



Novel layer-by-layer assembly of rGO-hybridised ZnO sandwich thin films for the improvement of photo-catalysed hydrogen production

Swe Jyan Teh, Chin Wei Lai, Sharifah Bee Abd. Hamid*

Nanotechnology & Catalysis Research Centre (NANOCAT), 3rd Floor, Block A, Institute of Postgraduate Studies (IPS), University of Malaya, 50603 Kuala Lumpur, Malaysia

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ABSTRACT

Metal oxide semiconductor materials such as ZnO have tremendous potential as light absorbers for photo-catalysed electrodes in the electrochemical reduction of water. Promoters such as rGO have been added to reduce the recombination losses of charge carriers and improve its photoelectrochemical activity. In this study, the effect of layer ordering on the charge transfer properties of rGO-hybridised ZnO sandwich thin films for the photo-catalysed electrochemical reduction of water was investigated. rGO-hybridised ZnO sandwich thin films were prepared via a facile electrode position technique using a layer-by-layer approach. The thin films were analysed using FESEM, XRD, Raman, PL, UV-vis, EIS and CV techniques to investigate its morphological, optical and electrochemical properties. The FESEM images show the formation of distinct layers of rGO and ZnO nanorods/flakes via the layer-by-layer method. XRD confirmed the wurtzite structure of ZnO. PL spectroscopy revealed a reduction of photoemission intensity in the visible region (580 nm) when rGO was incorporated into the ZnO thin film. Among the six thin films prepared, ZnO/rGO showed superior performance compared to the other thin films (0.964 mA/cm²) due to the presence of graphene edges which participate as heterogenous electrocatalysts in the photocatalysed electrolysis of water. rGO also acts as electron acceptor, forming an n-p heterojunction which improves the activity of ZnO to oxidise water molecules to O₂. EIS revealed that the application of rGO as back contact (rGO/ZnO, rGO/ZnO/rGO) reduces the charge transfer resistance of a semiconductor thin film. Alternatively, rGO as front contact (ZnO/rGO, rGO/ZnO/rGO) improves the photo-catalysed electrolysis of water through the participation of the rGO edges in the chemical activation of water. The findings from this study indicate that the layer ordering significantly affects the thin film's electrostatic properties and this understanding can be further advantageous for tunable applications.

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1. Introduction

Today, our modern society is habituated to a high degree of mobility, fast communication and daily comfort, all of which require considerable energy input. These energy inputs largely consist of fossil fuel, which in turn, after combustion, contributes to the greenhouse gases and increases the carbon footprint in the earth's atmosphere. The addition of greenhouse gases is said to be largely responsible for increasing extreme climate conditions, which have wrought havoc on many nations across the world in the past several years [1]. Many scientists are aware that the extraction and combustion of fossil fuels will release significant amount of greenhouse gases to the atmosphere and this is a major threat to the environment (Bockris, 2002; Ghicov and Schmuki, 2009). Environmental damage and atmospheric changes may soon

alter the weather and climate patterns of the earth, resulting in grave problems of all its inhabitants [2,3].

Many countries are including renewable energy as a source of electricity in a global effort to aid the earth and minimise environmental problems caused by greenhouse gas emissions [4]. Renewable energy sources are valued for its ability to generate electricity with low impact to the environment [5], but is also limited due to its intermittent nature [6,7]. Natural phenomena such as fluctuations in wind flow and limited hours of sunlight exposure result in fluctuations of energy supply. Thus, methods to harness and store energy from intermittent sources of renewable energy are necessary to maintain a reliable power supply [8–10].

The storage of energy derived from renewable sources can be achieved by storing it as electricity [11,12] or as chemical fuels [13]. The production of chemical fuels, such as hydrogen and methanol, using energy generated from renewable sources is an attractive energy storage option mainly due to its ease of mobility and low carbon emissions impact. To date, hydrogen (H₂) has been established

* Corresponding author.

E-mail address: sharifahbee@um.edu.my (S.B.Abd. Hamid).

as a potential future energy carrier and possibly the best substitute for fossil fuel to secure the future supply of a clean and sustainable energy [14–16]. The novel feature of using H₂ is that it can be produced from water by utilising our solar energy, which is readily available and renewable resources without carbon emission.

Much research has been pursued on the development of semiconductor electrodes for photocatalytic water splitting process, in order to bring H₂ production technology to the point of commercial readiness. By fabricating electrodes which directly utilises sunlight to catalyse the electrochemical water splitting process, this increases the H₂ production efficiency as well as reduces the overall cost of production.

Metal oxide semiconductor materials such as ZnO have tremendous potential acted as light absorbers for photo-catalysed electrodes in the electrochemical reduction of water. It is a well-known fact that ZnO has similar conduction and valence positions as anatase TiO₂, and therefore has been frequently considered an alternative to titanium dioxide (TiO₂) for photocatalytic applications. As a matter of fact, zinc oxide (ZnO) is of interest on account of its high electron mobility [17], the availability of low temperature synthesis methods, and the potential for controlling the morphology through simple processing from solution [18,19].

However, the widespread use of ZnO as photoelectrode, compared to TiO₂, is limited by its light conversion efficiency. The photoelectrochemical performance of ZnO is limited by low internal surface area and slow electron injection [20]. It was reported that the higher photogenerated electron transport rate contributed to the performances of ZnO, but in the case of TiO₂, it is the low recombination rate and fast electron injection [21].

The photoelectrochemical response of ZnO can be further improved through the formation of heterojunctions with p-type materials. Reduced graphene oxide (rGO) has gained much attention as a novel, non-metal material in electronic applications, due to its flexibility and high surface area [22]. The unique features of sp² hybridised carbon, the presence of oxygen functional groups and graphene edges allow rGO to be conductive yet catalytically active. Indeed, when a heterojunction is formed, photoexcited electrons formed at the surface of the n-type semiconductor are quickly transferred to the p-type rGO surface which acts as electron acceptor [23], resulting in enhanced photocurrent and photocatalytic activity [24,25].

Among the vast morphological types allowed in the preparation of ZnO nanostructures, ZnO nanowire and nanorod are the most capable candidates to be coupled with rGO film for enhancement in water photoelectrolysis. The direct electrical pathway provided by the nanowires ensures the rapid collection of carriers generated throughout the device [26]. Recent articles support the promoting properties of rGO towards the photoelectrocatalytic activity of ZnO nanorods. When distinct layers of rGO and ZnO were prepared, the addition of rGO to Ag-doped ZnO was able to improve the photoelectrochemical response of the Ag-doped ZnO thin film [27].

While p–n and n–p heterojunctions have been widely explored for the improvement of charge transfer efficiency in photoanodes, few studies have been carried out on the electronic properties of bipolar heterojunctions, i.e., n–p–n and p–n–p junctions in photoelectrocatalytic applications. Making intuitive guesses on their properties are more or less impossible, and a focused research on the area is essential for the fundamental understanding of the role of rGO in promoting photoelectrocatalytic activity. Sandwich materials have demonstrated improved photoelectrochemical response compared to a single layer. Previously, ZnO/rGO/ZnO has been applied in supercapacitor applications [28]. A three-component, layered TiO₂ thin film previously demonstrated improved photocatalytic activity for dye degradation, due to a synergetic effect arising from the appropriate alignment of three-component layers [29]. To the best of our knowledge, detailed studies on the effect

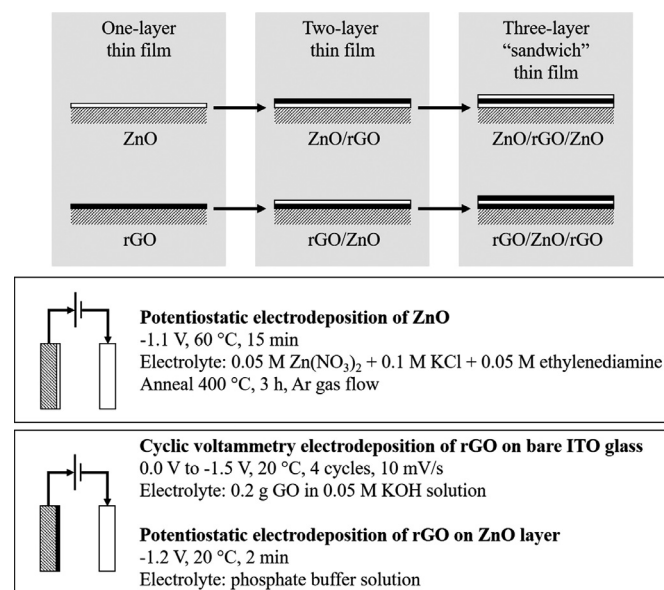


Fig. 1. Schematic representation of preparing the rGO-hybridised ZnO thin films using a layer-by-layer assembly method.

of rGO layer ordering their photoelectrocatalytic performance are lacking.

In this paper, the influence of layer ordering on the charge transfer properties and photoelectrocatalytic activity of rGO-hybridised ZnO sandwich thin films was investigated in detail in order to overcome drawbacks such as poor visible light response and recombination losses of charge carriers in photo-catalysed electrochemical reduction of water applications. This study aims to determine the optimum layer structure to obtain the best photo-catalytic electrochemical water splitting performance.

2. Experimental

2.1. Sample preparation

6 samples of thin films were prepared, with the sample name assigned according to the number of layers and order of the layering; beginning from the bottom layer: rGO, ZnO, rGO/ZnO, ZnO/rGO, rGO/ZnO/rGO and ZnO/rGO/ZnO. The samples were prepared in successive layer-by-layer assembly technique in a three-electrode cell using an Autolab PGSTAT302A electrochemical workstation. Platinum wire and Ag/AgCl were used as the counter and reference electrode, respectively. The steps to prepare each thin film sample is summarised in Fig. 1.

To deposit rGO on bare ITO glass, cyclic voltammetry method was applied between 0.0 V and -1.5 V at a scan rate of 10 mV/s over 4 cycles, using 0.2 g GO dispersed in 50 mL 0.05 M KOH solution as the electrolyte solution. To prepare the rGO coating on ZnO layer, GO was deposited by dip-coating the ZnO thin film in 0.2 g GO dispersed in 50 mL ethanol and allowed to dry between each immersion. Then, the dip-coated GO was reduced by applying a voltage of -1.2 V for 2 min in phosphate buffer solution as electrolyte.

The ZnO layer was deposited on bare- and rGO-coated ITO glass using a potentiostatic method, whereby a potential of -1.1 V was applied for 15 min in a 60 °C water bath and constant stirring. The electrolyte solution for the electrode position of ZnO layer consisted of 0.05 M Zn(NO₃)₂, 0.10 M KCl, and 0.05 M ethylenediamine (EDA). The as-prepared thin films were then annealed at 400 °C, at a heating rate of 1 °C/min and residence time of 3 h, under argon gas flow.

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