Structural and optical characterization of Zn(OH)$_2$ and its composites with graphite oxides

SM Z. Islam,$^{1,2}$ Taposh Gayen,$^2$ Alaa Moussawi,$^2$ Lingyan Shi,$^3$ Mykola Seredych,$^4$ Teresa J. Bandosz,$^4$ and Robert Alfano$^{1,2,*}$

$^1$Department of Electrical Engineering, The City College of New York, 160 Convent Avenue, New York 10031, USA
$^2$IUSL, Department of Physics, The City College of New York, 160 Convent Avenue, New York 10031, USA
$^3$Department of Bio-medical Engineering, The City College of New York, 160 Convent Avenue, New York 10031, USA
$^4$Department of Chemistry, The City College of New York, 160 Convent Avenue, New York 10031, USA
*Corresponding author: ralfano@sci.ccny.cuny.edu

Received December 4, 2012; revised February 14, 2013; accepted February 14, 2013; posted February 15, 2013 (Doc. ID 180995); published March 14, 2013

The optical properties of zinc (hydr)oxide and its porous composites with 2% and 5% graphite oxide (GO), thus forming ZnGO-2 and ZnGO-5, are investigated using reflectance spectroscopy and two-photon fluorescence (TPF) imaging. The bandgap energies for the Zn(OH)$_2$, ZnGO-2, and ZnGO-5 samples are determined to be in the range between 2.88 and 3.60 eV. The size of light-emitting regions (~from 4.5 to 45 μm) and pore size (~from 20 to 255 μm) are measured using the TPF imaging technique. © 2013 Optical Society of America

OCIS codes: 160.0160, 160.4236, 300.0300, 300.6170.

The subject of energy band structures and critical points of porous microcomposites has attained renewed interest because of the potential applications of these new optical materials in sensors and solar energy convertors [1,2]. The determination of the optical bandgap energies and transitions between critical points (i.e., between valence and conduction bands) are important because they not only control the efficiency for solar conversion and the shape of the optical emission spectrum, but also manifest the effect of structural and thermal disorder on the electronic properties of the composite materials [3]. Direct interband transitions are believed to be responsible for the peaks observed in the derivative of reflectivity with respect to energy of a number of semiconductors and composite materials in the spectral energy range between 1 and 12 eV [4]. Identification of these critical points would provide insight into the band structure of these materials over a wide spectral range of energies, as indicated in [4]. Wavelength modulation techniques using derivatives of normalized reflectance spectra [i.e., $(1/R) (dR/d\nu E)$] and two-photon fluorescence (TPF) imaging techniques have been identified as two most robust methods in the measurement and analysis of bandgap energies and porous and light-emitting regions.

In this Letter, the first-order derivative of reflectance, a modulation technique, as a function of photon energy has been employed to determine the bandgaps and critical transition energies for Zn(OH)$_2$ and its composites with 2% and 5% graphite oxide (GO) as zinc-graphite oxides (referred to as ZnGO-2 and ZnGO-5, respectively). The TPF imaging technique has been used to locate the light-emitting regions and determine the sizes of pores.

Using reflectance spectroscopy GaAs, Zn(OH)$_2$, ZnGO-2, and ZnGO-5 were studied in the energy range from 1.0 to 6.1 eV. The bandgaps for ZnO and GO are reported to be 3.3 [5] and 2.4 eV [6], respectively. The reflectance spectroscopy method has proven to be efficient, as no perturbation is necessary. The interpretation of data poses no ambiguity, but it demands careful elimination of background contributions and the sensitivity of the spectrometer needs to be maintained at a value of $\Delta R/R \geq 10^{-4}$. Using the energy derivative of normalized reflectance data, effects of surface conditions on reflectance measurements are greatly minimized. The reflectance data were obtained at room temperature.

Two-photon excitation microscopy is a fluorescence imaging technique that allows imaging up to a depth of approximately 1 mm. The application of two-photon excitation fluorescence microscopy has become a powerful tool for studying biological functions in live tissues and offers many advantages over conventional imaging techniques. TPF is a technique in which a fluorophor is excited by the simultaneous absorption of two photons. The familiar one-photon fluorescence process involves exciting a fluorophor from the electronic ground state to an excited state by a single photon. This process typically requires photons in the ultraviolet or blue/green spectral range. However, the same excitation process can be generated by the simultaneous absorption of two less energetic photons (typically in the infrared spectral range) under sufficiently intense femtosecond pulse laser illumination [7]. TPF imaging identifies light-emitting regions. It also identifies the pores and void regions of samples. Using this imaging technique, particle size and distribution can be estimated.

Samples of Zn(OH)$_2$, ZnGO-2, and ZnGO-5 have been investigated. GaAs served as a reference sample. ZnGO-2 and ZnGO-5 samples were prepared by synthesis of Zn(OH)$_2$ doped with 2% and 5% GO following reference [2]. GO was synthesized by oxidation of graphite (Sigma-Aldrich) using the Hummers method [8]. The composites were prepared by dispersing GO powder (2 or 5 wt. %) of the final mass of the material in 1.0 L zinc chloride solution (0.05 M). The resulting well-dispersed suspension was stirred for 4 h. Hydr(oxide) solution (0.05 M) was then added (2.0 L) at a rate of 2.0 mL per min using a Titronic Universal. Afterward, the obtained composites were extensively washed with distilled water until neutral pH was achieved and no traces of chloride ions were found. The suspension was centrifuged and a formed gel was dried at 100°C over 48 h. Zinc (hydr)oxide was
prepared in the same way, without the GO in ZnCl₂ solutions. Some details on Zn(OH)₂ are discussed in [2]. The samples were characterized at room temperature by reflectance spectroscopy (Varian’s Cary 500 Scan-Spectro-Photometer) between the spectral UV and NIR ranges. The samples were dispersed in de-ionized water with a fixed concentration (5 mg/ml) [2]. The samples used for reflectance and TPF imaging were all 8 mm in diameter and of 150 μm thickness. The device used to measure the reflectance spectra was designed to calculate absolute reflectance using a pair of matched mirrors as comparison mirrors to perform the calibration and measure the sample’s reflectance.

The reflectance spectra and their derivatives for three samples, Zn(OH)₂, ZnGO-2, and ZnGO-5 shown in Figs. 1(b)–1(d), are very much alike, reflecting the similarity of their band structures. Similar groups in different semiconductors or materials are believed to come from transitions in the similar general areas of the band structures. The bandgap energies of the three samples Zn(OH)₂, ZnGO-2, and ZnGO-5 have been labeled with E₀ and E₁ only. Critical points of transition that have been labeled as E₀, E₀ + Δ₀, E₁, E₁ + Δ₁, E₂, and E₂ were obtained using (1/R)(dR/dE) = 0 for GaAs in [9] and are compared with results reported in [9]. The critical point at E₀ (i.e., E₀) is identified as the bandgap energy, while the critical point at E₀ + Δ₀ corresponds to a transition from the split-off valence band at k = 0, which arises through the spin orbit interaction. The transitions at E₁ and E₁ + Δ₁ corresponding to Λ-point and L-point transitions are also due to spin-orbit splitting. Although the detailed band structure and notation given to GaAs are obtained from [9], the values of pertinent interband transitions are given in Table 1 for GaAs (as a reference), Zn(OH)₂, ZnGO-2, and ZnGO-5.

TPF imaging was performed with the Ultima Multi-Photon-Microscope (Olympus BX-51 of Prairie Tech. Inc., WI, USA). An excitation energy between 1.82 eV (680 nm) and 1.15 eV (1080 nm) was used to conduct TPF imaging. The samples, in particular, were excited with 100 fs laser pulses with an energy of 1.569 eV (i.e., 790 nm) using the Ti-sapphire (Chameleon Ultra II laser, Coherent Inc.) laser, and the fluorescence emitted from the specimen was collected by the photomultiplier tubes after passing barrier filters (450–490 nm).

The two-dimensional (2D) images (239.1 μm × 239.1 μm) produced on the screen (512 × 512 pixels) were recorded, as shown in Fig. 2. For 3D images, we collected Z-series image stacks with defined ranges for the start position, stop position, and step size.

The image stacks were analyzed using Image J software (National Institutes of Health). After importing images into image J, image properties of pixel width

<table>
<thead>
<tr>
<th>Materials</th>
<th>Previous Results (eV)</th>
<th>Present Results (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>E₀ = 1.5192e⁺</td>
<td>E₀ = E₉ = 1.50</td>
</tr>
<tr>
<td></td>
<td>E₀ + Δ₀ = 1.859µ</td>
<td>E₁ = 2.99</td>
</tr>
<tr>
<td></td>
<td>E₁ = 3.017µ</td>
<td>E₁ + Δ₁ = 3.245µ</td>
</tr>
<tr>
<td></td>
<td>E₂ = 3.8⁸</td>
<td>E₂ = 5.11</td>
</tr>
<tr>
<td>Zn(OH)₂</td>
<td>E₀ = E₉ = 2.97c</td>
<td>E₀ = E₉ = 2.98</td>
</tr>
<tr>
<td>ZnGO-2</td>
<td>E₀ = E₉ = 2.93c</td>
<td>E₀ = E₉ = 2.90</td>
</tr>
<tr>
<td>ZnGO-5</td>
<td>E₀ = E₉ = 2.84f</td>
<td>E₀ = E₉ = 2.88</td>
</tr>
</tbody>
</table>

*Ref. [9], measured at 4K.
*Ref. [4].
*Measured by us from absorption edge at room temperature.
direction were and they are clearly as they are deposited on the 318 /0.0006 [av. size, 982 Z ∼ 827 Y [av. size, m 2(c) (c) show that the holes are almost hexagonal in shape. with the pore size ranging ∼ are very similar. [min 20.0 and 551 135 and /0.0006 [av. size, 2(c) direc-

Those in the parent material Zn particles of the inorganic phases are smaller in size than 498 5 143 and /0.0006 [av. size, 2(c) 20.0 to 232 μm. A 3D image for each sample is shown in the insets on the upper-left corner of each figure. Upper-right corner of images show intensity bars of emitted regions of samples, where white color denotes region of maximum emitted light whereas light blue color denotes region of no light. The arrows shown in (a)–(c) show that the holes are almost hexagonal in shape.

(0.467 μm) and height (0.467 μm) in the X and Y directions, and voxel depth (1 μm) in the Z direction were provided. They were then converted into 8 bit images to reconstruct the 3D images. The clearest images were chosen for analysis.

TPF images shown in Figs. 2(a)–2(c) are very similar. These three samples indicate the presence of holes between the aggregates of particles. These holes are almost hexagonal in shape, and these three images also show light-emitting regions that are nothing but the aggregates of nanoparticles. Particle size distribution of luminscent light-emitting regions that are nothing but the aggregates of microparticles vary in size in the studied samples and this unique imaging technique shows the structural details of the composites that are reported for the first time. The current studies on these microcomposites have proven to be very useful as Zn(OH) 2, ZnGO-2, and ZnGO-5 hold promise as new materials for their unique capacities in harvesting solar energy and their storage purposes. The pore sizes are possibly suitable for doping with dye molecules and quantum dots to enhance solar conversion.

This work was supported in part by the army research grant W911NF-10-1-0030 and NSF collaborate grant 1133112.

References