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Synthesis and characterization of TUD-C impregnated with zinc oxide

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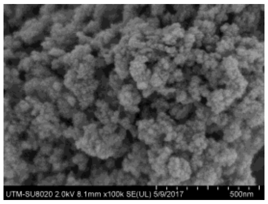
GRAPHICAL ABSTRACT



FE-SEM micrograph of TUD-C/5ZnO

ABSTRACT

Technische Universiteit Delft-Crystalline (TUD-C) is a zeolite composite with ZSM-5 nanocrystals embedded in a mesoporous matrix. TUD-C and TUD-C doped with zinc oxide were successfully synthesized using sol-gel and impregnation methods. A series of TUD-C impregnated with zinc oxide were synthesized via sol-gel method using zinc acetate dehydrate ($Zn(CH_3COO)_2.2H_2O$) as a zinc precursor and distilled water was used as solvent. The synthesized TUD-C and TUD-C doped with zinc oxide were characterized by using Nitrogen adsorption-desorption analysis, Fourier transform infrared spectrometer, Diffuse reflectance ultra violet-visible spectrophotometer, X-ray diffraction and Field Emission Scanning Electron Microscopy. From Nitrogen adsorption-desorption analysis, it was confirmed that TUD-C and all the TUD-C doped with zinc oxide samples have hierarchical mesoporous texture with high surface area which is 208.54 m^2/g for TUD-C and lesser for TUD-C doped with zinc oxide. The interpretation of Fourier transform infrared spectrometer analysis showed siloxane and hydroxyl (water) functional groups in all synthesized samples, indicating framework stretching vibration band of Si(Al)-O in tetrahedral $Si(Al)O_4$ in the TUD-C and H-bonded zeolitic water. Diffuse reflectance ultra violet-visible spectrophotometer analysis showed low values of bandgap for zinc oxide supported on TUD-C. The X-ray diffraction confirmed MFI framework of TUD-C in the samples. Field Emission Scanning Electron Microscopy showed the agglomeration formed in the samples. From the synthesized material, there are possible applications of TUD-C impregnated with zinc oxide such as used as photocatalyst and improved electrical properties material.

Keywords: TUD-C, zinc oxide, mesoporous, sol-gel method, characterization.

1. INTRODUCTION

Piezoelectric materials are the material that able to generate an AC (alternating current) voltage when subjected to mechanical stress or vibration, or to vibrate when subjected to AC voltage, or both [1]. From this property, this material is widely used as high voltages and power sources. A piezoelectric potential is produced in any bulk or nanostructured semiconductor crystal, for instance group III-V and II-VI materials, by polarization of ions under applied stress and strain. This property is usually found in zincblende and wurtzite crystal structures. Zinc oxide crystallizes in the wurtzite structure, available as large bulk single crystals, and II-VI oxide material making it having this piezoelectric property [2].

A dielectric is a material having poor conductor of electricity but an efficient supporter of electrostatic field. Dielectric material has property of ability to support an electrostatic field while dissipating minimal energy (heat). The lower the value of dielectric loss (which is the amount of energy lost as heat), the more effective is the dielectric material. In general, metal oxides have high dielectric constants.

Ferroelectric material exhibits permanent electric polarization that varies in strength with the applied electric field. All ferroelectric materials exhibit piezoelectric effect due to lack of symmetry. Some of the properties of ferroelectrics are spontaneous polarization in the absence applied electrical field and strong non-linear dielectric response to an applied electric field. Zinc oxide has piezoelectric, dielectric and ferroelectric properties.

Photocatalysis is a branch of science study about catalysts that speed up the chemical reactions that required light. A photocatalyst is a material that capable of absorbing light producing electron hole pairs that enable chemical transformations of the reaction participants and regenerate its chemical composition after each cycle of such interactions [3-8]. Metals oxide such as oxides of zinc, titanium, and vanadium are usually used as photocatalyst that are able to oxidize organic substrates [6-8]. Photocatalysis can degrade and mineralize most organic contaminants in water and air.

There is no report on the usage of TUD-C of design on piezoelectricity, dielectricity and ferroelectricity material. However, zinc oxide supported on zeolites is used as photocatalyst and it is known that TUD-C is a zeolite composite with ZSM-5 nanocrystals embedded in a mesoporous matrix. Then, this research was conducted to synthesize and characterize TUD-C and doped it with zinc oxide which is likely to have better electrical properties and could be used in the photocatalytic reactions.

2. EXPERIMENTAL

In this study, TUD-C and TUD-C impregnated with zinc oxide were prepared. Zinc oxide composition were 1 wt%, 2 wt%, 3 wt%, 4 wt%, and 5 wt%; where TUD-C was the support for zinc oxide. TUD-C was synthesized in a homogenous synthesis solution consisting of water, triethanolamine (TEA), tetraethylammonium hydroxide (TEAOH), tetraethyl orthosilicate (TEOS), and ZSM-5. The method used was sol-gel method. One beaker containing H_2O and TEA while in the other beaker containing TEOS and ZSM-5 were prepared. Both mixtures in each beaker was magnetically stirred for 1 hour to assure homogenous mixing. The water and TEA mixture was added drop-wise into TEOS mixture, forming solution A. Solution A was kept on stirring for 1 hour. Then, TEAOH was added drop-wise into solution A and continuously stirred for another 2 hour. Later, the solution was evaporated at ambient conditions for 24 h to incur a solid gel. Then, the solid gel was dried at 373 K for about 1-2 hours. Later, it was calcined in autoclave at 873 K for 12 hours to remove the organic contents. The Si/Al ratio is 30 for this study.

TUD-C doped with ZnO (1-5 wt%) were prepared using sol gel and impregnation method. High purity zinc acetate dehydrate was used as precursor of zinc was dissolved in distilled water. Precursor solution of ZnO was mixed with TEOS and ZSM-5 and stirred for 1 hour. In another beaker, H_2O and TEA mixture was stirred for 1 hour. The water and TEA mixture was added drop-wise into TEOS mixture, forming solution B. Solution B was kept on stirring for 1 hour. Then, TEAOH was added drop-wise into solution B and continuously stirred for another 2 hour. Later, the solution was evaporated at ambient conditions for 24 h to incur a solid gel. Then, the solid gel was dried at 373 K for about 1-2 hours. Later, it was calcined in autoclave at 873 K for 12 hours to remove the organic contents. All the samples went for characterization of Nitrogen adsorption-desorption analysis (BET), Fourier transform infrared spectrometer analysis (FTIR), Diffuse reflectance ultra violet-visible spectrophotometer analysis (DR UV-Vis), X-ray diffraction (XRD) and Field Emission Scanning Electron Microscopy (FESEM).

3. RESULTS AND DISCUSSION

3.1. Synthesis of TUD-C and TUD-C doped zinc oxide

A series of TUD-C (Si/Al = 30), TUD-C/1ZnO, TUD-C/2ZnO, TUD-C/3ZnO, TUD-C/4ZnO, TUD-C/5ZnO were successfully synthesized. White powder TUD-C and creamy white powder of TUD-C doped ZnO were obtained after calcination which was to remove organic contents. The creamy white powder of ZnO supported on TUD-C instead of theoretical white colour of ZnO was obtained maybe due to some Zn^{2+} content adsorbed in TUD-C instead of ZnO. It is known that ZnO turns to yellow upon heating and it lost oxygen and became Zn^{2+} ion.

3.2. Nitrogen adsorption-desorption (BET) analysis

The nitrogen adsorption desorption (BET) multipoint analysis were ran for all synthesized samples. The samples were dried overnight to remove water moisture on their surface. The instrument was degass to vacuum and nitrogen gas was flowed onto samples. The surface area, pore volume, and average pore diameter of TUD-C, TUD-C/1ZnO, TUD-C/2ZnO, TUD-C/3ZnO, TUD-C/4ZnO, and TUD-C/5ZnO were obtained in Table 1. The surface area for TUD-C is the highest with value of 208.54 m^2/g. After ZnO impregnation, the BET surface area decreases by the incorporation of this oxide to TUD-C. It can be seen physically of the samples where the TUD-C powder is finer than the TUD-C doped with ZnO powder.

Table 1: Surface area for TUD-C, TUD-C/1ZnO, TUD-C/2ZnO, TUD-C/3ZnO, TUD-C/4ZnO, and TUD-C/5ZnO

Sample	**Surface area (m^2/g)**	**Pore volume (cm^3/g)**	**Average pore radius (nm)**
TUD-C	208.54	0.33	2.31
TUD-C/1ZnO	198.56	0.42	3.30
TUD-C/2ZnO	148.24	0.25	0.97
TUD-C/3ZnO	163.42	0.19	1.82

TUD-C/4ZnO	174.49	0.32	0.97
TUD-C/5ZnO	199.56	0.39	0.97

The isotherms of all of the samples were plotted.

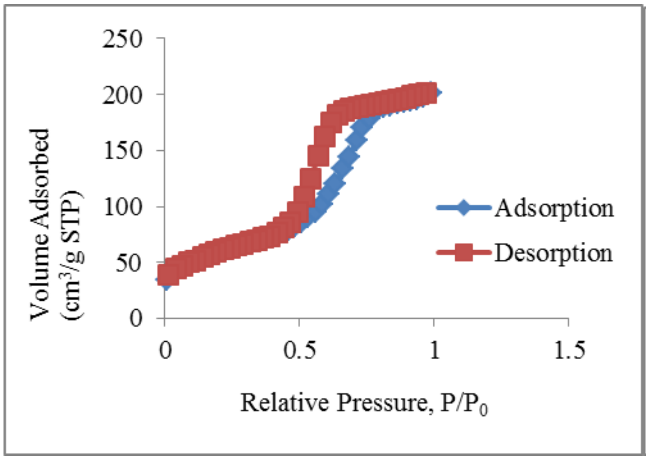


Figure 1: Isotherm plot of TUD-C

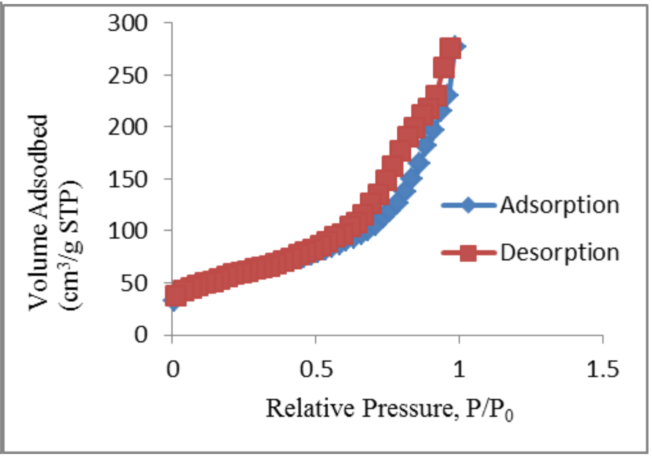


Figure 2: Isotherm plot of TUD-C/1ZnO

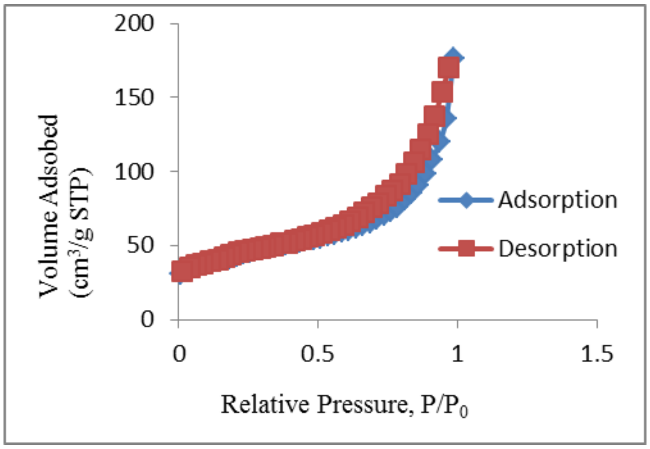


Figure 3: Isotherm plot of TUD-C/2ZnO

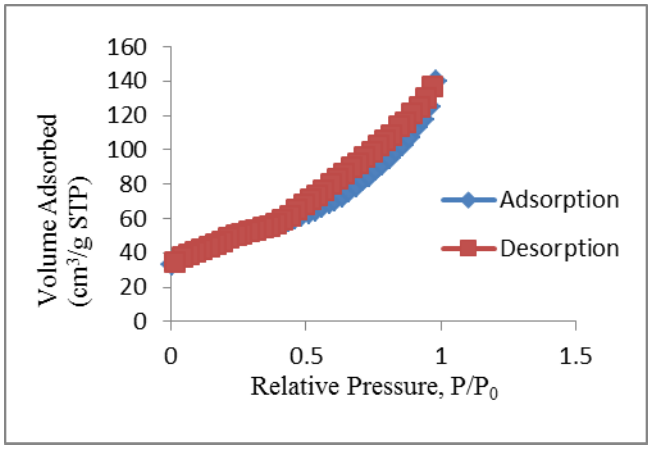
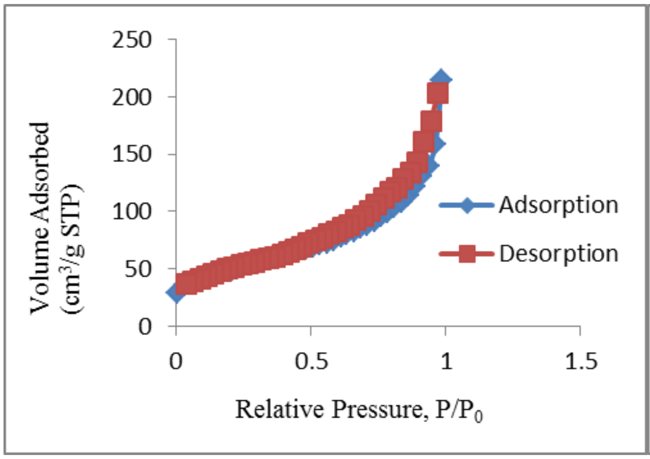


Figure 4: Isotherm plot of TUD-C/3ZnO



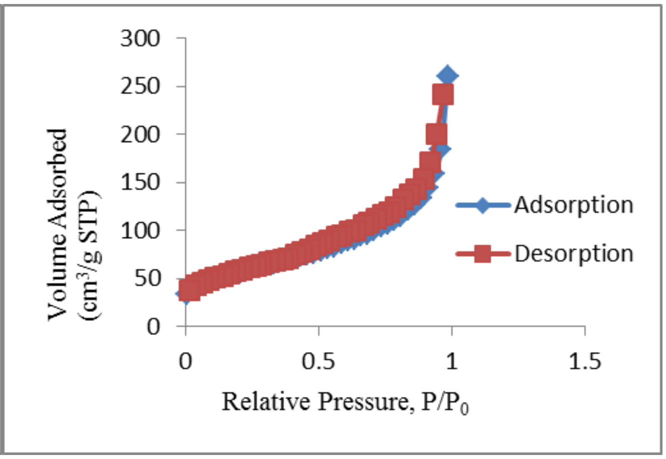


Figure 5: Isotherm plot of TUD-C/4ZnO **Figure 6**: Isotherm plot of TUD-C/5ZnO

From Figure 1, TUD-C sample exhibits Type IV isotherm which is mesoporous solid with H2 hysteresis loop which is associated with capillary condensation in 'ink bottle' pores (having narrow necks and wide body). From Figure 2 until Figure 6, the isotherms for TUD-C doped with ZnO are type IV which are mesoporous solids with H3 hysteresis loop which consist of slit shape pores, with non-uniform size and/or shape. This is the reason why the distribution of pore volume and average pore radius of TUD-C doped with ZnO do not have certain trend values as in Table 1. The format of matching curves between the supported TUD-C and the pure TUD-C indicates that the TUD-C texture remained after ZnO incorporation. Large surface areas of all samples indicating that they can be good catalysts.

3.3. Fourier transform infrared spectrometer (FTIR) analysis

Figure 7 shows the FTIR spectra of TUD-C, TUD-C/1ZnO, TUD-C/2ZnO, TUD-C/3ZnO, TUD-C/4ZnO, and TUD-C/5ZnO. The spectra show bands similarities. There should be ZnO peaks for the TUD-C impregnated with ZnO around 450 cm^{-1} but it may not appear there due to lack of ZnO composition in the samples. At 3249 cm^{-1}, it is weak O-H stretching region of H-bonded water (zeolitic). The spectra show the strongest peak at around 1086 cm^{-1} which is the framework stretching vibration band of Si(Al)-O in tetrahedral Si(Al)O_4 in the TUD-C. It can be concluded that the structure of TUD-C were not destroyed even after doping with ZnO. At 806 cm^{-1}, it is Si-O-Si symmetric stretching. Table 2 summarized the bands of FTIR spectra.

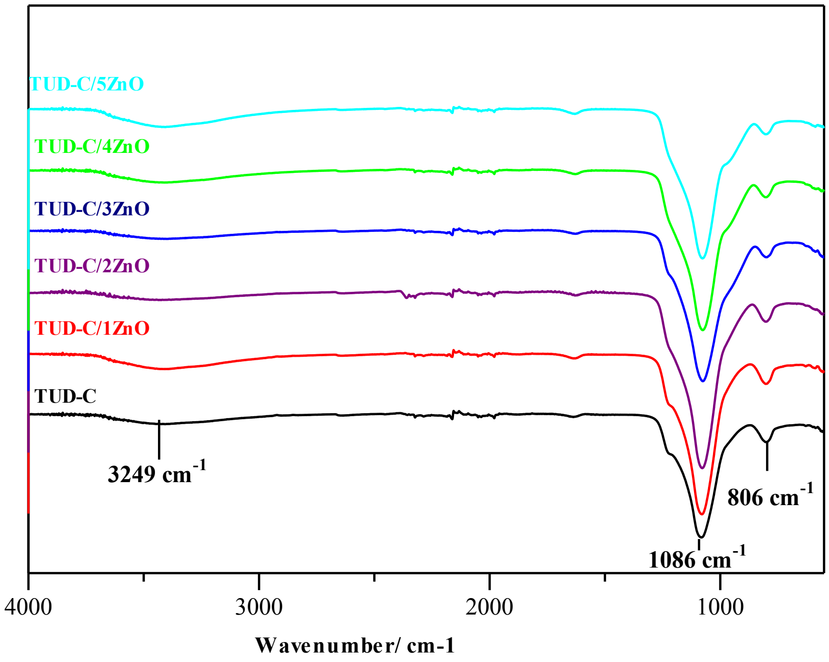


Figure 7: FTIR spectra of TUD-C, TUD-C/1ZnO, TUD-C/2ZnO, TUD-C/3ZnO, TUD-C/4ZnO, and TUD-C/5ZnO.

Table 2: The FTIR vibration bands of synthesized samples

Wavenumber (cm^{-1})	Functional Group
3249	O-H (stretching)
1086	Si-O-Si (asymmetric stretching)
806	Si-O-Si (symmetric stretching)

3.4. Diffuse reflectance ultra violet-visible spectrophotometer (DR UV-Vis) analysis

Figure 8 shows the DR UV-Vis spectra of TUD-C, TUD-C/1ZnO, TUD-C/2ZnO, TUD-C/3ZnO, TUD-C/4ZnO, and TUD-C/5ZnO samples. All the samples except TUD-C exhibited an absorption peak at around 480 nm. Theoretically, the DR UV-Vis peak of ZnO is in the range of 350-380 nm. The absorption peak is higher due to introduction of TUD-C as ZnO support. The bandgap energy, E_g can be determined by using Tauc plot, with the Equation 4.1:

$$\alpha h\nu = A\,(h\nu - E_g)^{n/2} \qquad (4.1)$$

α = Absorption coefficient

$h\nu$ = Photon energy

A = Constant

E_g = Optical band gap

n= Value depends on type of transition;

where n= 1 (direct transition), n= 4 (indirect transition)

The optical band gap, E_g was determined from the x-intercept of linear extrapolation in the Tauc plot of $(\alpha h\nu)^{2/n}$ versus hν. In this study, TUD-C has indirect transition and all samples considered having indirect transition due to the main composition of TUD-C instead of direct transition of ZnO. Table 4.3 shows the determined optical band gap of all samples. Figure 4.9- Figure 4.14 show the Tauc plots of the samples for bandgap determinations. Their x-intercepts are the value of band gap.

Table 3: The bandgap energy of the samples

Sample	Bandgap Energy (eV)
TUD-C	2.91
TUD-C/1ZnO	1.30
TUD-C/2ZnO	0.50
TUD-C/3ZnO	0.70
TUD-C/4ZnO	1.14
TUD-C/5ZnO	0.38

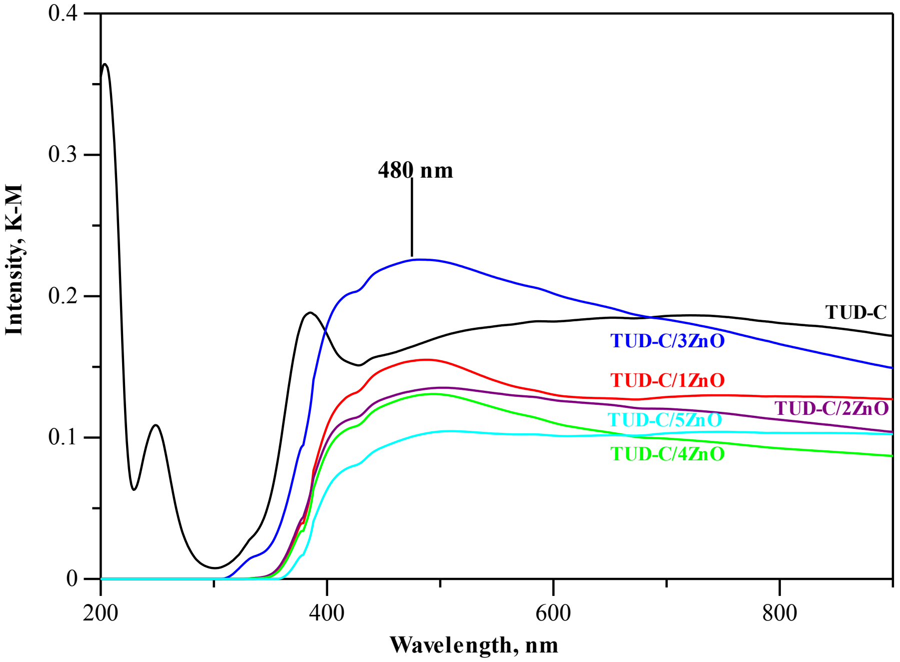


Figure 8: DR UV-Vis spectra of TUD-C, TUD-C/1ZnO, TUD-C/2ZnO, TUD-C/3ZnO, TUD-C/4ZnO, and TUD-C/5ZnO

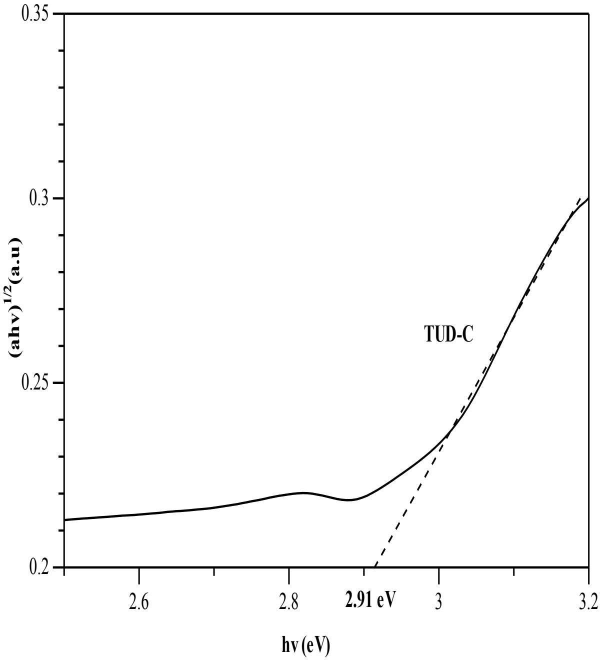


Figure 9: Tauc plot of TUD-C

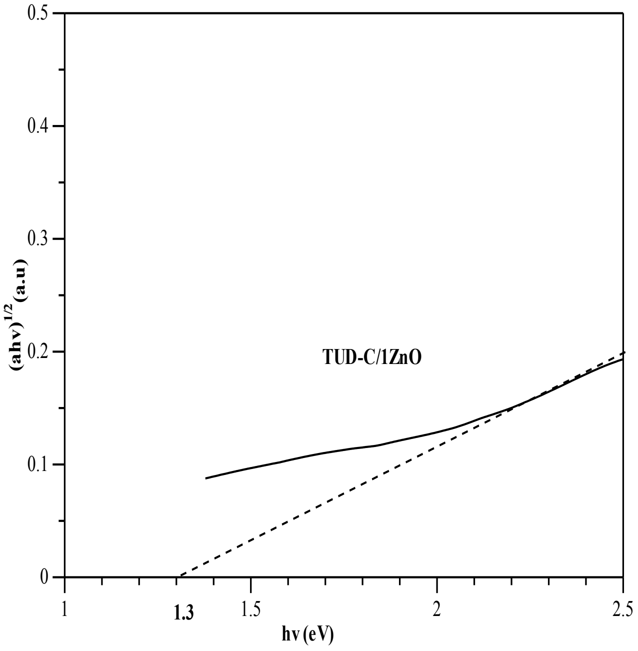


Figure 10: Tauc plot of TUD-C/1ZnO

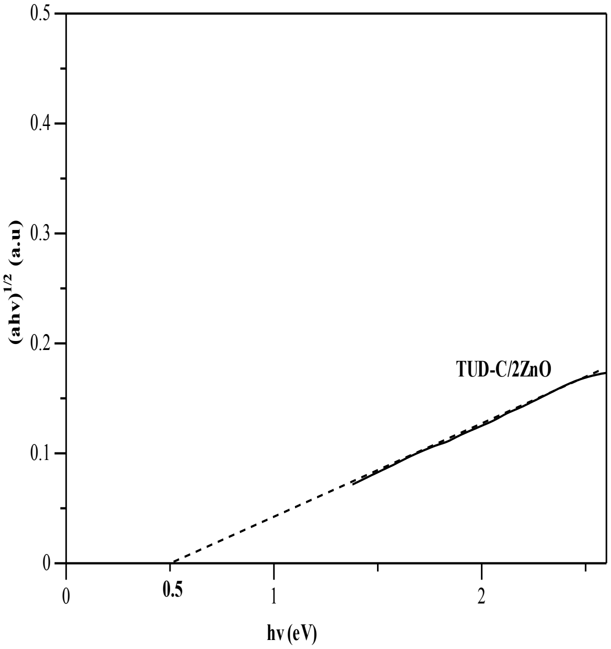


Figure 11: Tauc plot of TUD-C/2ZnO

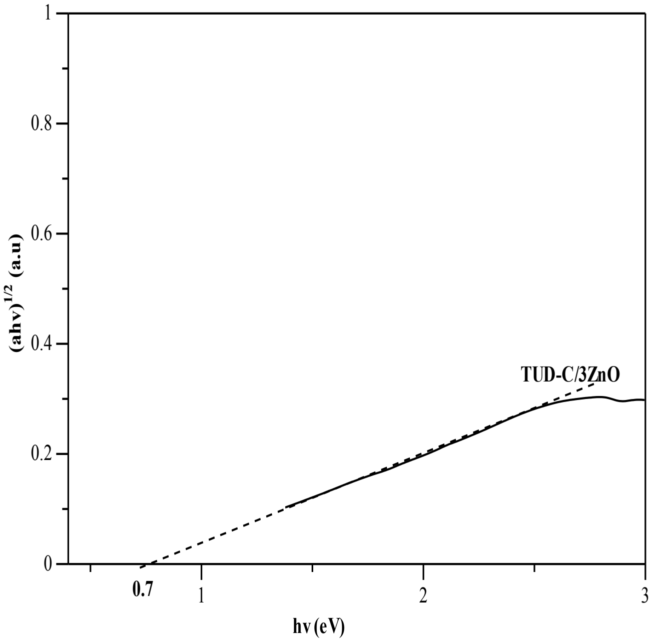


Figure 12: Tauc plot of TUD-C/3ZnO

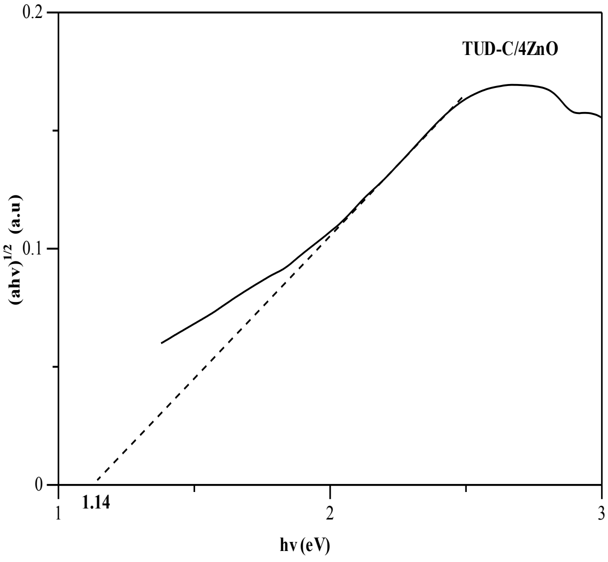


Figure 13: Tauc plot of TUD-C/4ZnO

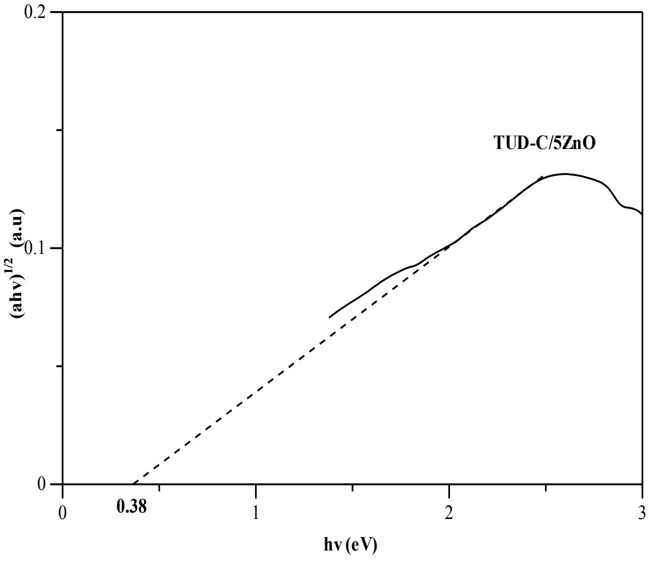


Figure 14: Tauc plot of TUD-C/5ZnO

3.5 X-ray Diffraction (XRD) analysis

Figure 15 shows the XRD diffractograms of TUD-C, TUD-C/1ZnO and TUD-C/2ZnO. XRD analysis determined the phase present in the samples. The XRD patterns of the samples were recorded in the fraction angle range from 0° to 90°. From the figure, there are sharp peaks at low angle 2 Theta = 8.0^o and 9.0^o confirming the formation of MFI framework of TUD-C in the samples. Peaks of ZnO are not detected in the diffractograms. It could be due to low amount of ZnO or well dispersion of ZnO on the surface of TUD-C.

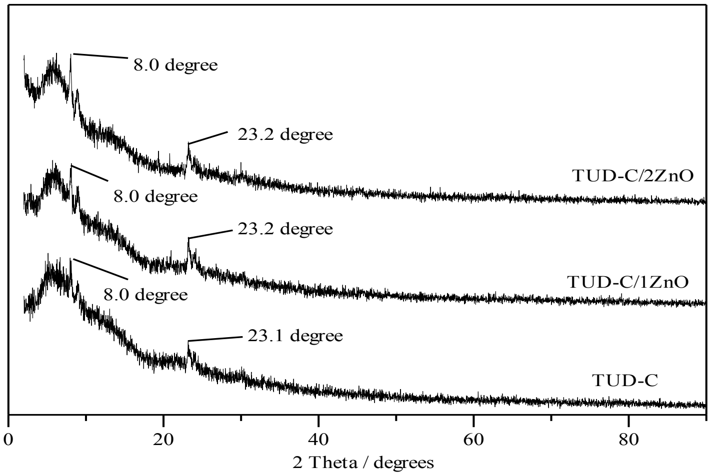
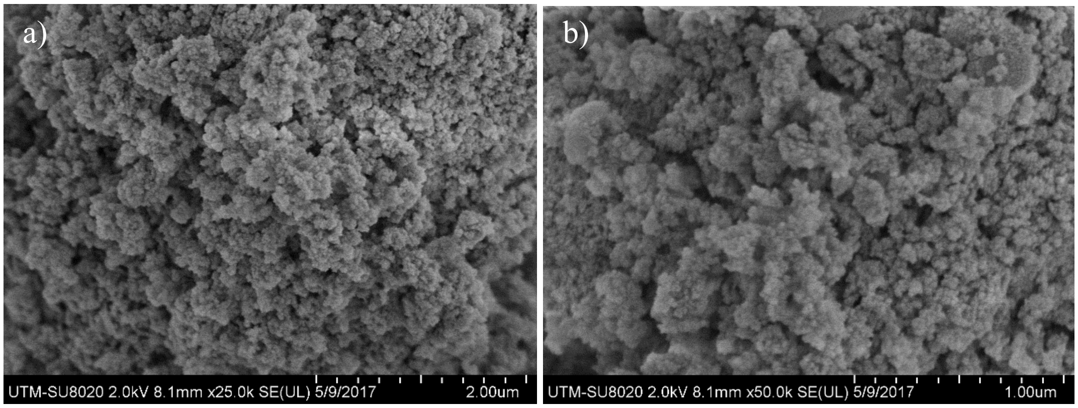


Figure 15: XRD patterns of TUD-C, TUD-C/1ZnO and TUD-C/2ZnO

3.6 Field Emission Scanning Electron Microscopy (FESEM) analysis

FE-SEM micrographs of TUD-C/5ZnO synthesized in different magnifications are shown in Figure 16. The images suggested that the sample was in nanoscale. Agglomeration was formed in the sample.



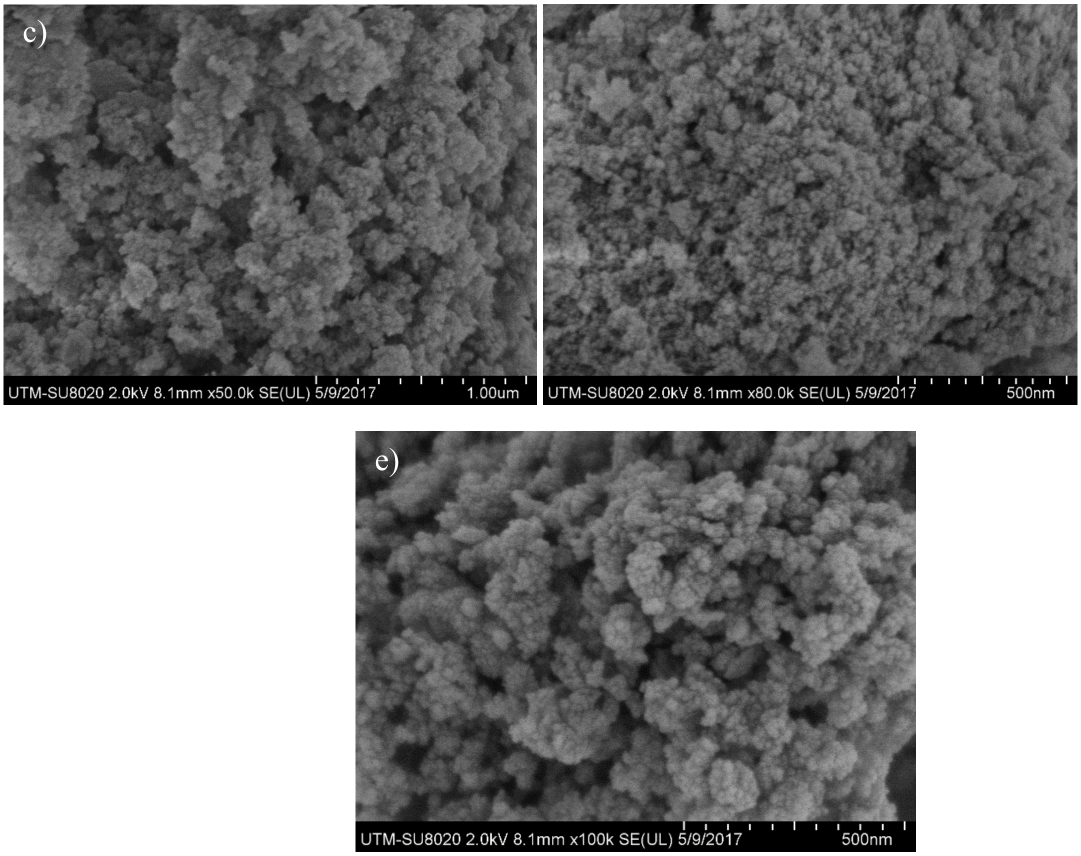


Figure 16: FE-SEM micrographs of TUD-C/5ZnO synthesized in different magnifications (a) 2.00µm, (b-c) 1.00µm and (d-e) 500nm

4. CONCLUSION

The study shows that the synthesis of TUD-C and TUD-C impregnated with zinc oxide have been successfully prepared by combination of sol-gel and impregnation method using zinc acetate dehydrate as zinc precursor with distilled water as solvent. TUD-C, TUD-C/1ZnO, TUD-C/2ZnO, TUD-C/3ZnO, TUD-C/4ZnO, and TUD-C/5ZnO were successfully characterized by BET, DR UV-Vis, and FTIR analyses. Synthesized white powder TUD-C and creamy white powder of TUD-C doped ZnO were obtained after calcination which was to remove organic contents. The creamy white powder of ZnO supported on TUD-C instead of theoretical white colour of ZnO was obtained maybe due to some Zn^{2+} content adsorbed in TUD-C instead of ZnO. Nitrogen adsorption desorption analysis showed all samples have type IV with hysteresis loop meaning that all samples have mesoporous structure. The surface area decreased after impregnation of zinc oxide with TUD-C. DR UV-Vis spectra show absorption peak at around 480 nm for all samples except TUD-C. The values of bandgap for doped TUD-C were lower than TUD-C. However, those values are too low and there might be some error. FTIR spectra show bands similarities. There were existence of H-bonded zeolitic water, framework stretching vibration band of Si(Al)-O in tetrahedral $Si(Al)O_4$ in the TUD-C and Si-O-Si symmetric stretching according to their peaks. XRD diffractograms show sharp peaks at low angle 2 Theta = 8.0^o and 9.0^o confirming the formation of MFI framework of TUD-C in the samples. It confirms the crystalline structure in the first three synthesized samples. FE-SEM micrographs of TUD-C/5ZnO synthesized showing the sample is nanoscale in size. From there, there exists pores of the sample (mesoporous) and agglomeration was formed in the sample.

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