy (EIS) and voltammetry. In addition, the influence of pH toward the photoanode performance was also investigated and it was noticed that a high pH condition was favorable higher photocurrent response from the EIS measurements. The main reason could be attributed to the decrease of recombination process at the photoanode with fast quenching of the photogenerated holes with OH^- ions at high pH. The experiment was also run for CO_2 photoreduction and increased photocurrent was observed.

1. Introduction

With the increase of population growth, sky-rocketing dependence on fossil fuels are placing unprecedented constraints on energy supplies for domestic, commerce and industrial sectors. The dependency on fossil fuels enhances carbon dioxide (CO_2) emission to the atmosphere which eventually plays a major role in long term climate change and global warming [1,2]. Since the CO_2 molecule is highly stable, it requires very high energy input for the successful recycling to synthetic fuels. The photoelectrocatalytic reduction of CO_2 is a very promising catalytic process where direct solar energy is utilized to activate the photocatalyst for the desired reactions [3,4]. Much of the important research in photoelectrochemistry is aimed to develop these photocatalysts by utilizing semiconductors with a suitable energy band-gap and favorable electron transfer kinetics [5]. For this purpose, TiO_2 nanomaterials have shown some promise although some significant improvements are mandatory for a successful photocatalytic activity. Recently researchers have reported about graphene-TiO_2 nanocomposites for the application of various optical and electronic devices. This composite material has also shown tremendous photocatalytic activity and charge transfer properties [6,7].

The most important mechanism for the photo-assisted reduction of CO_2 is the photogeneration of electrons and holes on the electrode surface. Upon illumination with photon energies higher than the band gap energy of the semiconductor photocatalyst, the photogenerated electrons are excited from the valence band to conduction band, while the holes migrate to the surface [8]. The photogeneration of electrons and holes and their subsequent redox reactions can be summarized as follows:

$$TiO_2(e_{CB}{}^- - h_{VB}{}^+) \rightarrow e_{CB}{}^- + h_{VB}{}^+ \quad (1)$$

The holes oxidize the H_2O molecule:

$$2H_2O + 4\,h^+ \rightarrow 4H^+ + O_2 \quad (2)$$

A small biased potential is necessary to drive the oxidation process at the photoanode. This helps to reduce the recombination of electron ($e_{CB}{}^-$) and hole ($h_{VB}{}^+$) and results in an improved photocatalytic performance. At the same time, the photoexcited electrons are drawn to the counter cathode where the actual CO_2 electroreduction occurs.

Several reports have been published on CO_2 photo-conversion process using TiO_2 photocatalysts. The doping of TiO_2 with various metal, non-metal and other semiconductors has been performed to extend the absorption range in the visible region [9]. Recently, graphene showed tremendous performance in photocatalytic activity due to its high optical transmittance, large specific surface area and unique electronic properties [10]. It was demonstrated earlier that the electrochemical redox reactions could be

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http://dx.doi.org/10.1016/j.apsusc.2015.02.162
0169-4332/

enhanced when the electrocatalyst was illuminated with a suitable wavelength [11,12]. C. Zhai et al. showed that, reduced graphene oxide with titania nanotube arrays can increase the PEC process efficiency to a great extent [13]. However, it is still unclear how graphene–TiO_2 semiconductor composites can play an effective role as a photoelectrocatalyst for CO_2 photoreduction.

In this paper, we report the synthesis, characterization of graphene-TiO_2 photoanode and the effect of pH on its performance as a photoelectrocatalyst. CO_2 photoreduction experiment was also carried out and the response was examined.

2. Experimental methods

2.1. Materials

Graphite flakes, with 7–10 μm nominal size were procured from Alfa Aesar. Tetra-n-butyl ortho titanate [$Ti(OBu)_4$] was procured from Sigma–Aldrich and all other chemicals used in this work were of analytical grade. The indium tin oxide (ITO) coated conducting glass plates (0.7 mm thickness) were procured from Osaka, Japan. Deionized water (18.2 MΩ cm) used in the experiments was Milli-Q system (Millipore, Bedford. with Mega-Pure System, Model MP-290). The light source, 150 W (Xe arc lamp) solar simulator was from OSRAM photo optic (Germany). It had a consistent spectrum profile of AM 1.5G i.e. almost the same characteristic features of 1 Global radiation solar light (i.e. intensity $100\,mW\,cm^{-2}$) under standard air condition. Carbon dioxide used throughout the experiments was of 99.9% purity.

2.2. Graphene-titania nanocomposite and photoanode preparation

The graphene incorporated titania (TiO_2) anatase nanocrystals were prepared via sol-gel method. Prior to this, graphene oxide was prepared by the modified Hummer's method and high quality graphene was prepared from graphene oxide via the hydrazine treatment [14]. For the preparation of the graphene-TiO_2 nanocomposite, 4 ml TBOT, 20 ml absolute ethanol and acetic acid were mixed in a beaker. Acetic acid was used to control the pH of the solution. 0.01 g fine graphene powder, 5 ml ethanol and 3 ml of deionized water were added in another beaker and kept under sonication. This solution was added drop-wise to the first solution. The total mixture was stirred for 30 min and kept for 24 h for the gel formation. The gel was dried at 70 °C overnight. The dry porous gel was milled using mortar and pestle. The dried catalyst powder was calcined at 600 °C for 4 h.

Prior to the electrophoretic deposition of the photocatalyst material on ITO coated glass substrate, the thin substrates were cleaned with acetone, dehydrated alcohol and ultrapure water respectively. The electrophoretic deposition technique was performed on 1 cm × 1 cm active electrode surface, using a DC power supply at 60 V for 1 min. The electrolyte composition was 0.1 mg powder catalyst/ml solvent.

2.3. Photocatalysis experiments and instrumentation

XRD spectra were recorded with a powder X-ray diffractometer (type Bruker D8 Advance equipped with EVA diffract software, Germany) over the range $10^\circ \leq 2\theta \leq 80^\circ$, operating at 40 kV and 40 mA, with Cu Kα radiation ($k = 1.5418$ Å). A scanning electron microscope (SEM, Quanta FEI 200) was used to probe the coating materials on the surface of ITO coated glass substrates. The UV–vis spectrophotometer was from PerkinElmer, Lambda 35 series, equipped with a 10 mm path length quartz cell, was used for the UV spectroscopy measurement. Fourier transformed infrared (FTIR) spectroscopy was recorded using a Bruker IFS 66V/S using a KBr technique.

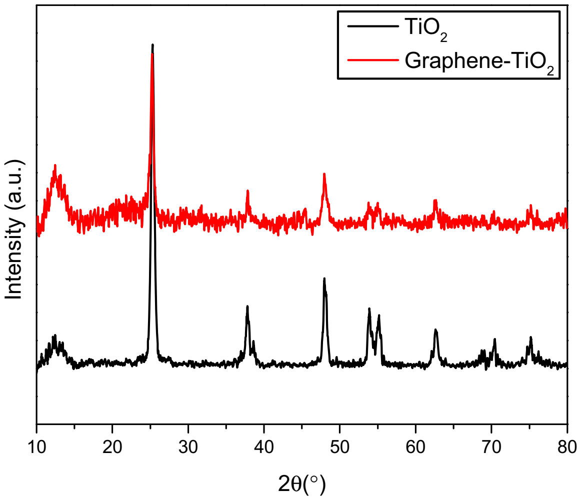

Fig. 1. XRD patterns of TiO_2 and Graphene-TiO_2.

All photoelectrochemical experiments were carried out with an Autolab PGSTAT302N potentiostat/galvanostat (EcoChemie, The Netherlands) with a three-electrode quartz cell. Graphene-TiO_2/ITO modified electrodes were used as the working electrode (WE). A saturated calomel electrode (SCE) and platinum wire were the reference and counter electrodes respectively. Electrochemical impendence spectroscopy (EIS) was performed at the open circuit potential (OCP) in the dark and under solar simulator irradiation. Simulation of the experimental data was done using analogue circuits with the NOVA 1.10 software installed in a computer, interfaced with the potentiostat. The frequency range was between 10^{-1} Hz to 10^5 Hz, with amplitude of 5 mV around OCP. A 0.1 M Na_2SO_4 solution was used as a supporting electrolyte in 0.5 M triethanolamine (TEA) aqueous solution. In the CO_2 photoreduction experiment, CO_2 gas was bubbled in the electrolyte for 1 h before the voltammetry experiment. The incident light intensity was $100\,mW\,cm^{-2}$ on WE in the cubic quartz cell. The photocurrent was measured for the graphene-TiO_2 modified nanocomposite electrode at an applied potential of 0.02 V (SCE). Raman spectroscopy was performed with Renishaw Invia Raman Microscope using ($\lambda = 514$ nm) laser excitation.

3. Results and discussions

3.1. Structural characterization

XRD was performed on the prepared graphene-TiO_2 nanocomposite sample to study the crystallinity of the nanocomposites. From the JCPDS data (reference code 21-1272), the peaks at 25.38° (1 0 1), 37.82° (0 0 4), 48.18° (2 0 0), 55.2° (2 1 1), 62.9° (2 0 4), 69.92° (2 2 0) are the characteristic diffraction patterns of the TiO_2 anatase phase. A thick broader peak was observed at 24° degree which is attributed to the crystalline graphene structure [15]. The peak was not obvious due low graphene content in the sample. A peak for unreduced GO was also observed at 11°. A small peak was observed in TiO_2 sample as well. It was appeared may be due to unwanted background noise at lower 2θ value. Fig. 1 shows the diffraction patterns and the phase change from anatase to rutile was not observed in the nanocomposite sample although the calcination temperature was 600 °C. In fact, the phase transformation of TiO_2 from anatase to rutile occurs between 500–700 °C [16]. The average crystallite