Thermal Stability of ZnO Nanoparticle Bound Organic Chromophores

Kenneth Skorenko, Rose T. Bernier, Jian Liu, Bradley Galusha, Frank Goroleski, Brendan P. Hughes, William E. Bernier, Wayne E. Jones Jr.*

Department of Chemistry, Binghamton University, 4400 Vestal Parkway E, Binghamton NY, 13902

*Corresponding Author: Wjones@binghamton.edu

Abstract

Thermally stabilized metal-organic chromophores have been generated through an electrochemical oxidation of zinc metal to form a ZnO-chromophore nanomaterial. The chromophores are surface bound to ZnO by a polar covalent metal-to-chromophore bridge which minimizes thermal degradation pathways of the organic molecule. The binding occurs between the Zn and carboxylic acid functional groups on the organic chromophore as confirmed using IR spectroscopy monitoring the loss of the COO⁻ peak at 1720 cm⁻¹. The new composite material demonstrates a thermal stability up to 300 °C based on the results of TGA/MS and DSC. The photostability of these materials in either the solution or solid state was monitored using UV/Vis/NIR spectroscopy. When incorporated into a polymer composite there is a dramatic increase in photo stability compared to the pure chromophore or the metal-chromophore nanomaterial.

Keywords: Thermally Stabilized, Pigments, Chromophore, Dye, Absorbing, Metal Oxide

1.0 Introduction

Organic cyanine chromophores contain strong characteristic absorptions which allow them to be used in a variety of optical based applications such as light filtering, infrared labeling, bio-imaging, optical switches, photovoltaic devices, and within clothing for true color control. [1-5] There are many applications for which cyanine based dyes have not been used, such as light filtering in laser shields, displays and passive solar devices due to their low thermal and photo stability. These applications use plastics as a medium with the chromophores applied by a surface coating method on an appropriate substrate. Applying organic absorbers as a coating leaves them susceptible to scratching and degradation from Ultraviolet (UV) light, water and oxygen. However, the process of encapsulating the absorber into the plastic medium would lead to degradation of the chromophore due to high processing temperature. [6-8] Many high density plastics, such as polycarbonate and acrylate, used in commercial applications tend to have higher processing temperatures, greater than 200 °C while organic chromophores tend to degrade between 120 and 150 °C, limiting their use in many commercial applications.

As one example of typical organic chromophore degradation, **Fig. 1A** shows the UV/Visible (Vis) spectra of an organic cyanine chromophore that has been heated from 50 to 300 °C in 50 °C increments. [9] The commercial name for this chromophore is Dye 847 and the structure is shown in **Fig. 1B**. The spectra shows a large intensity decrease in the absorption characteristics of the chromophores between 100 and 150 °C, well below standard processing temperatures for many commercial applications. [1] Generally only dyes with strong intermolecular forces and high levels of aggregation are thermally stable. [10] While cyanine chromophores tend to have low thermal stability, they are desired due to the wide range of

absorptions that are selective and extend into the near IR, as well as the ease of fabrication and low cost of the dyes. [7]

The energy generated during heating causes bonds in the cyanine dyes to cleave, limiting the stability of these organic molecules.[11,12]At high temperature there is enough vibrational energy to break bonds between atoms causing degradation of the molecule and then loss of its favorable absorbance characteristics. [12-14] By binding the molecule to ZnO nanoparticles, the mass of the molecule is increased and new alternate pathways for the vibrational energy to dissipate are created. The binding between the chromophore and ZnO nanoparticles occurs between the carboxylic acid of the molecule and the ZnO of the nanoparticle creating a C-O-Zn bridge leading to chemical binding on the nanoparticle.[15-17]The new vibrational pathways between the molecule and nanoparticle and the increased heat capacity of the new optical nanomaterial is hypothesized to result in increased thermal stabilization.

ZnO has been studied extensively due to its electrical and optical properties. It has been used in many applications ranging from photovoltaic, and nano-energy generators to UV absorbing sunscreens. [17-20] ZnO has a wide band gap, allowing for high transparency in the visible region of the electromagnetic spectrum. It also has a low coefficient of thermal expansion coupled with the high surface area of the nanoparticles makes ZnO a prime candidate for a thermally stabilized optically absorbing nanomaterial. [17-20]ZnO nanoparticles can be generated using an electrochemical deposition method, which allows for a C-O-Zn bridge during the nanoparticle formation in the presence of carboxylic acids. Electrochemical deposition also allows for control of size and concentration of ZnO nanoparticles generated. [16] While ZnO has also been used as a photo catalyst for photodegradation of organic molecules, this process relies

on the metal oxides ability to hydrolyze water. [6] However, when encapsulated in a solid plastic matrix the water exposure is limited.

Here the thermal and optical properties of a new composite nanostructure are reported which incorporate a model cyanine dye with ZnO nanoparticles. Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis/Mass Spectrometry (TGA/MS), Infrared (IR) and UV/Vis/Near IR spectroscopy are used to characterize binding between the organic dye and the nanoparticle, as well as to monitor thermal degradation. The chromophore is measured both as solid particles and as particles encapsulated in a polyvinyl chloride (PVC) laminate as a model system for current industrial applications.

2.0 Methods

2.1 Materials

Zinc metal and stainless steel foil (Type 304) were purchased from Alpha Aesar and cut to size for use in electrochemical deposition. Chromophores were acquired from Crysta-Lyn Chemical Company and used as received. Screen printing solvent, TechMark TM-MMX was purchased from Fujifilm USA and used as received. All other solvents and other chemicals were reagent grade, purchased from Sigma Aldrich, stored at room temperature and used as received.

2.2 Generation of Nanomaterial

The ZnO nanoparticles are generated via electrochemical deposition carried out under oxidizing conditions (EDOC). Zn metal (99.999%) was used as a sacrificial anode and stainless steel was used as a cathode. The electrodes were immersed in a solution of 0.1 M tetrabutylammonium bromide in isopropanol with 0.01 M cyanine molecule (Dye 847) dissolved in solution. Using a Keithley programmable current source, a variable current was applied

between the two electrodes to maintain a constant voltage as measured using a Keithley 182 Voltmeter. The current was adjusted so the voltage was steady between 25 and 30 V. Oxygen was supplied to the system at steady rate of 1.2 ml/min. This continued for four hours producing dark blue product in the presence of the chromophore or a white ZnO nanoparticle without the chromophore added.

To produce a dried solid powder, the product was separated using a fritted Buchner funnel with pore size < 200 nm. The particles were then washed with methanol until the resulting filtrate contained no excess chromophore as determined by an absence of blue color. A 200 nm filter allowed collection of the product.

2.3 Lamination

The PVC lamination process was performed using a high pressure melt of two PVC films. The absorbing nanomaterial was screen-printed, using a 13 line per inch mesh, onto a side of PVC material and then sandwiched between another PVC film. The films were then placed in a Wuhan A4 Water and Air Cooling Card Laminator and pressure applied using a hand crank, which caused two metal plates to compress the material. The metal plates were then heated to 140 °C at a ramp rate of 20 °C / min and then held at 140 °C for 1 min. The plates were subsequently water cooled over 20 min to 60 °C. The metal plates were separated and the resulting in a composite laminate of PVC films and the chromophore or dye nanomaterial.

The screen printing process required the use of a screen printing ink. The absorbing nanomaterial (200 mg) was dispersed in 1 ml of acetone, which was added to 9 ml of TechMark-MMX, a PVC based solvent. The mixture was then dispersed using physical mixing and sonication for 10 min. The resulting mixture was then screen printed as described previously.

When the pure chromophore was used in the lamination process, the chromophore (20 mg) was dissolved in 4-hydroxy-4-methyl-2-pentane and added to TechMark-MMX in a ratio of 1 to 9.

To prevent aggregation of the dye nanocomposite in the laminate films, a different purification technique was used which prevented drying of the nanomaterial. After EDOC of the nanomaterial occurred, the solution was collected and distributed between centrifuge tubes. This was centrifuged for 20 min at 3000 RPM to settle the solid material. The solution was then decanted and the solid was washed with methanol. This solution was dispersed using a vortex mixer and then centrifuged again for 20 min at 3000 RPM. This process continued until there was no visible chromophore in solution after centrifuging. The nanoparticles were then washed three more times using acetone as the eluent under the same conditions. This solution was then used to generate the ink for the screen printing process.

2.4 Instrumentation

Solid State UV/Vis spectrographs of films were collected using Perkin Elmer Lambda 25 spectrometer and blanked with either glass or PVC sheets that had undergone the same processing steps as the samples. Scanning Electron Microscopy (SEM) images were taken on a Zeiss Supra 55VP using a field emission microscope. Samples were coated with a 5 nm layer of gold. TGA/MS data was taken using a Netzsch TGA/MS with programmable thermal conditions. The thermal conditions were determined using Thermal Instruments TGA Series Q50 with an isothermal mode that activated when the sample mass change was greater than 1% and deactivated when the mass change was less than 0.05 %. TGA data can be seen in the supplemental. The mass spectral data was determined using a quadrupole mass spectrometer setup, which was set to scan from 0.5 to 30.5 AMU on one sample and 30.5 to 60.5 AMU on a separate absorber nanomaterial sample. Both samples used the same thermal conditions.

Differential Scanning Calorimetry (DSC) measurements were done using a Thermal Instruments, TA Q50 series. The DSC sample holder was an aluminum pan, physically sealed by crimping the edges of the lid and holder, temperature was increased at 10 °C per min with air as reference. IR spectra were measured using a Bruker Equinox 55. The IR spectra were taken with 32 scans at a resolution of 4 cm⁻¹.

3.0 Results and Discussion

3.1 Dye Binding

The blue nanomaterial composite powder was readily produced on a gram scale as described above. It was characterized by IR spectroscopy as shown in **Fig 2**. For comparison purposes, the spectra of the pure dye and pure ZnO prepared under identical conditions are included. The IR spectra confirm the binding of a carboxylate ion from the chromophore to the zinc oxide nanoparticles. The peak at ~ 1720 cm⁻¹ is related to the carboxylate group in chromophore 847. Upon binding the dye to ZnO nanoparticles and washing off the excess reactant the peak at 1720 cm⁻¹ was not observed. The IR spectra confirmed the presence of the dye before washing and after washing so it was concluded that the binding between the carboxylate of the dye and the surface of the zinc had occurred.

SEM was used to determine the size of the dye composite nanomaterial and is shown in **Fig. 3A**. The presence of excess aggregation was observed, likely due to the removal of the surfactant during the washing procedure. The material was milled and Transmission Electron Microscopy (TEM) was used to determine size of the smaller particles, as seen in **Fig. 3B**. The average size of individual nanoparticles was ~ 150 nm in the largest dimension and ~50 nm in the smallest. The particles are not uniform in shape. The aggregates of the nanoparticles were easily dispersed back into solution with sonication at room temperature.

3.2 Thermal Stability

To measure the thermal stability of the 847 nanomaterial a series of measurements were performed using DSC, TGA and TGA/MS. The purpose of this characterization was to understand how the chromophore was degrading in order to improve overall thermal stability, as shown in **Figure 4**.

The TGA of the pure chromophore, the dye nanocomposite and ZnO nanoparticles are shown in **Fig. 4A**. The data shows that pure samples of chromophore 847 degrade significantly during heating, with over 30 % of the weight lost by 210 °C, whereas the chromophore bound nanomaterial undergoes little degradation, with a gradual loss that matches pure ZnO particles. This loss is likely due to solvent and residual surfactant. Both the chromophore bound nanomaterial and pure ZnO nanomaterial have a significant loss at 180 °C which is likely due to the loss of tetrabutylammonium bromide. The second weight loss seen in ZnO at 200 °C is likely tetrabutylammonium bromide. This peak is not noticed in the nanomaterial and however there is a peak at 230 °C which could be the start of chromophore degradation or excess TBAB similar to that of the ZnO, however the distinction between the two is not clear.

The results of DSC are shown in **Fig. 4B** where both samples have an endothermic peak starting at 180 °C and peak max at 220 °C. Since the peak at 220 °C occurs in both ZnO and the dye nanocomposite, this peak is not related to the degradation of dye. The lower intensity of the peak at 220 °C on the nanomaterial is due to a lower concentration of tetrabutylammonium bromide that can bind since the nanomaterial has chromophore bound to the surface. To better understand the degradation pathway, TGA/MS was used to measure the atomic mass of the off-gassing species during thermal degradation.

Using the TGA results, TGA/MS data was taken of the dye nanocomposite **Fig. 5** to measure the off-gassed species. The TGA/MS was blanked in O₂ to account for atmospheric gases in the chamber. The counts shown on the Y axis relate to the ion counts of a specific Atomic Mass Unit (AMU) determined by the mass spectra, while the temperature was determined by the TGA.

The off-gassing of CO₂ allows the tracking of the degradation of the molecule, by binding to ZnO thermal properties are enhanced. The TGA/MS of chromophore 847 bound to ZnO, shown in **Fig. 5**, shows no major CO₂ peaks until ~290 °C, confirming higher thermal stability of the chromophore. The lack of CO₂ off gassing before 300 °C in the chromophore bound sample is not due to the lower concentration of the chromophore since the release at 300 °C (1.48 E-11) of the dye nanocomposite is similar to the release at 300 °C (1.58 E-11) of the pure chromophore. TGA/MS data of the chromophore from 1-30 and 30 – 60 AMU as well as TGA/MS of the 847 nanomaterial from 1-30 can be found in the supplemental information section. The TGA of the chromophore indicates that degradation of the chromophore starts at ~120 °C. This relates to AMU 15, 18 and 44, which correspond to hydroxide, water and carbon dioxide, indicative of a combustion reaction consistent with the breakdown of the carboxylate functional group of the chromophore. During the heating process of the chromophore, the presence of HCl formation was measured, AMU 36, indicating the breakdown of the center ring structure of the chromophore. This can also be seen in **Fig. 1**, where under heating there was a loss of the main peak and a blue shifted peak around 580 nm formed. A blue shift would be expected if the molecule had a shortened conjugation pathway. The 847 nanomaterial shows no peak associated with the release of HCl indicating that the center ring structure stays intact during the thermal process.

There are minor peaks in the nanomaterial that are associated with the release of CO₂ and H₂O before 300 °C. To understand the extra peaks that show up in dye nanocomposite, TGA/MS of just ZnO shows H₂O peaks occurring at 160, 220, 260 and 300 °C, which correlate to similar peaks on the dye nanocomposite. This same trend occurs with the CO₂ peaks at 60, 120 and 260 °C, which are also seen in the dye nanocomposite. However, the major difference between the two materials is that the ZnO nanoparticle does not show the drastic loss of CO₂ at 290 °C which can be seen in the dye nanocomposite. This is then due solely to the degradation of the chromophore. It is also worth noting the lower intensities of CO₂ and H₂O on the nanomaterial before the peak at 290 °C. These peaks are likely due to tetrabutylammonium bromide and the intensity is expected to be lower on the dye nanocomposite since there is chromophore bound to the surface of the ZnO.

3.3 ZnO/Chromophore Photostability

The photo-stability of the chromophore absorber can be measured using UV/Vis spectroscopy by tracking the intensity of the peak maximum to measure photo-degradation. **Fig. 6** shows the rate of photo-degradation of the chromophore. The rate constants are listed in each graph. The samples were either laminated or unlaminated, then exposed to light or left in the dark. As seen in **Fig. 6C,D** when the unlaminated chromophore is exposed to sunlight there is rapid degradation of the chromophore.

Prior studies have shown that cyanine and merocyanine dyes are susceptible to complete degradation in under an hour under high intensity Hg lamp irradiation. [21-22] It can be shown that the mechanism for this process involves oxidation of the cyanine under ambient conditions. Our results are consistent with this mechanism along with the stability observed when heat

lamination is used to achieve greater photostability. [22-24] The rates of these processes range from 10^{-3} to 10^{-1} mol·min⁻¹. The 847 dye and dye nanoparticle composite were irradiated under 150W Xe Lamp and the rate of decomposition was found to be similar. In comparison, we see that the rate of decomposition of the laminated nanocomposite is on a timescale of weeks in the presence of sunlight. Detailed studies under more intense laser irradiation are on-going.

Laminate films have decreased amount of UV light that can interact with the chromophore due to the absorption from PVC. When looking at **Fig.6**, we see that the laminated chromophores photodegrade at a much slower rate. The lamination process also prevents air exposure to the chromophore/nanomaterial limiting the degradation due to oxidation. There was thermal degradation of the chromophore, as seen in **Fig. 6A**, during the lamination process, which shows a loss of 0.2 absorption (24% of the intensity at λ max) from the thermal heating. **Fig. 7** shows the rate of photo-degradation of the dye nanocomposite. When the pure chromophore is compared with the dye composite nanomaterial the loss of intensity during the lamination process is resolved, as seen in **Fig. 7A**. The dye nanocomposite showed a 10% increase in absorbance, 0.06. Since the baseline did not show the same increase, it may be concluded that this increase in absorbance is not due to aggregation but to an increase in solubility of the nanocomposite during the heating process in lamination. Additionally, the binding of the dye nanocomposite shows a decrease in the rate of photo-degradation, from -0.0544 /week for the dye chromophore compared to -0.0351 / week for the dye composite nanomaterial. **Fig.7 C,D** show that the photo-degradation does not occur when removed from sunlight for the dye nanocomposite as well.

4.0 Conclusion

The preparation of organic cyanine dye metal oxide nanocomposite has led to a significant overall increase in the thermal stability of the absorbing chromophores. Using an electrochemical deposition ZnO nanoparticles were prepared under oxidative conditions producing large aggregates, which were composed of smaller clusters of ~200 nm particle size. Methods have been reported to produce sizes of less than 200 nm before drying. IR data supports a polar covalent bonding interaction through the carboxylic acid allowing for vibrational interactions between the ZnO and dye. Thermal gravimetric analysis data demonstrates a large increase in the thermal stability from ~ 160 °C for the unbound chromophore to 260 °C when bound as a nanocomposite. UV/Vis spectroscopy also shows increased photo-stability when incorporated into a UV absorbing polymer as a laminate suggesting that ZnO nanoparticles could have applications with chromophores that need to withstand high processing temperatures.

Acknowledgements

This work was supported by the Research Experiences for Undergraduates (REU) Program of the National Science Foundation under Award Number 1263004, equipment support from the National Science Foundation under Award Number CHE-0922815 (DUE-0942672 (DUE-0942672), Strategic Partnership for Industrial Resurgence (SPIR) and the Center for Autonomous Solar Power (CASP).

References

- [1] Emam MEM, Kenawy IMM, Hafez MAH. Study of the thermal decomposition of some new cyanine dispersed dyes. *J. Therm. Anal. Calorim.* 2001;63:75-83.
- [2] Khazraji AC, Hotchandani S, Das S, Kamat PV. Controlling dye (merocyanine-540) aggregation on nanostructured TiO₂ films. an organized assembly approach for enhancing the efficiency of photosensitization. *J. Phys. Chem. B* 1999;103:4693-4700.

- [3] Giese RL, Mukhopadhyay S, Risko C, Marder SR, Brédas J. Design of polymethine dyes for all-optical switching applications: guidance from theoretical and computational studies. *Adv. Mater.* 2014;26:68–84.
- [4] Guo Z, Park S, Yoon J, Shin I. Recent progress in the development of near-infrared fluorescent probes for bioimaging applications. *Chem. Soc. Rev.* 2014;43:16–29.
- [5] Luo S, Zhang E, Su Y, Cheng T, Shi C. A review of NIR dyes in cancer targeting and imaging. *Biomaterials* 2011;32:7127–7138.
- [6] Ullah R, Photocatalytic degradation of organic dyes with manganese-doped ZnO nanoparticles. *J. Hazard. Mater.* 2008;156:194–200.
- [7] Yang S, Tian H, Xiao H, Shang X, Gong X, Yao S, Chen K. Photodegradation of cyanine and merocyanine dyes. *Dyes Pigm.* 2001;49:93–101.
- [8] Wang J, Tsuzuki T, Tang B, Hou X, Sun L, Wang X. Reduced graphene oxide/ZnO composite: reusable adsorbent for pollutant management. *ACS Appl. Mater. Interfaces* 2012;4:3084–3090.
- [9] K.S. Skorenko. Fabrication of solid state dye sensitized solar cells utilizing vapor phase polymerized poly(3,4-ethylenedioxythiophene) hole conducting layer. [dissertation] Binghamton: Binghamton University; 2015.
- [10] Kim YD, Kim JP, Kwon OS, Cho IH. The synthesis and application of thermally stable dyes for ink-jet printed LCD color filters. *Dyes Pigm.* 2009; 81: 45 – 52.
- [11] J.T. JE, Y.J. Huh, M.K. Ma. “Thermal degradation of organic dyes for recordable optical media”. *Mol Cryst Liq Cryst A*. 1998, (316), 375 – 380
- [12] Johns IB, McElhill EA, Smith JO. Thermal stability of organic compounds. *Ind. Eng. Chem. Prod. Res. Dev.* 1962;1:2–6.
- [13] Bojdys MJ, Jeromenok J, Thomas A, Antonietti M. Rational extension of the family of layered, covalent, triazine-based frameworks with regular porosity. *Adv. Mater.* 2010;22:2202–2205.
- [14] Chowa JC, Yu JZ, Watson AJG, Ho SSH, Bohannan TL, Hays MD, Fung KK. The application of thermal methods for determining chemical composition of carbonaceous aerosols: A review. *J. Environ. Sci. Health, Part A: Environ. Sci. Eng. Toxic Hazard. Subst. Control* 2007;42:1521–1541.
- [15] Persson P, Ojamäe L. Periodic Hartree–Fock study of the adsorption of formic acid on ZnO(1010). *Chem. Phys. Lett.* 2000;321:302–308.
- [16] Lenz A, ZnO nanoparticles functionalized with organic acids: an experimental and quantum-chemical study, *J. Phys. Chem. C*. 2009;113:17332–17341.
- [17] Rossini JE, Binding and static quenching behavior of a terthiophene carboxylate on monodispersed zinc oxide nanocrystals. *J. Phys. Chem. C* 2011;115:11–17.

- [18] Wong KK, Effect of ZnO nanoparticle properties on dye-sensitized solar cell performance. ACS Appl. Mater. Interfaces 2012;4:1254–1261.
- [19] Xu L. Hierarchical ZnO nanostructures obtained by electrodeposition. J. Phys. Chem. C. 2007;31:11560-11565.
- [20] Liu HT, Zeng XF, Zhao H, Chen JF. Highly transparent and multifunctional polymer nanohybrid film with superhigh ZnO content synthesized by a bulk polymerization method. Ind. Eng. Chem. Res. 2012;51:6753–6759.
- [21] Horiuchi H, Ishibashi S, Tobita S, Uchida M, Sato M, Toriba K, Otaguro K, Hiratsuka H. Photodegradation Processes of Cyanine Dyes in the Film State Induced by Singlet Molecular Oxygen. J. Phys. Chem. B. 2003;107:7739-7746.
- [22] Yang S, Tian H, Xiao H, Shang X, Gong X, Yao S, Chen K. Photodegradation of cyanine and merocyanine dyes. Dyes and Pigments, 2001;49:93-101.
- [23] Horiuchi H, Ishida S, Matsuzaki K, Tani K, Hashimoto T, Hotta H, Tsunoda K, Kodaira T, Okutsu T, Hiratsuka H. Suppression Mechanism of the Photodegradation of J-Aggregate Thin Films of Cyanine Dyes by Coating with Polysilanes. J. Phys. Chem. C. 2011;115:6902–6909.
- [24] Irick G, Zannucci JS. Photosensitized fading of dyes in polymer films and fabrics. Research Disclosure. 1976;145:37-38

Figure 4:

Figure 5:

Figure 6:

Figure 7:

Graphical Abstract

DYPI-D-15-00857R1

Title: Thermal Stability of ZnO Nanoparticle Bound Organic Chromophores