Synthesis of TiO2 NRs - ZnO Composite for Dye Sensitized Solar Cell Photoanodes

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Abstract. Composite of TiO2 NRs - ZnO were synthesized for DSSCs photoanode materials. TiO2 NRs was synthesized from TiO2 anatase by mechnochemical technique using ball milling process with agitation speed of 1000 rpm. While, the further hydrothermal refluxing process was conducted at 120°C under various concentration of NaOH in aqueous solution. The starting material of ZnO was prepared from ZnSO4.7H2O as a precursor. The hydrothermal treated TiO2 was added to the ZnO powder in a certain composition of 1:1, 1:2 and 2:1 (w/w), and the mixtures were then annealed at 400°C. The resulting material was characterized by X-ray diffraction (XRD), Surface area analyzer (SAA), Transmission electron microscopy (TEM), and Thermogravimetry/Differential thermal analysis (TG/DTA). The TiO2 revolution occurs from anatase phase into brookite phase. Rutile TiO2 phase was increasing when the NaOH was added at about 12 M. Nanograf of TEM showed the optimum condition for the formation of TiO2 NRs was obtained when 12 M NaOH was used. Structural transformation to 1D nanorods of TiO2 capable increase surface area up to 79 m²/g. TiO2 NRs-ZnO composite was prepared from TiO2 NRs and ZnO using comparation of TiO2 NRs: ZnO = 1:1, 1:2, dan 2:1. Anatase phase TiO2 as a single phase TiO2 was obtained in the TiO2–ZnO composite (1:1 w/w) upon heating the sample until 400°C. Difference TiO2 NRs-ZnO composite materials were investigated as good photovoltaic materials. Evaluation of the performance of DSSCs was conducted by I-V Keithley 2602A measurement indicate that photoanode built of TiO2 NRs - ZnO thin film has a higher solar cell efficiency than that of TiO2 thin film photoanode.

1. Introduction
Nanomaterials are tremendous interest due to their noticeable application in electronics, optics, and photonics as well as photocatalytic materials. Zinc oxide as a direct wide-band gap semiconductor with a bandgap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature is discovered to be importance semiconductor photocatalysis in recent years. In general, the photocatalytic activity is based on the generation of electron/hole pairs and limited by the recombination of electron/hole pairs. Many methods, such as doping, metal modification, and coupling of composite semiconductors, have investigated to suppress the recombination and increase the life time of separation electron and hole, hence to improve the photocatalytic properties. Among them the coupling of different semiconductor seems useful to achieve the recombination of electron/hole separation and prevent the recombination
electron hole pairs efficiently [1]. Difference TiO$_2$/ZnO composite materials were investigated as a good photocatalytic as well as a good photovoltaic materials.

Different author apply various methods of modification like ball milling [2], doping and codoping [3, 4] to obtain efficient photocatalysis under visible light with ZnO, TiO$_2$ and TiO$_2$-ZnO composites. Application of supported bycomponent catalysts from two semiconductors oxide also alter the electronic properties, as compared to the initial materials, in turn affecting charge photogeneration, charge separation and transfer, as found for ZnO overlayers on TiO$_2$. Although researcher focused on the fabrication of TiO$_2$/ZnO composite materials, and their photoactivity, there is still a need to study the structure and growth properties influence on the photocatalytic as well as photovoltaic activity.

Jayasankar et al. (2012) [5] have extend the hybrid sol–gel–powder method to the processing of thick, macro-meso-porous TiO$_2$, ZnO and ZnO–TiO$_2$ composite films, and show that these films can be advantageously applied for the photocatalytic degradation of dye molecules, as one of possible applications. The results presented hereafter show a procedure for mixing TiO$_2$ and ZnO nanopowders with optimized TiO$_2$ and ZnO precursor solutions, respectively, to process thick films with homogeneously distributed nanoparticles and porosity. ZnO–TiO$_2$ composite thick films were also investigated. The films were processed via spin coating and annealed at a fairly low temperature of 400°C to yield approximately 4 mm thick films in one coating sequence. Over the past several years, we have developed ZnO nanorod arrays suitable for both polymer-inorganic cells and dye-sensitized cells. Several groups have built polymer-inorganic cells from their own ZnO rod arrays, but in general the devices perform [6].

Nanoparticles (NPs) decorated ZnO/TiO$_2$ core/shell nanorod arrays were fabricated on transparent conductive glass substrates by sequential plasma deposition and post-annealing processes for dye-sensitized solar cells (DSSCs) applications. The NPs decorated ZnO/TiO$_2$ nanorods were composed of single-crystalline ZnO nanorods, homogeneously coated thin TiO$_2$ shells and entirely covered anatase TiO$_2$ NPs. The photocurrent density of the composite electrode was largely enhanced due to the enlarged surface area, the dark current was suppressed and the open-circuit voltage was increased because of the energy barrier formed at the interface between the ZnO core and the TiO$_2$ shell [7].

DSSCs based on one-dimensional (1D) ZnO nanostructures, which exhibit significantly higher electron mobility than that of both TiO and ZnO NPs films [8], have recently been attracting increasing attention [8, 9]. However, the power conversion efficiency of these DSSCs based on ZnO nanorods was still at a relatively low level (−1.5%) [8]. Insufficient internal surface area of those 1D nanostructures is considered to be one of the key factors in limiting the energy conversion efficiency. For improving the surface area without sacrificing electron transport efficiency, nanorods/nanoparticle composite films [7], were employed to be used as the photoanode of DSSCs. The photocurrent density and efficiency of these cells were largely increased because of the enriched surface area for better dye loading and lightharvesting.

2. Experimental

2.1. Synthesis of TiO$_2$ NRs –ZnO
Treated TiO$_2$ ball mill was refluxed under NaOH solution of 8, 10, and 12M for 24 hours. Then the powder resulted was filtered and neutralized to pH 7 using 0.1 M HCl to obtain a solid after dried at 60°C for 12 hours. While, the ZnO nanoparticle was synthesized by ZnSO$_4$.7H$_2$O precursor using NaOH alcoholic solution. Those precursor was also refluxed for 2 hours at 60°C until ZnO powder formed. Then the solids obtained were dried at a temperature of 60 - 70°C. Composites of TiO$_2$ NRs - ZnO were prepared at ratio of TiO$_2$ NRs : ZnO = 1 : 1, 1 : 2 and 2 : 1 (w/w) in ethanol, respectively. Then, it was stirred for 10 minutes at room temperature. TiO$_2$ NRs - ZnO composites were annealed at a temperature of 400°C. the TiO$_2$ NRs-ZnO was charactarized by XRD, TG/DTA, SEM and TEM.

2.2. Fabrication of DSSCs
DSSCs fabrication used FTO glass as a substrate. Nanorods composite of TiO$_2$ –ZnO at various compositions as about 5 grams was dissolved in 2 mL of ethanol to obtain a paste. The pasta was then
coated on FTO glass with slip coating method. Pt paste was also superimposed on another FTO glass to built counter electrode thin film. Both FTO based electrode was heated at a temperature of 400°C for 15 minutes. Composite materials photoanoda was soaked in a dye solution of N3 ruthenium complexes for 24 hours. Then, both electrodes were sealed and given a distance to immerse the electrolyte solution. Electrolyte was prepared from potassium iodide (KI) of 0.8 grams and iodine (I₂) of 0.127 grams dissolved in 10 mL acetonitrile. After the electrolyte was immersed, the DSSCs was characterized by an I–V Keithley 2602A measurement.

3. Result and Discussion

3.1. Synthesis of TiO₂ NRs –ZnO

Material TiO₂ nanorods (NRS) has been synthesized from TiO₂ nanoparticle that has been treated ball milling with agitation speed of 1000 rpm. Figure 1 shows the results of X-ray diffraction characterization of TiO₂ before and after ball milled treatment. Transformation of the X-ray diffraction pattern (Figure 1) shows the revolution in anatase phase TiO₂ into brookite phase TiO₂. This mechanical-chemical technique of TiO₂ preparation has also been carried out by Dutta et al. (2002) [10] and Rezaee et al. (2011) [11]. Dutta et al (2002) [10] have reported the phase transformation of TiO₂ crystals that can occur through mechanical-chemical ball milling treatment. Those processes were influenced by the rotational speed and agitation time.

![Figure 1. X-ray diffraction pattern of TiO₂ (a) before ball milled process (b) after ball milled process](image)

We used ball milled TiO₂ for preparation of TiO₂ NRs. Synthesis of TiO₂ NRs has been done by hydrothermal refluxing method at a temperature of 120°C using a strong base of NaOH at a concentration of 8, 10, and 12 M for 24 hours. TiO₂ after calcination at 400°C were characterized using XRD shown in Figure. 2.

![Figure 2. XRD pattern of TiO₂ NRs treated by NaOH solution at (a) 8M, (b) 10M, and (c) 12M](image)
The NaOH solution used to synthesize TiO$_2$ NRs influence the TiO$_2$ structure. XRD pattern of TiO$_2$ NRs (Figure 2) shows the most abundance of anatase TiO$_2$ phase. Rutile TiO$_2$ phase was increasing when the NaOH was added at about 12 M. These results are related to the synthesis results reported by Tsai and Teng (2006) [12] that the nano TiO$_2$ powder can be synthesized from a mixture of rutile and anatase phase at various concentration of NaOH. Representative transmission electron microscopy (TEM) images of treated TiO$_2$ under NaOH solution are provided in Figure 3. An overview of the nanorods at low magnification in Figure 4c shows that the sample almost exclusively contains nanorods with an average length of 80 nm and diameters of 50 nm. But in the lower NaOH concentrations (Figure 3a and Figure 3b) 1D nanorods weren’t appear.

![Figure 3](image_url)

**Figure 3.** TEM micrographs of the TiO$_2$ treated using NaOH solution of (a) 8 M, (b) 10 M, dan (c) 12 M

Structural transformation of the ball milled TiO$_2$ to 1D TiO$_2$ NRs was characterized from pore size distribution data’s (Figure 4). 1D TiO$_2$ NRs have an average surface area 79 m$^2$/g, but ball milled TiO$_2$ only have it about 7.56 m$^2$/g. It was concluded that structural transformation to 1D nanorods capable increase the surface area. Increasing of surface area characteristic will be increase dye adsorption onto TiO$_2$ surface. It will gain well perform for dye sensitized TiO$_2$ photoanode.

![Figure 4](image_url)

**Figure 4.** Pore size distribution of (a) ball milled anatase TiO$_2$ nanoparticle (b) TiO$_2$ NRs

TiO$_2$ NRs–ZnO composite was prepared from TiO$_2$ NRs and ZnO using molar ratio of TiO$_2$ NRs : ZnO = 1:1, 1:2, and 2:1, respectively. Thermogravimetry and Diferential Thermal Analysis (TG/DTA) (Figure. 5) show the crystallization process in the range temperature of 30 – 900°C. Mass decrease in the range of 60 – 150°C and 200 – 350°C can be ascribed to release H$_2$O content dan decomposition of organic volatile compound (Figure 5a). DTA/TGA curves showed significant differences of each sample (Figure 5). TiO$_2$ NRs (sample A) showed a shoulder exothermic peak at 250°C and a sharp and strong exothermic peak at 360°C, and at 700°C, they can be ascribed to dehydroxylation, anatase and rutile formation, respectively. It seems that those process not similar if TiO$_2$ NRs was composed by 3D ZnO (Figure. 5b). The exothermic peak at 350°C was shoulder and no exothermic peak at 700°C ascribed to rutile formation.

The samples were also characterized by X-ray powder diffraction (XRD) (Figure 6). Anatase phase TiO$_2$ as a single phase TiO$_2$ was obtained in the TiO$_2$–ZnO composite (1:1 of w/w ratio) upon heating the sample until 400°C. TiO$_2$ NRs have a crystal size 45.4nm, while crystal size of TiO$_2$ NRs–ZnO
composite only gain a crystal size of 41.5nm. Those conclude that there is constrain crystal growth in the composite.

![TG/DTA curves](image)

**Figure 5.** TG/DTA curves of (a) TiO$_2$ NRs (b) TiO$_2$ NR$_2$ - ZnO composite, recorded in air ambient.

![XRD patterns](image)

**Figure 6.** XRD patterns of (a) TiO$_2$ NRs –ZnO composite, (b) TiO$_2$ NRs, and (c) ZnO NPs

3.2. *Performa TiO$_2$ nanorods - ZnO composite for DSSCs photoanode*

Figure 7 shows the current ($I$) - voltage ($V$) curves of the dye sensitized solar cells based on the TiO$_2$ NRs-ZnO composite with N3 dye. The values of short-circuit current density ($I_{sc}$), open-circuit voltage ($V_{oc}$), $P_{max}$, and overall power conversion efficiency ($\eta$) are summarized in Table 1.

![Current - voltage curves](image)

**Figure 7.** Current - voltage curves of the dye sensitized solar cells (DSSCs) based on (A) TiO$_2$ NRs photoanode, and TiO$_2$ NRs-ZnO composite photoanode (B) molar ratio of TiO$_2$ NRs:ZnO composite = 1:1, (C) molar ratio of TiO$_2$ NRs:ZnO composite = 1:2, (D) molar ratio of TiO$_2$ NRs:ZnO composite = 2:1.
Table 1. Performance of the solar cells with the electrode made of TiO2 (A) TiO2 NRs photoanode, and TiO2 NRs-ZnO composite photoanode (B) molar ratio of TiO2 NRs:ZnO composite = 1:1, (C) molar ratio of TiO2 NRs:ZnO composite = 1:2, (D) molar ratio of TiO2 NRs:ZnO composite = 2:1.

| Sample | Parameter | I(sc) (µA) | V(oc) (mV) | I(max) (µA) | V(max) (mV) | P(max) (mW) | η (%) |
|--------|-----------|------------|------------|-------------|-------------|-------------|-------|
| A      |           | 0.785      | 0.092      | 3.57        | 200.01      | 0.715       | 0.36  |
| B      |           | 1.28       | 0.313      | 11.8        | 200.07      | 2.37        | 1.18  |
| C      |           | 1.15       | 0.045      | 6.66        | 175.84      | 1.17        | 0.59  |
| D      |           | 2.04       | 0.164      | 9.12        | 0.187,53    | 1.71        | 0.86  |

It should be noted that the enhanced power conversion efficiency in TiO2 NRs-ZnO composite solar cells could be attributed to (1) the suitable oriented TiO2 nanorods and 3D ZnO for the hybrid solar cell, exciton diffusion length, and their compositions (2) the oriented TiO2 nanorods and 3D ZnO reduced the electron recombination by provided a direct pathway for fast electron transport to the charge collecting electrode. In addition, the further improved the photoelectrochemical electrode (PCE) could be with the consideration of the ideal TiO2 nanorods grown perpendicular to the ITO substrates via manipulating the densities of TiO2 nanorods [13].

4. Conclusion

Material TiO2 NRs has been synthesized from TiO2 nanoparticle that has been treated ball milling, then has been further treated by hydrothermal refluxing method at a certain temperature and NaOH 12 M. Structural transformation to 1D nanorods capable increase surface area. Increasing of surface area may be increase dye adsorption onto TiO2 surface and TiO2 NRs have a crystal size of 45.4 nm, while that in TiO2 NRs–ZnO composite only gain a crystal size of 41.5nm. Difference TiO2 NRs-ZnO composite materials were investigated as a good photovoltaic materials. The enhanced power conversion efficiency in this TiO2 NRs–ZnO composite solar cells could be attributed to the suitable oriented TiO2 NRs–ZnO for the hybrid solar cell, exciton diffusion length, and the oriented TiO2 nanorods reduced the electron recombination by provided a direct pathway for fast electron transport to the charge collecting electrode.

References

[1] Zhao L, Xia M, Liu Y, Zheng B, Jiang Q and Lian J 2012 Mater. Trans. 53 463-468
[2] Uzunova-Buinova M, Dimitrove D, Radev D, Bojinova A and Todoravsky D 2008 Mater. Chem. Phys. 110 291
[3] Lorret O, Francova D, Waldner G and Stelzer N 2009 Appl. Cat. B. 91 39
[4] Donkova B, Dimitrov D, Kostadinov M, Mitkova E and Mehndjiev D 2010 Mater. Chem. Phys. 123 563
[5] Jayasankar M, Hazem S, Salah H, Matthias D and Es-Souni M Catal. Sci. Technol. 2 379-385
[6] Greene L E, Law M, Yuhas B D and Yang P 2007 J. Phys. Chem. C. 111 50
[7] Wang M, Huang C, Cao Y, Yu Q, Deng Z, Liu Y, Huang Z, Huang J, Huang Q, Guo W and Lian J 2009 Appl. Phys. 42 155
[8] Law M, Green L, Johnson J, Saykally R and Yang P 2005 Nature. Mater 4 455-459
[9] Wahyuningsih S, FAdilah G, Hidayat R and Ramelah AH 2016 Procedia Chemistrty 19 632-637
[10] Dutta H, Sahu P, Pardhan S K and De M 2002 Mater. Chem. Phys. 77 153-164
[11] Rezaee M, Khoie S M M and Liu K H 2011 Cryst. Eng. Comm. 13 5055-5061
[12] Tsai C C and Teng H 2006 Chem. Mater 18 367-373
[13] Yodyingyong S, Zhou X, Zhang Q, Triampo D, Xi J, Park K, Limketkai B and Cao G 2010 J. Phys. Chem. C. 114 21851–21855