

Time-resolved photoluminescence of Zn(OH)₂ and its composites with graphite oxides

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Time-resolved photoluminescence is used to determine carrier recombination through radiative and nonradiative processes in zinc hydroxide Zn(OH)₂ and its porous composites with graphite oxide (GO). The decay times, measured by a streak camera, are found to be larger for zinc hydroxide (~1215 ± 156 ps) than its composites (~976 ± 81 ps for ZnGO-2 and 742 ± 59 ps for ZnGO-5), but no significant changes in rise times (from 4.0 to 5.0 ps) are recorded. The dominant mechanism for the radiative process is attributed to free carrier recombination, while microporous networks present in these materials are found to be pathways for the nonradiative recombination process via multiphonon emission. © 2013 Optical Society of America

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The study of relaxation processes of photogenerated excess carriers (i.e., electrons and holes) in micro/meso-porous composite materials is important both from the basic physics point of view and for its applications in solar and photodetector devices [1–3]. The radiative process involves exciton and free carrier recombination, and nonradiative (NR) processes involve carrier–phonon and carrier–carrier interactions, and their mechanisms include carrier capture via defect levels (such as pores, voids, stacking faults, etc.) and carrier escape through multiphonon emissions (MPEs). It is of great importance to determine not only the band gap energies and absorption coefficients of zinc hydroxide, Zn(OH)₂ and its composites with graphite oxide (GO), but also their radiative and NR relaxation processes. The composites of Zn(OH)₂ studied herein are ZnGO-2 (with 2 wt. % GO) and ZnGO-5 (with 5 wt. % GO). Mabayoje *et al.* [1] have shown that such materials exhibit photoactivity in the visible light, which suggests their applications as sensors and solar energy harvesting components [2]. The new composites, obtained via an *in situ* precipitation method, involve synthesis of oxygen-containing functional groups from GO and a zinc hydroxide precursor, leading to the formation of interface bonds between the inorganic and graphene-based phases [3]. This interface decisively determines the texture and porosity of the heterogeneous composite materials. The porous structure of the composites significantly influences the carrier relaxation processes. The unique characteristics, such as improved structural and electrical properties, stem from the layered structure of the composites with chemically active oxygen groups at the basal planes of GO. The micro/meso-sizes pores of the composites can accommodate photoactive units (i.e., quantum dots, dye molecules) and offer versatile applications. The quantum efficiency and operating lifetime of the sensors and solar energy converters depend strongly on NR recombination processes,

as the functional nonlinearity of devices has been attributed to the loss mechanisms associated with NR recombination processes [4]. No work of time-resolved photoluminescence (TRPL) has yet been reported on these micro/meso-porous composite materials despite their potential applications as solar adsorptive and sensing devices.

In this Letter, the room-temperature TRPL technique is used to characterize radiative and NR recombination processes in zinc hydroxide Zn(OH)₂, and its composites ZnGO-2 and ZnGO-5. Light-emitting regions and a network of pores of these composite materials are identified via a two-photon fluorescence (TPF) imaging technique. The details of the TPF setup have been reported in an earlier work [5]. Samples of zinc hydroxide and its composites, ZnGO-2 and ZnGO-5, used in these TRPL experiments were synthesized by a scheme reported elsewhere [1–3]. GO was synthesized by oxidation of graphite (Sigma-Aldrich) following the Hummers method [6]. Some details on Zn(OH)₂ and its composites are discussed in [1–3]. Room-temperature PL spectra are found to be in the spectral range between 420 and 550 nm and have already been reported [5].

The experimental setup used for the TRPL experiment is shown in Fig. 1. The 395 nm pulses obtained by frequency doubling the 790 nm, 100 fs, 82 MHz repetition rate pulses from a mode-locked Ti:sapphire laser in a beta barium borate (BBO) crystal were used to excite the samples. The laser beam power density just before impinging on samples was measured to be 34 W/cm². The time evolution of the luminescence was recorded by a streak camera (Hamamatsu model C5680) with a typical temporal resolution of 4 ps. A short-pass filter was used after the second-harmonic BBO crystal to block the 790 nm laser beam, and a long-pass filter was used in front of the streak camera to block the 395 nm laser beam reflected by the sample. A series of band-pass filters, with

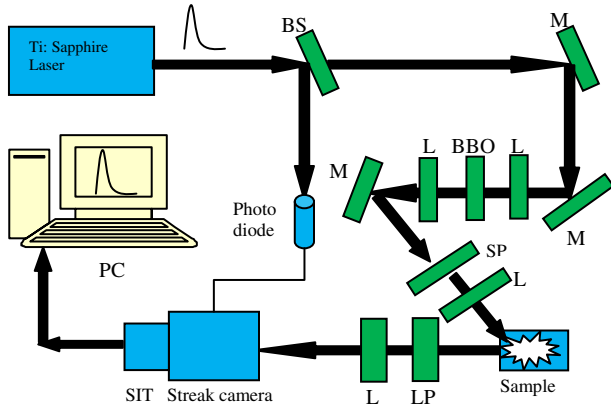


Fig. 1. Schematic diagram of the experimental setup used for time-resolved photoluminescence measurements. M, mirrors; BS, beam splitter; LP, long-pass filter; SP, short-pass filter; BBO, second-harmonic generator; L, lenses; SIT, silicon intensified target.

center wavelengths ranging from 400 to 450 nm and a full width at half-maximum (FWHM) of 10 nm, were used to select the luminescence wavelength range of interest. TRPL spectra of three samples were measured at room temperature by a streak camera. The temporal profiles of PL for three samples Zn(OH)₂, ZnGO-2, and ZnGO-5 are shown in Fig. 2. It shows that all PL traces decay exponentially following their fast nonexponential part. The decay trace can be described by the following equations [7]:

$$I(t) = A_1[e^{-kt^{1/3}-t/\tau_0} - e^{-t/\tau_1}] + A_2[e^{-t/\tau_0} - e^{-t/\tau_1}], \quad (1a)$$

taking, $A_1 = A_2 = A$

$$I(t) = A[e^{-kt^{1/3}-t/\tau_0} + e^{-t/\tau_0} - 2e^{-t/\tau_1}], \quad (1b)$$

where $I(t)$ is the PL intensity at time t ; A_1 and A_2 , the rate constants, show hop-induced energy transfer among acceptors and trap-limited local dynamics, respectively, and these two energy pathways are assumed of equal probability; k is the fast fluorescence diffusion acceptor to acceptor decay rate component at the onset of the relaxation process, which depends on concentrations of

acceptors and the local environment; and τ_1 is the rise time of excited carriers. The TRPL decay phenomena in this material system are found to be consistent with Eq. (1). The first exponential term in Eq. (1b) contains k related to the 2D diffusive decay rate constant, which is strongly influenced by its local environment. The PL lifetime (τ_0) reflects the competition between radiative and NR recombination processes. The PL rise and decay times and the k values (that give best fits) are provided in Table 1. The experimental rise and decay profiles match perfectly well with the fitting curves based on Eq. (1). The PL decay time of Zn(OH)₂ is found to be much greater than its composites, ZnGO-2 and ZnGO-5. This indicates that the NR recombination is more dominant in composite materials than in Zn(OH)₂, which is attributed to the presence of voids and pores, which are more abundant in the composite materials than in Zn(OH)₂, resulting in the short lifetime. The pore sizes and their area coverage in Zn(OH)₂, ZnGO-2, and ZnGO-5 have been reported [5]. The areas of pores in ZnGO-2 and ZnGO-5 are found to be 827 and 982 μm^2 , respectively, as opposed to a much smaller area of 498 μm^2 in Zn(OH)₂ (Fig. 3).

Likewise, the average sizes (i.e., diameter) of micro/meso-pores are found to be $\sim 11.94 \pm 3.21 \mu\text{m}$, $\sim 17.83 \pm 4.52 \mu\text{m}$, and $\sim 23.48 \pm 5.18 \mu\text{m}$, respectively, for Zn(OH)₂, ZnGO-2, and ZnGO-5. Based on TPF images (Fig. 3) of the samples, a model is proposed following the work of Swenberg [7], where light upon emitting from light-emitting regions can transfer either (1) locally as an emitter or (2) nonlocally as a 2D diffusive exciton where motion is a series of uncorrelated hops among acceptors. This model is suitable, as the materials studied herein are amorphous, marked by a lack of translational symmetry of the lattice, and is connected by a network of voids and pores. There have been attempts to explain energy transport, electron-scavenger reaction, and excitonic lifetimes in such materials in terms of hopping and trapping in fractal structures [8]. The decay phenomenon of excited carriers, having carrier density $\sim 1.6 \times 10^{16} \text{ cm}^{-3}$, is an ensemble average over all possible configurations of the acceptors (i.e., voids and pores) distributed over the structure. At high pump

Table 1. Lifetime (τ_0), Rise Time (τ_1), and Fluorescence Decay Rate Constant (k) of Zn(OH)₂, ZnGO-2, and ZnGO-5 Provided Best Fit to Fluorescence (TRPL) Profiles

Sample	Lifetime(τ_0) ps	Rise Time(τ_1) ps	k
Zn(OH) ₂	1215 ± 156	5	0.5
ZnGO-2	976 ± 81	4.5	0.4
ZnGO-5	742 ± 59	4	0.5

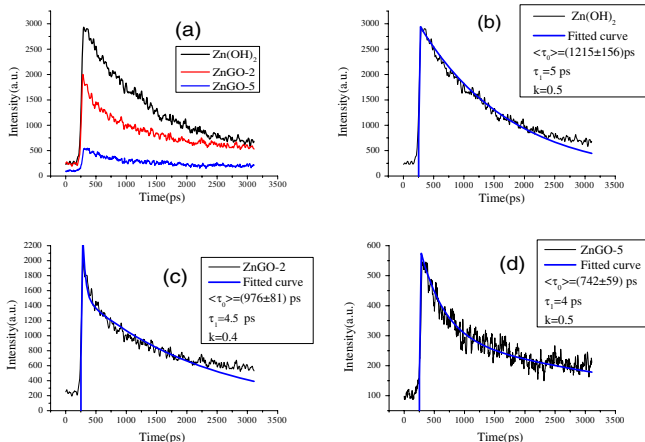


Fig. 2. TRPL spectra of Zn(OH)₂, ZnGO-2, and ZnGO-5 are shown together in (a), and Zn(OH)₂, ZnGO-2, and ZnGO-5 are shown separately in (b)–(d).

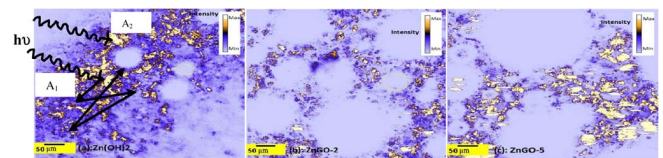


Fig. 3. TPF images show light-emitting regions (i.e., aggregates of particles) and distribution of pores (i.e., white areas) of many sizes in Zn(OH)₂, ZnGO-2, and ZnGO-5, and pathways of light traveling and trapping.

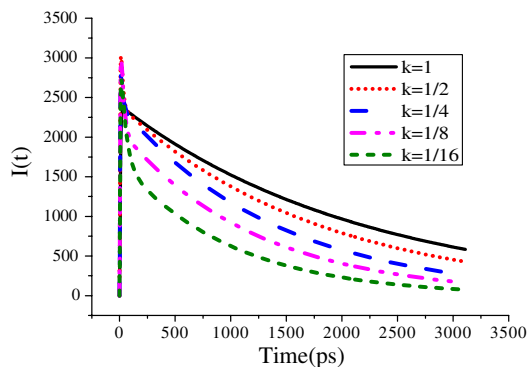


Fig. 4. Fluorescence intensity profiles for different values of fluorescent decay rate constant (k).

intensities, Auger [4] and bimolecular relaxation [7] occurs. Using much lower pump intensity in this study, the carrier dynamics conformed neither with the bimolecular model, as the laser intensity was rather low, nor with the Auger recombination model, as it was an energy-intensity-independent study. The fast component of the highly non-exponential term depends on the dimension and spatial arrangement of the acceptor arrays, which are voids and pores for this material system. The TPF images (Fig. 3) show the pathways to trapping among the various pores and sites to quenching for PL spectra. Larger pores in ZnGO-5 and ZnGO-2 give shorter lifetimes. Whether the pathways to trapping are coherent or incoherent depend on the concentrations as well as the separation distance among the acceptors [7]. The model adopted herein is similar to the “lake model” [7] in photosynthesis where energy transfer is allowed to happen between different sites. An excitation-intensity-dependent study will shed more light on both the nature of energy transport and whether it is

a diffusion-limited process. Figure 4 shows time dependence intensity profiles with the variation of decay rate constants. A higher decay rate constant shows an overall slower decay rate, implying higher separation distances between acceptors and their lower concentrations.

In conclusion, TRPL phenomena in the disordered, micro/meso-porous composite materials have been studied with a streak camera, and shorter lifetimes in the composite materials compared to those in zinc hydroxide have been attributed to the presence of higher and larger pores as opposed to $\text{Zn}(\text{OH})_2$. These micro/meso-porous composite materials will play many roles in devices for harvesting and storing solar energy.

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