

## The effect of nano-Zinc oxide on the self-cleaning properties of cotton fabrics for textile application

Praripatsaya Panutumrong<sup>1</sup>), Tanapak Metanawin<sup>2</sup>), Siripan Metanawin<sup>3</sup>),  
and Narongchai O-Charoen<sup>1</sup>)

*1)Department of Materials and Metallurgical Engineering, Faculty of Engineering,  
Rajamangala University of Technology Thanyaburi, 12110, Thailand*

*2 Department of Materials and Production Technology Engineering, Faculty of Engineering, King  
Mongkut's University of Technology North Bangkok, Bangkok, 10800, Thailand  
tmw@kmutnb.ac.th*

*3Department of Textile Engineering, Faculty of Engineering, Rajamangala University of  
Technology Thanyaburi, PathumThani, 12110, Thailand*

### Abstract

*The self-cleaning properties of nano-zinc oxide on cotton fabrics have been investigated. The cotton fabric has been prepared by pad-dry method. The nano-zinc oxide was encapsulated in the polystyrene particle by mini-emulsion process prior used. The loading amount of zinc oxide particles into the mini-emulsion were various from 1% wt to 40%wt. The particles sizes of ZnO-encapsulated polystyrene mini-emulsion were determined using dynamic light scattering. It was showed that the particle size of the mini-emulsion was in the range of 124-205 nm. The topography and morphology of ZnO-encapsulated polystyrene which coated on cotton fabrics was observed using scanning electron microscopy. The crystal structure of ZnO-coated on cotton fabrics was explored by X-ray diffraction spectroscopy. The photocatalytic activities of zinc oxide were present through the self-cleaning properties. The presents of the zinc oxide on cotton fabrics significantly showed the improving of the self-cleaning properties under UV radiation.*

**Keywords:** nano-Zinc oxide, self-cleaning properties, textile application

## 1. Introduction

Hybrid polymer materials are increasingly attracted scientific and technologically interested by virtue of their unique structures and significant advantages over many existing materials science. Particularly, hybrid polymer materials at nanometer scale, the design and synthesis of nanoscale objects require a good deal of control over interfaces in order to build up and organize the nanostructures.[1] Furthermore, the combination

of multitechnologies such as nanotechnology, biotechnology and polymer technology can offer multi-functional, versatile, stable, resistant and non-toxic products which results in outstanding properties in the wide range of high value industrials, foods and medicals applications such as anti-microbial, anti-oxidant, anti-bacterial and self-cleaning properties.[1, 2]

Recently, much interest in new materials that can demonstrate photocatalytic behavior under the proper illumination conditions for applications in textile industrials.[3] For this reason, metal oxide such as nanotitanium dioxide (nano-TiO<sub>2</sub>) and nano zinc oxide (nano-ZnO) have attracted great attention as a semiconductor photocatalyst due to its widely used materials, low cost, good stability, and ease of preparation.[4] One of an interesting application of metal oxide is self-cleaning ability.[1, 5, 6]

Nano zinc oxide (nano-ZnO) exhibits low dielectric constant, large electromechanical coupling coefficient, high luminous transmittance, high catalysis activity, intensive ultra-violet and infrared absorption, and etc. Therefore, nano-ZnO can potentially be applied to self-cleaning ability and UV- shielding materials.[7] The features of large volume to area ratio. However, ZnO nanoparticles are prone to aggregate due to the large surface area and high surface energy. In order to improve the dispersion, it is necessary to modify the surface of ZnO nanoparticles.[8-10]

The development of designing and modifying of nano-ZnO particles for high protection against UV radiation (both UVA and UVB falls into the regions of the solar spectra of 315-400nm and 280-315nm, respectively) is an objective sought not only by the solar cell industry but also by the textile industrial in the framework of new products classified as technical textiles. Several studies have reported that ZnO coating of cotton textiles could be performed using different pretreatments and techniques such as RF-plasma, MW-plasma, UV-irradiation, dip-pad-dry-cure and dip-coating to improve the adhesion of the coating and the life cycle of washings.[11]

In this investigation, cotton fabrics were coated with the hybrid polymeric material of ZnO through mini-emulsion polymerization using dip-pad-dry process. This study was set out to investigate the synergistic role of the encapsulation of nano-ZnO on cotton fabrics and to elucidate the impacts of this hybrid polymeric material on self-cleaning ability.

## **2. EXPERIMENT**

### **2.1 Materials**

The styrene monomer (Sty), hexadecane (HD), sodium dodecylsulfate (SDS) and potassium persulfate (KPS) were purchased from Aldrich at the highness purity. Zinc oxide is CAS#1314-13-2. All samples were used as received. All other chemicals were used as supplied by the companies.

### **2.2 Preparation of encapsulated-ZnO/polystyrene miniemulsion polymerisation**

The mixture of Zinc dioxide (1-40%wt), styrene monomer (2.5g) and hexadecane (0.104g) was added into the mixture of distilled water (10cm<sup>3</sup>) and sodium dodecylsulfate (0.030g). The mixture was stirred under nitrogen gas for 15 minutes. The mixture was sonicated for 15 minutes. After that the potassium persulfate (0.042g) was added into the reaction and the temperature was raised up to 70°C for 0-48 hours.

### **2.3 Hybrid miniemulsion coated on cotton fabrics**

The cottons were cut into the dimension of 5x5cm<sup>2</sup>. The cottons were treated in the oven at 80°C for 10 minutes to remove the surface impurities. The coating process is called Dip-Pad-Dry method by immersed

the cotton in the miniemulsion for 3 minutes with stirred in ambient temperature for 3 minutes. The coated cottons fabrics were dried in an oven at 80°C for 3 minutes.

## **2.4 Characterizations**

### **2.4.1 Dynamic light scattering (DLS)**

Dynamic light scattering was performed on DelsaTMNano C particle analyzer from Beckman Counter, USA. DelsaTMNano C particle analyzer equipped with 30mW 658nm Laser diode operated at the angle 165°

### **2.4.2 Scanning electron microscope (SEM)**

The SEM images were recorded by using Jeol JSM-6510 or Jeol JSM-5410LV, Japan. The samples were coated with gold.

### **2.4.3 X-ray diffraction (XRD)**

The XRD patterns were recorded on PANalytical X Pert Pro MPD model pw3040/60 with Cu-K $\alpha$  X-ray source (the Netherlands). The diffractometer was scanned from  $2\theta=5^{\circ}$ - $80^{\circ}$  with a scanning rate of 0.02cm<sup>-1</sup>.

### **2.4.4 Fourier transform infrared (FTIR)**

The FTIR measurements were conducted using PerkinElmer model Frontier at the resolution 4cm<sup>-1</sup> in wave number region 4000-650cm<sup>-1</sup>.

### **2.4.5 Self-cleaning Test**

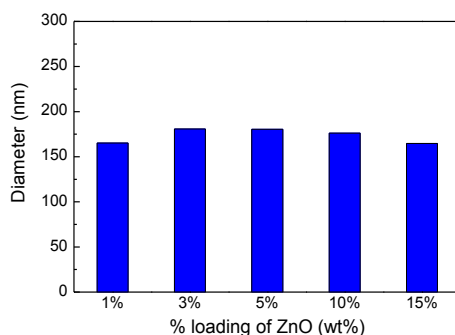
In order to investigate the self-cleaning characteristics of encapsulated-ZnO/polystyrene mini-emulsion, colorant stains were created on the samples. Coffee stains were used as colorant organic stains. Aqueous solution of coffee stains was prepared by mixing 5.5 g coffee in 50 cm<sup>3</sup> of deionized water. Stained samples were irradiated using a UV-A lamp (Philips, the Netherlands), with 365 nm wave length radiation and light intensity of 11.6 mW/cm<sup>2</sup>. The self-cleaning property was evaluated based on the colour removal of coffee stains on fabrics.

## **3. RESULTS AND DISCUSSIONS**

### **3.1 Characterization of styrene miniemulsion**

#### **3.1.1 Dynamic light scattering (DLS)**

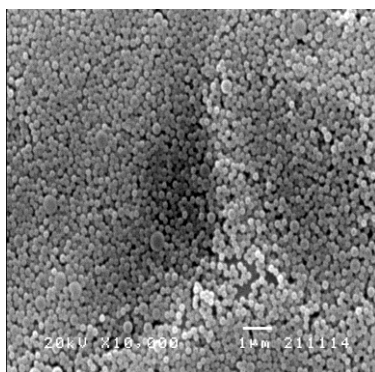
Zinc oxide was encapsulated in polystyrene nanoparticles via miniemulsion polymerization with 4 hours polymerization time. The loading amounts of ZnO from 1wt% to 40%wt were explored. It was found that the polystyrene miniemulsion were able to encapsulate ZnO maximum at 15%wt. This is because the miniemulsion broke down if the loading amount of ZnO was more than 20%wt. Fig. 1 demonstrated the hydrodynamic diameters of the encapsulated-ZnO/polystyrene miniemulsion. It was found that the diameter of the miniemulsion particles was slightly increased with raising the polymerization time. The hydrodynamic diameter of hybrid PS miniemulsion was in range 165nm-180nm for 4 hours of polymerization time



**Fig.1. Hydrodynamic diameter of encapsulated-ZnO/polystyrene miniemulsion with loading 1-15%wt ZnO.**

### 3.1.2 Scanning electron microscope

The scanning electron microscope was employed to observe the microstructure of the encapsulated-ZnO/polystyrene miniemulsion. The encapsulate-ZnO/polystyrene with 10%wt loading was prepared by a dropped of the miniemulsion on SEM stub and dried in the oven overnight. Fig.2 presents the SEM image of the well-defined structure of the miniemulsion.

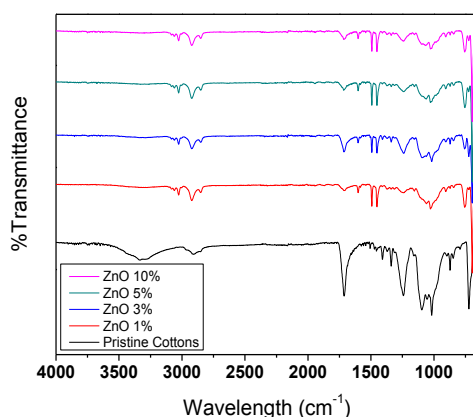


**Fig. 2. SEM image of encapsulated-ZnO/polystyrene miniemulsion with 10% loading of ZnO.**

## 3.2 Characterization of cottons coated with encapsulated-ZnO/PS miniemulsion

### 3.2.1 Fourier Transform Infrared Spectrophotometer (FTIR)

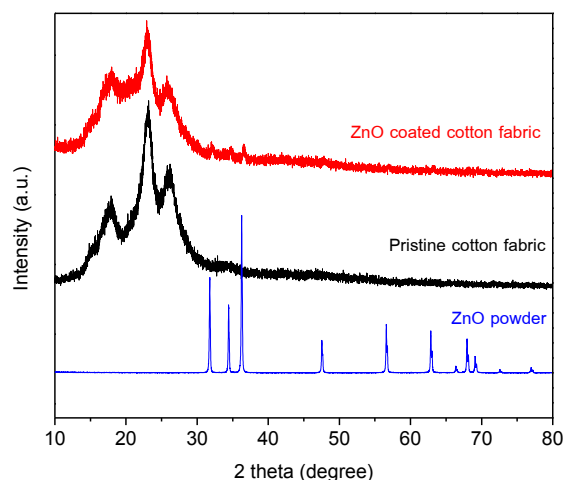
The functional-group of the pristine cottons fabrics and the encapsulated-ZnO/PS miniemulsion coated on cottons fabrics were investigated using the Fourier Transform Infrared, as seen in Fig.3. The absorption peaks at  $696\text{cm}^{-1}$  was attributed benzene ring folding. The peaks at  $754.5\text{cm}^{-1}$  was attributed to C-H bending of benzene ring. The C-C stretching of the benzene ring absorptions vibrated at  $1492\text{cm}^{-1}$  and  $1601\text{cm}^{-1}$ , respectively. All the absorption bands of the benzene ring and ZnO in this hybrid particles remained unchanged but the C=O bond vibration at  $1712.3\text{cm}^{-1}$  deteriorated to the shoulder part in hybrid particles. The absorption band of COO-Zn at  $1452\text{cm}^{-1}$  demonstrates interactions between carboxyl groups and ZnO. These FTIR spectra confirmed that ZnO was integrated into the miniemulsion



**Fig.3. Shows the FTIR spectra of the pristine cottons fabric and cottons fabrics coated with loading 1-10%wt ZnO/PS miniemulsion.**

### 3.2.2 X-ray diffraction (XRD)

To compare the crystal structure of pristine ZnO powder and the encapsulated-ZnO/PS miniemulsion on the cottons fabric, XRD technique were employed. As seen in Fig.4, peaks of pristine ZnO are presented at  $2\theta = 31.7^\circ, 34.4^\circ, 36.2^\circ, 47.5^\circ, 56.6^\circ$  and  $62.8^\circ$  representing ZnO.[7] As presented in Fig.4, the XRD spectrum of the encapsulated-ZnO was found very tiny peak at  $2\theta = 31.7^\circ, 34.4^\circ$  and  $36.2^\circ$ . This is because of the ZnO were encapsulated in PS miniemulsion. Thus, these XRD spectra confirmed that ZnO were encapsulated in PS miniemulsion and found on the cottons fabrics.

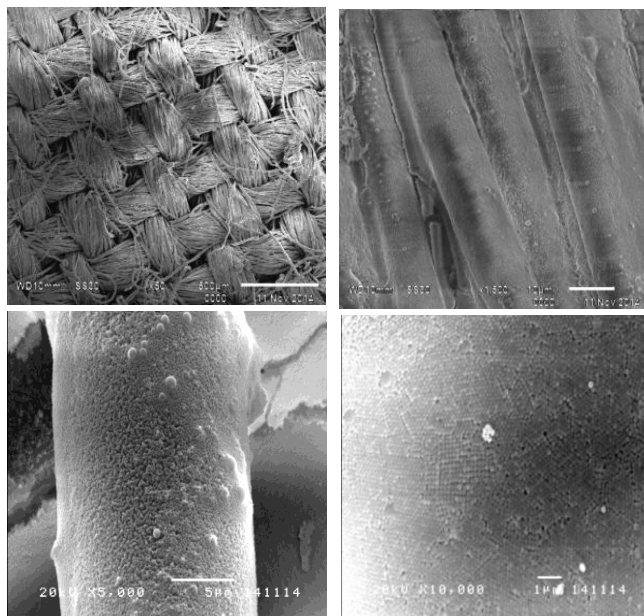


**Fig. 4. XRD spectra of pristine ZnO and cotton coated with encapsulated-ZnO/PS miniemulsion.**

### 3.2.3 Scanning electron microscope

The microstructure of the ZnO hybrid nano polymer coated on cottons fabrics were observed using SEM (Fig.5). The SEM image indicates that the particles presented well-define structure and having spherical shape. The hybrid miniemulsion had a good adhesion on the fibers of cottons fabrics. The ZnO hybrid

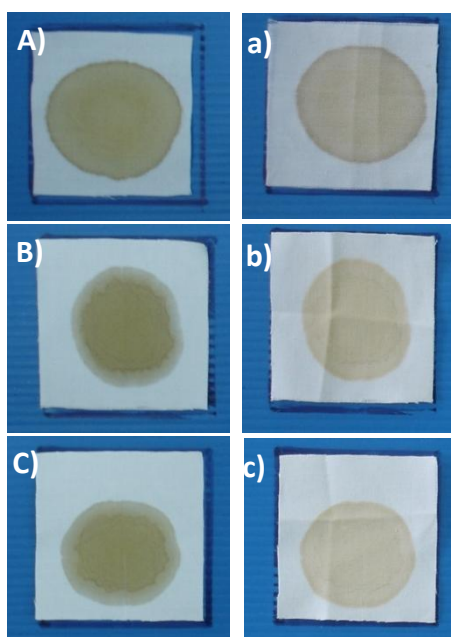
nanopolymer prepared using miniemulsion polymerization which was coated on cotton fabric have the small size and high surface area. The small crystalline size attained is beneficial for the photocatalytic induced discoloring of the coffee stain.

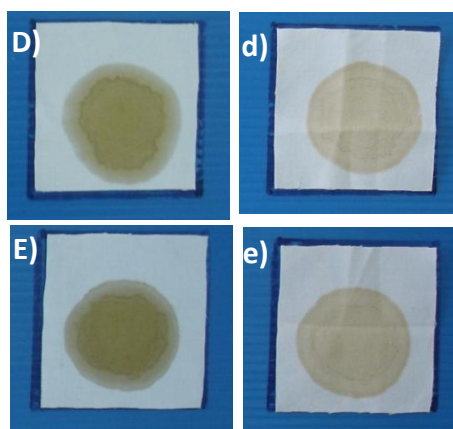


**Fig.5. SEM images of loading 10%wt of ZnO a) 50x, b) 1,500x, c) 5,000x and d) 10,000x**

### 3.2.4 Self-cleaning test

The self-cleaning properties of the encapsulated-ZnO/PS miniemulsion stained with coffee solution were examined under  $11.6 \text{ mW/cm}^2$  UV radiation. The result shown that the coffee stained on the cotton fabrics were decreased when increased loading amount of ZnO from 1% wt to 10% wt. As demonstrated in Fig.6, the coffee stain on cotton coated with hybrid ZnO miniemulsion containing 10%wt of ZnO were relatively removed under  $11.6 \text{ mW/cm}^2$  UV radiation for 84 hours.





**Fig.6. The photography of the self-cleaning test under 11.6 mW/cm<sup>2</sup>UV-A radiation for 84 hours. (Before test: A-E, after test: a-e) when A-a) Pristine cottons fabric, B-b)Coated with 1%wt ZnO, C-c)Coated with 3%wt ZnO, D-d) Coated with 5%wt ZnO, and E-e) Coated with 10%wt ZnO.**

#### 4. CONCLUSION

In this work, the development of designing and modifying of nano-ZnO particles were investigated by using miniemulsion polymerization. The self-cleaning properties are also concern. Then the hybrid polymers were coated on the cotton fabrics by using Dip-Pad-Dry method. The variation of the ZnO content from 1%wt up to 40%wt in the encapsulated of hybrid polymer was study. It was notice that the synthesis was successful. However, the maximum loading of ZnO in the polystyrene miniemulsion were 15%wt due to the break out of the miniemulsion at the loading amount of ZnO more than 20%wt. The hydrodynamic diameters of the encapsulated-ZnO/polystyrene miniemulsion were determined using DLS. It was found that the diameter of the miniemulsion particles was slightly increased with raising the polymerization time and with loading amount of ZnO from 1-15%wt. The hydrodynamic diameter of hybrid nano-ZnO was in range 165nm-180nm for 4 hours of polymerization time. The photocatalytic studied of the coated fabric with hybrid polymer significantly show the improving in self-cleaning properties with increase in the amount of hybrid polymer on the cotton. The FTIR and XRD confirm the present of the hybrid polymer on the cotton fabrics. SEM micrographs show the morphology of the hybrid nano-ZnO at different ratios on the cotton fabrics.

#### ACKNOWLEDGEMENT

I would like to thank King Mongkut's University of Technology North Bangkok for financial support.

#### REFERENCES

- [1] Zhang, M., et al., "Titania-Coated Polystyrene Hybrid Microballs Prepared with Miniemulsion Polymerization," *Langmuir*, Vol. 20, pp. 1420 – 1424, 2014.
- [2] Ana M. Peiro´, et al., "Hybrid polymer/metal oxide solar cells based on ZnO columnar structures," *J. Mater. Chem.*, Vol. 16, pp. 2088–2096, 2006.

- [3] Meilert, K.T., D. Laub, and J. Kiwi, "Photocatalytic self-cleaning of modified cotton textiles by TiO<sub>2</sub> clusters attached by chemical spacers," *J. Mol. Catal. A. Chem.*, Vol. 237, pp. 101–108, 2005.
- [4] Fateh, R., R. Dillert, and D. Bahnemann, "Self-Cleaning Properties, Mechanical Stability, and Adhesion Strength of Transparent Photocatalytic TiO<sub>2</sub>–ZnO Coatings on Polycarbonate," *Appl. Mater. Interfaces*, Vol. 6(4), pp. 2270-2278, 2014.
- [5] Kapridaki, C. and P. Maravelaki-Kalaitzaki, "TiO<sub>2</sub>-SiO<sub>2</sub>-PDMS nano-composite hydrophobic coating with self-cleaning properties for marble protection," *Progress in Organic Coatings*, Vol. 76, pp. 400-410, 2013.
- [6] Y. Paz, et al., "Photooxidative self-cleaning transparent titanium dioxide films on glass," *J. Mater. Res.*, Vol. 10(11), pp. 2842-2848, 1995.
- [7] Elamin, N. and A. Elsanousi, "Synthesis of ZnO Nanostructures and their Photocatalytic Activity," *J. Appl. Indus. Sci.*, Vol. 1, pp. 32-35, 2013.
- [8] Hamrouni, A., H. Lachheb, and A. Houas, " Synthesis, characterization and photocatalytic activity of ZnO-SnO<sub>2</sub> nanocomposites," *Mater. Sci. Eng. B.*, Vol. 178, pp. 1371-1379, 2013.
- [9] Sun, J.-H., et al., "Preparation and photocatalytic property of a novel dumbbell-shaped ZnO microcrystal photocatalyst," *J. Hazard. Mater.*, Vol. 172, pp. 1520–1526, 2009.
- [10] Yassitepe, E., et al., " Photocatalytic efficiency of ZnO plates in degradation of azo dye solutions, J. Photochem," *Photobiol. A.* 198, pp. 1–6, 2008.
- [11] Hong, R.Y., et al., " Synthesis, surface modification and photocatalytic property of ZnO nanoparticles," *Powder Technol.*, Vol. 189, pp. 426–432, 2009.