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Energy Procedia 56 (2014) 378 – 385

Energy

**Procedia**

11th Eco-Energy and Materials Science and Engineering (11th EMSES)

## Effect of SiO<sub>2</sub> and TiO<sub>2</sub> Nanoparticles on the Performance of Dye-Sensitized Solar Cells using PVDF-HFP/PVA Gel Electrolytes

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### Abstract

In this work, we aimed to study the effect of nanoparticles on the efficiency of dye-sensitized solar cells (DSSC) using polymer gel electrolytes (PGE) of PVDF-HFP/PVA blends. The concentration of polymer blend was fixed at 10 wt% with ratios of 8:2. The TiO<sub>2</sub> and SiO<sub>2</sub> nanoparticles was varied at 0.25 - 2.0 wt%. It was found that the efficiencies ( $\eta$ ) of the cells using liquid electrolyte and PGE were 3.49±0.05% and 3.26±0.09%, respectively. While the efficiencies of DSSCs using nanocomposite electrolytes was considerably decreased. The best efficiency of DSSCs using PGE containing 0.25 wt% TiO<sub>2</sub> and 0.5 wt% SiO<sub>2</sub> were found to be 2.71±0.10% and 3.03±0.09%, respectively. This may be due to the higher viscosity of the nanocomposite gels and phase separations between nanoparticles and polymer matrices. Furthermore, the electrical resistances of electrolytes were investigated by Electrochemical Impedance Spectroscopy (EIS). The EIS showed that DSSC using ionic liquid electrolyte (ILE) shows the lowest  $R_{ct2}$  and  $R_{diff}$ , and the interfacial resistances. While the DSSC containing nanoparticles exhibits the higher  $R_{ct2}$  and  $R_{diff}$ , corresponding to their DSSC efficiency. This result corresponding with their DSSCs efficiencies. The functional groups of polymer gel electrolytes were investigated by Fourier transform infrared spectroscopy (FT-IR) and the thermal properties of polymer gel electrolytes were analysis by differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) applications in dye-sensitized solar cells (DSSCs).

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Peer-review under responsibility of COE of Sustainable Energy System, Rajamangala University of Technology Thanyaburi (RMUTT)

*Keywords:* Nanoparticle, Nanocomposite, Polymer gel electrolyte, Dye-sensitized solar cells

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## 1. INTRODUCTION

Over the past decades, dye-sensitized solar cells (DSSCs) have attracted wide-spread scientific and technological interests due to its low cost and high energy conversion efficiency. DSSC prepared with liquid electrolyte has reached the efficiency of as high as 15% [1]. However, due to the usage of the liquid electrolyte, it has the disadvantages of easy evaporation and leakage after long-term lab tests which affect to reduce the long stability of the DSSC [2]. Thus, considerable efforts have been made to replace the liquid electrolyte with a solid state electrolyte or quasi-solid-state electrolyte [3], [4]. As a solid-state electrolyte, polymer electrolyte is usually formed by dissolving alkali metal salts into polymer matrix. However, the performance of a DSSC with polymer electrolyte is hampered by the low ionic diffusion in the polymer matrix [5], [6]. Therefore, quasi-solid-state electrolyte, such as polymer gel electrolyte, is formed by liquid electrolyte trapped in the polymer networks. It's has been suggested as the best choice for use in DSSCs because high stability and superior ionic diffusion [7]. The polymer gel electrolyte combines the advantages of solid and liquid electrolytes, such as high stability and superior ionic diffusion, and can also facilitate the penetration of the electrolyte into the mesoporous TiO<sub>2</sub> film. It has been expected to be a promising candidate for the ideal electrolyte [8], [9]. For instance, Haijun used alkaline polyvinyl alcohol and potassium iodide (PVA–KOH–KI) as gel electrolyte for quasi-solid-state supercapacitor. The specific capacitances of the supercapacitor is 236.90 F.g<sup>-1</sup>, increasing by 74.28% compared to the PVA–KOH system at the same current density [10]. Zhipeng used Poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) gel electrolyte for DSSC. The photoelectric conversion efficiency was 5.72% [11]. Other investigations of polymer gel electrolyte were focused on the nanostructure fillings into the electrolyte, such as SiO<sub>2</sub>, TiO<sub>2</sub> nanoparticles, carbon nanotubes, and so on [12] - [15]. For example, Wang et al. used silica nanoparticles as gelator to solidify ionic liquid-based electrolytes [16] and they concluded that addition of nanosilica has no adverse effect on the conversion efficiency, keeping a good consistency with diffusion coefficient test.

In this work, we have expected that the blending of two polymer matrices (PVDF-HFP and PVA) could reduce the crystalline phase of polymer gel and could enhance the capacity of liquid electrolyte which would result in the higher efficiency and the long-term stability of DSSC. Moreover, adding nanoparticles into polyblend gels could also improve the efficiency of DSSC. Thus, in this paper, we prepared the polymer gel electrolytes of PVDF-HFP/PVA blends at concentration of 10 wt% with a fixed ratio of PVDF-HFP/PVA at 8:2. Also, the influence of addition of TiO<sub>2</sub> and SiO<sub>2</sub> nanoparticles at concentration of 0.25 - 2.0 wt% to form nanocomposite gel electrolytes was studied and discussed.

## 2. EXPERIMENTAL

### 2.1 Materials and electrolyte preparation

Polyvinyl alcohol (PVA, Mw. 88000) Acros organics. Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP, Mw. 10000) Aldrich. IonLic DMPII was purchased from Solaronix. I<sub>2</sub>, 4-tert-butylpyridine (TBP) and N-Butyl-1H-benzimidazole (NBB) was provided by Aldrich. Guanidine thiocyanate (GuNCS) and 1-Methyl-2-pyrrolidone (NMP) was supplied by Acros organic. N719 dye was purchased from Solaronix (Switzerland). FTO conducting glasses (16 Ω sq<sup>-1</sup>) and H<sub>2</sub>PtCl<sub>6</sub> was supplied by Chameleon Reagent.

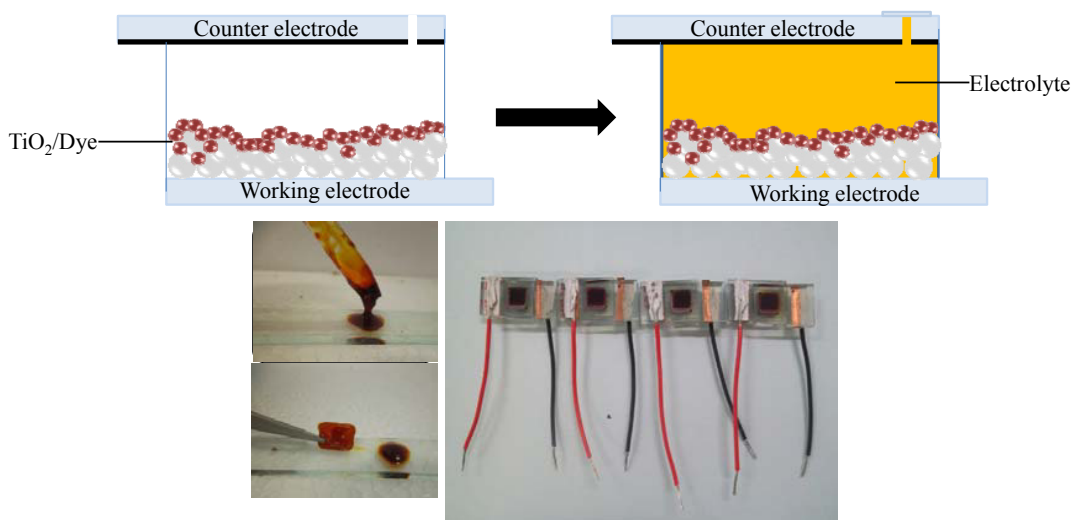
Firstly, the liquid electrolyte (LE) was prepared by mixing the amount of 1.0 M DMPII, 0.15 M I<sub>2</sub>, 0.5 M TBP and 0.1 M GuNCS dissolved in NMP. The mixture was stirred at room temperature for 2 h. Next, the ionic liquid electrolyte (ILE) was composed of 0.6 M DMPII and 0.45 M NBB dissolved in NMP. It was homogeneously stirred at room temperature for 7 h. After, the polymer gel electrolyte (PGEs) was prepared following the compositions listed in Table 1. All components in each electrolyte were homogeneously with ILE and stirred at room temperature for 7 h. Finally, to prepare the nanocomposite gel electrolyte, 10wt%PVDF-HFP/PEO (8:2) was chosen as polymer matrix. TiO<sub>2</sub> and SiO<sub>2</sub> nanoparticles were then added at 0.25, 0.5, 1.0 and 2.0 wt% into polymer matrix. After that, 2 ml ILE was filled and homogeneously stirred at room temperature for 7 h.

**Table 1.** Amounts of polymers used to prepare 10wt% gel electrolyte in 2mL ILE solvent.

Sample name	Weight (g)			
	PVDF-HFP	PVA	TiO <sub>2</sub>	SiO <sub>2</sub>
PVA	-	0.2	-	-
PVDF-HFP	0.2	-	-	-
PVDF-HFP: PVA (8:2)	0.16	0.04	-	-
add TiO <sub>2</sub> 0.25wt%	0.16	0.04	0.005	-
add TiO <sub>2</sub> 0.5wt%	0.16	0.04	0.01	-
add TiO <sub>2</sub> 1.0wt%	0.16	0.04	0.02	-
add TiO <sub>2</sub> 2.0wt%	0.16	0.04	0.04	-
add SiO <sub>2</sub> 0.25wt%	0.16	0.04	-	0.005
add SiO <sub>2</sub> 0.5wt%	0.16	0.04	-	0.01
add SiO <sub>2</sub> 1.0wt%	0.16	0.04	-	0.02
add SiO <sub>2</sub> 2.0wt%	0.16	0.04	-	0.04

## 2.2 DSSC Fabrication

The TiO<sub>2</sub> film electrode was prepared by screen printing the TiO<sub>2</sub> paste on the FTO glass followed by sintering at 500 °C for 30 min and cooling to 80 °C. Then, the TiO<sub>2</sub> film electrode was sensitized by immersion into a 0.3 mM solution of N719 dye in anhydrous ethanol at room temperature for 24 h. The Pt counter electrode was prepared by dropped 36μl of 7mM H<sub>2</sub>PtCl<sub>6</sub> in acetylacetone on FTO glass and also preheated to 385 °C for 30 min allowed to cool down to 110 °C. A single hole (ca. 0.5 mm diameter) was drilled in the Pt electrode to allowed for electrolyte filling. Finally, the DSSCs were fabricated by the assembly of the working electrode and counter electrode with thermoplastic film (Surlyn 30μm) and the internal spacer between the electrodes was filled with the prepared electrolytes as presented in Figure 1.

**Figure 1.** Cell assembly of the DSSCs.

## 2.3 Electrochemical Characterization

The current-voltage (I-V) measurements were carried out with an active area of 0.16 cm<sup>2</sup> by a Kiethley 2400 source meter, Kiethley 617 programable electrometer measured unit under AM 1.5 global simulated sunlight (100 mW/cm<sup>2</sup>) which was produce by a 500 W Oriel Solar Simulator (New Port BB-L, USA). The incident light

intensity was calibrated to 1 sun by a photovoltaic reference cell system (91150, Oriel instruments, USA). Electrochemical impedance spectroscopy (EIS) was measured in 1 sun illumination in an open-circuit at 0.6 - 0.7 V and with a frequency range from 105 to 101 Hz at an amplitude of 10 mV. The obtained spectra were fitted by ZIVE ZMAN 2.2 software. Moreover, the gel electrolytes were also characterized by FT-IR, DSC and TGA.

### 3. RESULTS AND DISCUSSION

#### 3.1. Properties of polymer gel electrolytes

FT-IR spectra of polymer electrolytes are shown in Figure 2. They exhibit absorption peaks at  $\sim 3400\text{ cm}^{-1}$  corresponding to the O-H stretching of PVA. C-H stretching peak of NBB is found at  $\sim 2800\text{ cm}^{-1}$ . The absorption peaks at  $\sim 1850\text{ cm}^{-1}$  is the result of C=O of 1-methyl-2 pyrolidone used as a solvent. PVDF-HFP shows the absorption peak at  $\sim 1180\text{ cm}^{-1}$  corresponding to the bending vibration of C-F bond. These evidences have confirmed that the polymer gel electrolytes were successfully prepared.

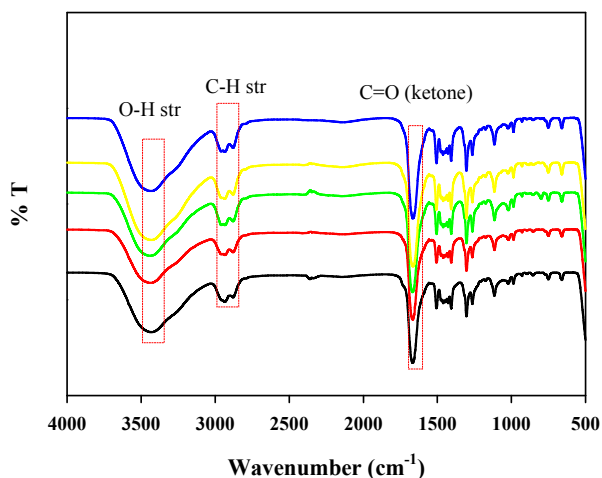


Figure 2. FT-IR spectra of polymer gel electrolytes.

From DSC measurements, it is found that the melting temperatures ( $T_m$ ) of PVDF-HFP/PVA blends were in the range of 179 - 195 °C which were lower than  $T_m$  of both neat polymers of PVDF-HFP (207 °C) and PVA (196 °C). This could be due to the reduction of crystallinity of PVDF-HFP/PVA gel. While,  $T_m$  of nanocomposite gel electrolytes was further slightly dropped as shown in Figure 3. From TGA data, see Figure 4, weight loss of polymer electrolytes was started at about 100 °C corresponding to moisture loss and the highest weight loss was found in the range 150–320 °C, corresponding to the polymers decomposition. However, the thermal stability of blend polymers was found to be higher than neat pair polymers and considerably decreased with addition of low amount of nanoparticles (<1 wt%).

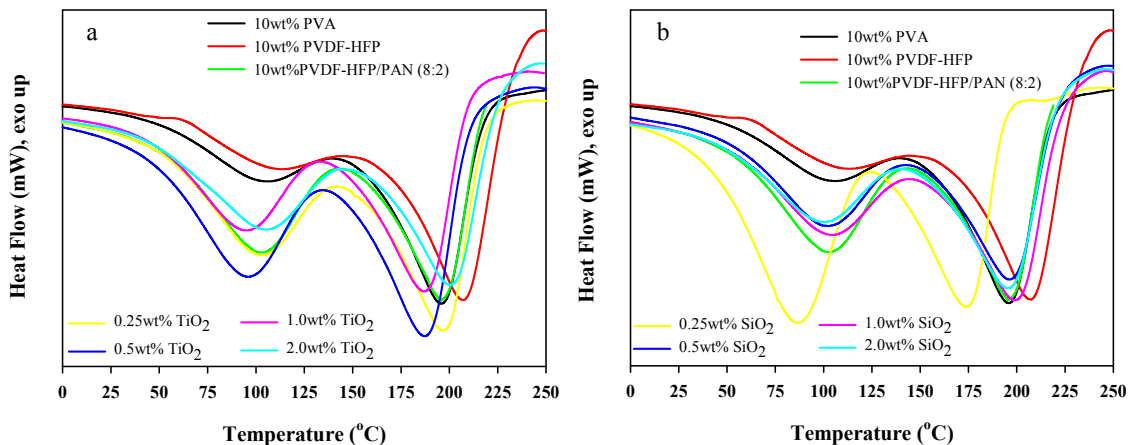


Figure 3. DSC thermograms of nanocomposite gel polymer electrolytes containing (a) TiO<sub>2</sub> and (b) SiO<sub>2</sub> nanoparticles.

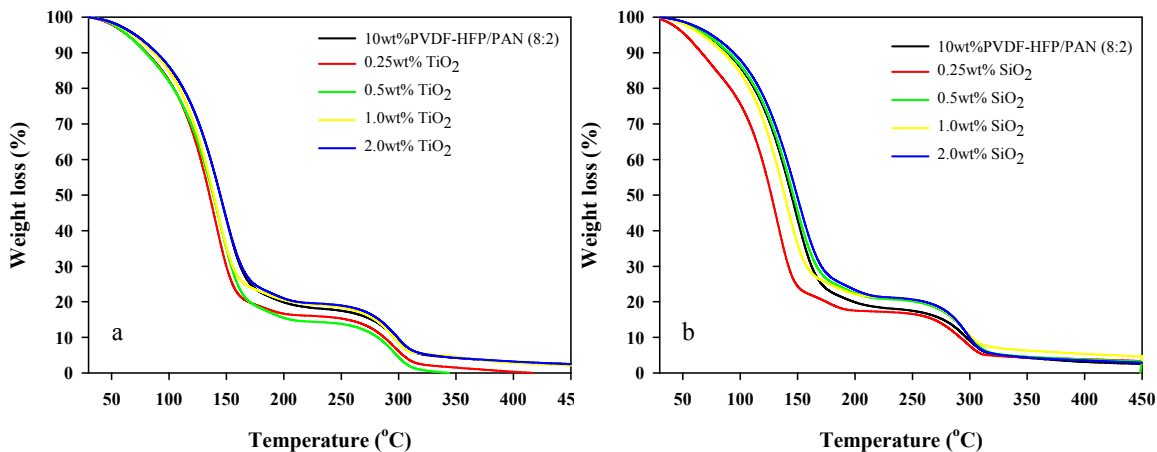


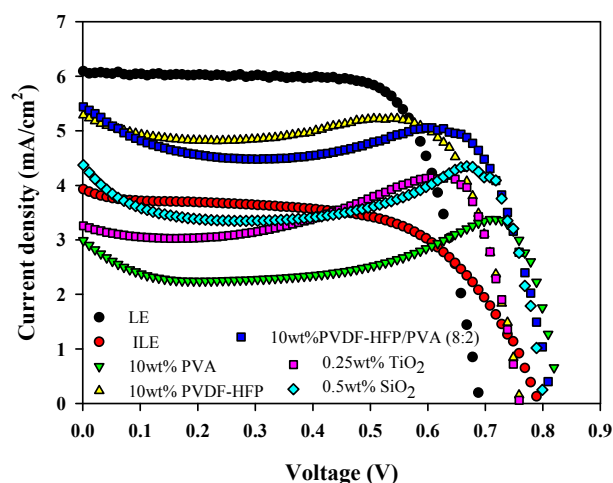
Figure 4. TGA thermograms of nanocomposite gel polymer electrolytes containing (a) TiO<sub>2</sub> and (b) SiO<sub>2</sub> nanoparticles.

3.2. Photovoltaic performance

Figure 5 shows the current-voltage characteristics of DSSCs employing various polymer gel electrolytes including nanocomposite gel electrolytes. All electrical properties of DSSCs are listed in Table 2. It is seen that the cell employing LE shows the efficiency of 3.02%. While, the efficiency of cell fabricated using ILE is 3.49% which is slightly increase due to the ILE was higher conductivity. Moreover, the efficiency of DSSCs fabricated using 10wt% PVDF-HFP/PVA (8:2wt%) gel electrolyte was 3.26% which the higher than that of LE. For the nanocomposite gel, it was found that the efficiency of DSSC tended to decrease with increasing contents of TiO<sub>2</sub> and SiO<sub>2</sub> nanoparticles. This may be due to the higher viscosity of polymer gels and harder transportation of ionic species after addition of nanoparticles into polymer gel electrolyte. With addition of 0.25 wt% TiO<sub>2</sub> and 0.5 wt% SiO<sub>2</sub> nanoparticles into such blend electrolytes, the efficiencies of DSSCs employed such nanocomposite gels are found to decrease to be 2.71% and 3.03%, respectively.

• **Table 2.** Electrical properties of DSSCs using different electrolytes.

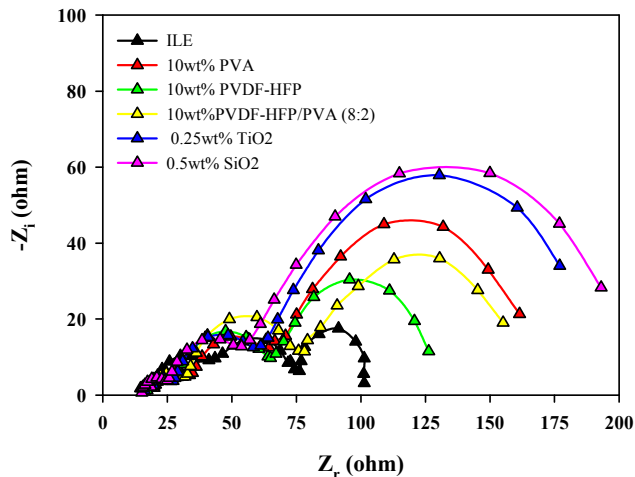
Sample	$\eta$ (%)	$I_{sc}$ (mA)	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	$ff$
ILE	3.49	1.12	6.98	0.79	0.63
PVA	2.45	0.48	3.17	0.83	0.99
PVDF-HFP	3.03	0.85	5.29	0.76	0.75
8:2	3.26	0.87	5.45	0.81	0.74
0.25wt% TiO <sub>2</sub>	2.71	0.52	2.61	0.76	1.09
0.5wt% TiO <sub>2</sub>	2.18	0.33	2.06	0.80	1.34
1.0wt% TiO <sub>2</sub>	2.57	0.58	3.57	0.85	0.85
2.0wt% TiO <sub>2</sub>	2.29	0.43	2.67	0.83	1.04
0.25wt% SiO <sub>2</sub>	2.54	0.68	4.30	0.82	0.73
0.5wt% SiO <sub>2</sub>	3.03	0.70	4.39	0.80	0.86
1.0wt% SiO <sub>2</sub>	2.95	0.65	4.07	0.82	0.88
2.0wt% SiO <sub>2</sub>	1.58	0.35	2.21	0.79	0.91



**Figure 5.** I-V curves of DSSCs using different electrolytes..

### 3.3. Electrochemical properties

The EIS under illumination exhibits three semicircles, as shown in Figure 6. The high-frequency range represents the charge transfer at the Pt counter electrode ( $R_{ct,pt}$ ), the middle-frequency range is related to the charge transport ( $R_i$ )/recombination ( $R_{ct}$ ) at the TiO<sub>2</sub>/electrolyte interface, and the low-frequency range is assigned to the ionic diffusion in the electrolyte. The EIS can be fitted with an equivalent circuit on the basis of the transmission line model [7], [17], [18]. Lower resistance causes higher electron transfer, i.e. high  $\eta$ , in DSSC. The ohmic serial resistance ( $R_s$ ) (intersection of high-frequency circle and x-axis) is mainly associated with the sheet resistance of the FTO substrate. The DSSC using ILE shows the smallest semicircles representing  $R_{ct2}$  and  $R_{diff}$ , and the interfacial resistances were general lower for DSSC using ILE as electrolyte. While the DSSC containing nanoparticles exhibits the higher  $R_{ct2}$  and  $R_{diff}$ , corresponding to their DSSC efficiency.



**Figure 6.** Nyquist plots of the EIS spectra measured for DSSCs using different electrolytes under AM 1.5 illumination at open circuit.

#### 4 CONCLUSION

We have successfully prepared the nanocomposite gel electrolytes employed in DSSCs. It is found that  $T_m$  of gel electrolytes was slightly dropped with addition of  $\text{TiO}_2$  and  $\text{SiO}_2$  nanoparticles. While the thermal stability of blend polymers was also slightly improved with addition of nanoparticles higher than 1wt%. The efficiency of DSSCs employed 10wt% PVDF-HFP/PEO (8:2wt%) gel showed the efficiency of 3.26% which lower than that of ILE. Moreover, the efficiencies of DSSCs using  $\text{TiO}_2$  and  $\text{SiO}_2$  nanocomposite gels was decreased to be 2.71% and 3.03%, respectively. This could be due to the more retarder of ionic species in higher viscosity of polymer gels after addition of nanoparticles into polymer gel electrolyte and the phase separation between nanoparticle and polymer matrix.

#### Acknowledgment

This work was financial supported by National Nanotechnology Centre (NANOTEC) of Thailand (P-10-11346). National Research Council of Thailand (NRCT) and Centre of Excellence for Innovation in Chemistry (PERCH-CIC), Commission of Higher Education, Ministry of Education and Ubon Ratchathani University are also acknowledged for some partial supports.

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