UV At Work

VARIAN

No: 081

The measurement of absorption edge and band gap properties of novel nanocomposite materials

TichLam Nguyen[a], and Andrew R. Hind PhD[b]

[a] Department of Applied Chemistry, RMIT University, GPO Box 2476V, Melbourne, Victoria, Australia

[b] Varian Australia Pty Ltd, PO Box 222, Clayton South, Victoria, Australia

E-mail: uv@varianinc.com

Abstract

Ultraviolet-visible (UV-Vis) diffuse reflectance measurements of novel nanocomposite structures have been acquired using a Cary 500 spectrophotometer equipped with a Praying Mantis diffuse reflectance accessory (DRA). Based upon the onset of the diffuse reflectance spectra of the powdered materials, the absorption edge and band gap energies of the nanocomposites were determined and compared.

Introduction

Nanocomposites materials are of interest to researchers the world over for various reasons. One driver for such research is the perceived potential for application of these types of nanostructured materials in next-generation electronic and photonic devices. Particles of a nanometer size exhibit unique properties such as quantum effects, short interface migration distances (and times) for photoinduced holes and electrons in photochemical and photocatalytic systems,[1,2,3] and increased sensitivity in thin film sensors.

Intercalation systems provide numerous possibilities for nanocomposite synthesis strategies aimed at the controlled preparation of complex organised structures at the nanoscale level at low temperature. Layered materials with wide band gap semiconductor properties are of potential industrial importance with respect to their application as chemical sensors. Layered phases with appropriate band structures and electronic conductivity exhibit specific redox properties, with the physical properties of the guest matrix modified by the intercalation process. This process is in turn associated with electron/ion transfer and, under the right conditions; hole-electron recombination may be suppressed by charge transfer from the guest to the host semiconductor layer. Photoelectrochemical processes at semiconductor colloid/electrolyte interfaces, such as the splitting of water and reduction of carbon dioxide, have received special attention because of their possible application for the conversion of solar energy into chemical energy.[1]

The present study aimed to directly measure the absorption edge and band-gap energies of these nanostructured materials, based on the onset of UV-Vis diffuse reflectance spectra. This investigation forms part of the semiconductor and microdevice chemistry research program being undertaken by the Department of Applied Chemistry, RMIT University.

Theory

The Praying Mantis DRA is designed to measure diffuse reflectance. Light is projected onto the horizontally positioned sample, and diffusely reflected light is collected by the two large hemispherical mirrors positioned above the sample. This reflected light is then directed toward the instrument detector (Figure 1). The Praying Mantis is ideal for the measurement of samples that must be kept horizontal (such as powders, liquids or pastes), as well as very small samples (image at the sample position is only 3 mm in diameter).

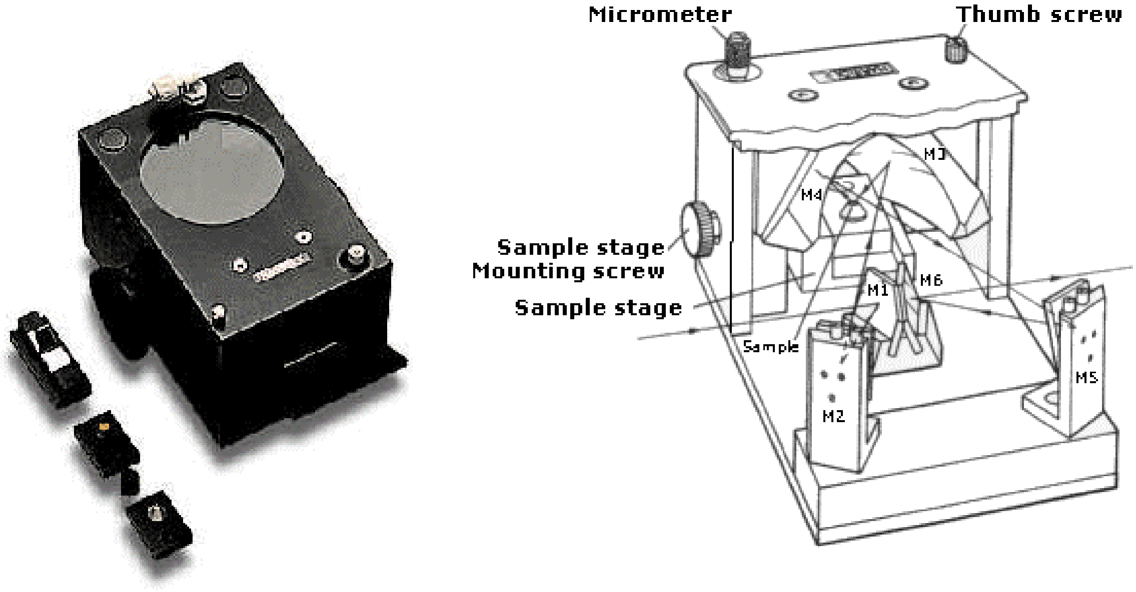

Figure 1. *The Praying Mantis diffuse reflectance accessory and optical diagram*

The absorption edge or band edge is defined as the transition between the strong short-wavelength and the weak long-wavelength absorption in the spectrum of a solid, generally a semiconductor. The spectral position of this edge is determined by the energy separation between the valence and conduction bands of the material in question.[4] In the case of transparent solids, the absorption edge can be measured using transmittance techniques. Diffuse reflectance measurements provide a more appropriate means of measurement for powdered materials.

Materials and Methods

(For part numbers please see Reference 5)

Equipment:

- Varian Cary 500 UV-Vis-NIR Spectrophotometer
- Praying Mantis DRA
- Cary 400/500 Extended Sample Compartment

Protocol

The Praying Mantis DRA was installed into the Cary 500 spectrophotometer and aligned.[6] The 'Scan' software was opened and the appropriate operating parameters set in the 'Cary' window (Figure 2). In addition, the 'SBW' (spectral bandwidth; nm), 'Beam mode' and 'Slit height' were set to '2.000', 'Double', and 'Reduced' respectively in the 'Options' window. Finally, 'Zero/baseline' correction was selected in the 'Baseline' window.

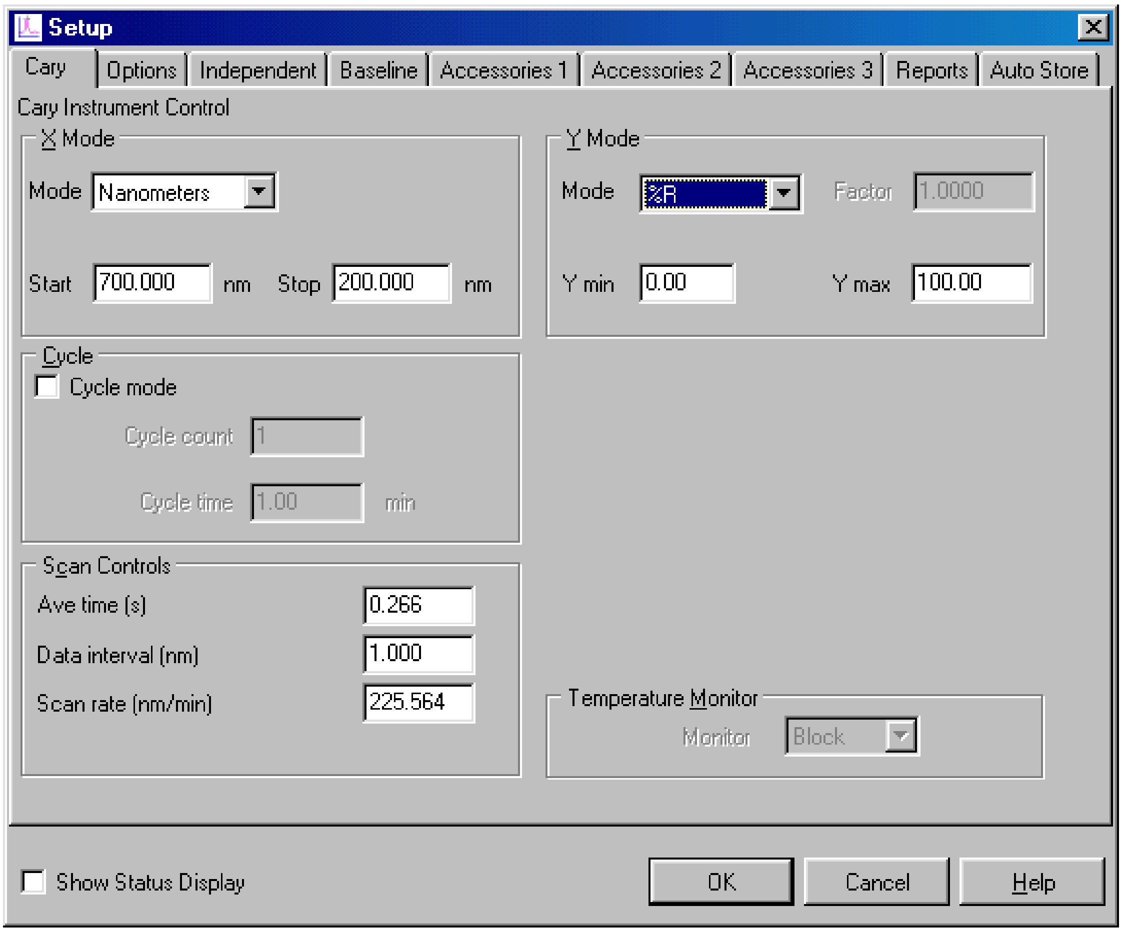

Figure 2. *Instrumental parameters for nanocomposite analysis*

The powdered samples were analyzed using the standard sampling cup supplied with the Praying Mantis accessory. In each instance, the cup was overfilled using the sample funnel and then the surface scraped flat by running a flat blade along the top surface of the sample cup. Attempts were made to make this process as reproducible as possible in order to reduce the likelihood of inter-sample variations in surface flatness and packing density (important for quantitative analyses). All sample spectra were acquired with respect to a powdered Teflon™ background, with the sample cup filled in the same manner as described above.

Results and Discussion

Diffuse reflectance spectra of the nanocomposite materials investigated (including precursors) can be seen in Figure 3. Based on these reflectance spectra the absorption edge for each compound was determined. Using these absorption edge values, the band gap energy was calculated in each instance (Table 1).

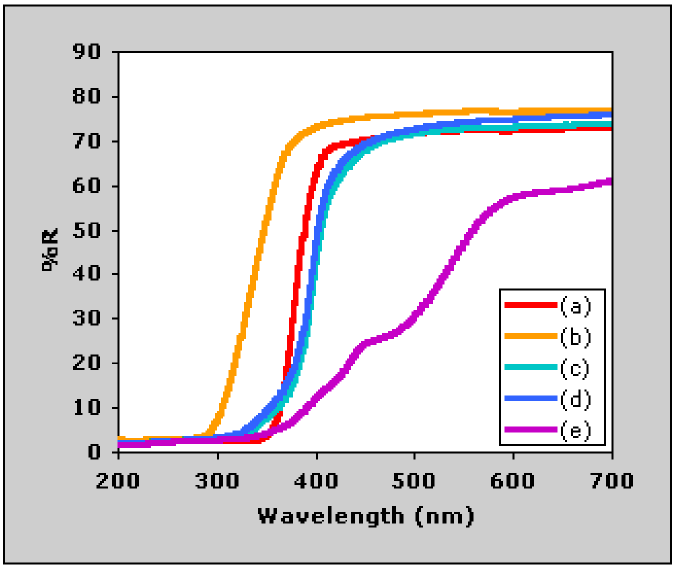

Figure 3. *Diffuse reflectance spectra of nanocomposite materials:* TiO_2 *(a),* $K_2Ti_4O_9$ *(b),* $(C_3H_7NH_3)_2Ti_4O_9$ *(c),* $C_6H_{12}(NH_3)_2Ti_4O_9$ *(d), and* $(Fe_3(CH_3COO)_7OH)Ti_4O_9$ *(e).*

Compound	Absorption Edge (nm)	Band Gap Energy (E_g; eV)
TiO_2	370	3.35
$K_2Ti_4O_9$	310	4.00
$(C_3H_7NH_3)_2Ti_4O_9$	387	3.20
$C_6H_{12}(NH_3)_2Ti_4O_9$	384	3.23
$(Fe_3(CH_3COO)_7OH)Ti_4O_9$	510	2.43

Table 1. *Absorption edges and band gap energies of nanocomposites and precursors.*

The results obtained for the precursor 'semiconductor' material TiO_2 are in general agreement with results reported previously.[1,7] Band gap values for TiO_2 can vary depending on particle size of the material, with smaller band gap values indicative of relatively densely packed crystalline structures.[7] The production of the precursor layered compound $K_2Ti_4O_9$, resulted in an increase in band gap energy relative to the TiO_2 starting material, this trend again being consistent with the literature.[1] In contrast, the intercalation of alkylamino and iron containing species resulted in a significant reduction in band gap energies, with the two alkylamino compounds exhibiting very similar properties in this respect. The iron containing species was found to have the lowest band gap energy of the materials investigated.

Conclusion

Using a Cary 500 spectrophotometer equipped with a Praying Mantis diffuse reflectance accessory, ultraviolet-visible (UV-Vis) diffuse reflectance spectra of novel nanocomposite materials have been acquired. Based upon these diffuse reflectance spectra of the powdered materials, absorption edge and band gap energies of the nanocomposites have been calculated and compared.

The authors would like to acknowledge the Department of Applied Chemistry (RMIT University) and the Cooperative Research Centre for Microtechnology. They would also like to thank Varian Australia Pty Ltd for the use of the Cary 500 UV-Vis-NIR spectrophotometer and Praying Mantis diffuse reflectance accessory.

References

1. Uchida, S., Yamamoto, Y., Fujishiro, Y., Watanabe, A., Ito, O., and Sato, T., 'Intercalation of titanium oxide in layered $H_2Ti_4O_9$ and $H_4Nb_6O_{17}$ and photocatalytic water cleavage with $H_2Ti_4O_9$/(TiO_2, Pt) and $H_4Nb_6O_{17}$/(TiO_2, Pt) nanocomposites', *J. Chem. Soc., Farady Trans.*, 93(17) **1997** 3229.

2. Sato, T., Yamamoto, Y., Fujishiro, Y., and Uchida, S., 'Intercalation of iron oxide in layered $H_2Ti_4O_9$ and $H_4Nb_6O_{17}$: Visible-light induced photocatalytic properties', *J. Chem. Soc., Farady Trans.*, 92(24) **1996** 5089.

3. Sato, T., Masaki, K., Sato, K., Fujishiro, Y., and Okuwaki, A., 'Photocatalytic properties of layered hydrous titanium oxide/CdS-ZnS nanocomposites incorporating CdS-ZnS into the interlayer', *J. Chem. Tech. Biotechnol.*, 67 **1996** 339.

4. Perkampus, H.-H., 'Encyclopedia of Spectroscopy', VCH, **1995** (ISBN 3-527-29281).

5. Part numbers:

Varian Cary 500 UV-Vis-NIR Spectrophotometer:	00 100710 00
Praying Mantis DRA:	00 100469 00
Cary 400/500 Extended Sample Compartment:	00 100466 00
Cary WinUV Scan Software	85 101584 00

6. Cary WinUV Scan Software, 'Cary Help', Version 2.0

7. Hsien, Y.-H., Chang, C.-F., Chen, Y.-H., and Chen, S., 'Photodegradation of aromatic pollutants in water over TiO_2 supported on molecular sieves', *Applied Catalysis B: Environmental*, 31 **2001** 241.