

Materials Analysis using Photon-in Photon-out Spectroscopy

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Introduction

Recent interest in nanotechnology and Organic Light Emitting Devices (OLED) has prompted intense research in the electronic structure and optical properties of relevant materials. Here we report recent development and applications of X-ray excited optical luminescence (XEOL) [1-5]. XEOL, using tunable synchrotron light as an excitation source, monitors the optical response following inner shell excitation of an element in a light emitting material in both the energy and time domain. XEOL from several prototype materials will be presented to illustrate its application in material analysis.

Methods and Materials

Methods: In XEOL measurements [1-2], we first record the x-ray absorption near edge structures (XANES) of an element, e.g. carbon K-edge in OLED materials and Si K-edge in silicon nanostructures. Photon energies from below to above the edge are then selected to excite the system. Photoluminescence is recorded with conventional optical monochromator and photomultiplier (PMT) instrumentation. The total luminescence yield (zero order) or the partial luminescence yield (PLY), is in turn used to obtain the XANES. In time-resolved studies, the short synchrotron light pulse is used as a strobe. Here, the PMT signal (~2 ns resolution) is used as the start and the synchrotron pulse (bunch clock) as the stop [3,4]. The time interval between the strobes is used to monitor the intensity decay. A time window (e.g. 0 - 10 ns after excitation) can be selected between pulses. The light emitted within this window is used to record time-resolved XEOL (TRXEOL) and optical XANES. Timing measurements reported here were conducted at the Advanced Photon Source (APS) in a top-up mode, and the Synchrotron Radiation Center (SRC), University of Wisconsin-Madison and the Canadian Light Source (CLS) using a single bunch. The pulse width was <100 ps in all cases and the repetition rate at APS, SRC and CLS was 153 ns, 300 ns, and 570 ns, respectively. A schematic is shown in Fig.1 where the green arrow represents the SR pulse and the red arrow the emission upon the relaxation of the excited state.

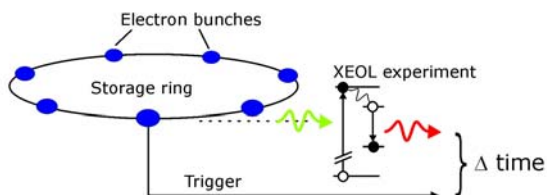


Fig.1 Schematic for time-resolved XEOL measurements

Materials: Si nanowire, Ir(ppy)₃, (ppy = 2-phenylpyridine) and TbCl₃ were used in the measurements reported here. Si

nanowire was prepared in our laboratory. As-prepared SiNW is encapsulated with a thin layer of oxide [6]. Other samples were obtained commercially.

Results

The optical luminescence from Si nanowires (SiNW) excited at the Si K-edge of Si (1840.5 eV) and SiO₂ threshold resonance (1847 eV) is shown in Fig.2 together with decay curves (inset).

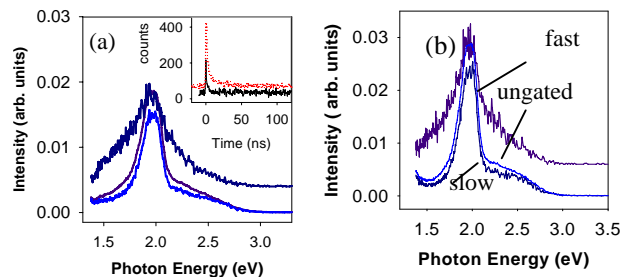


Fig.2 TRXEOL with ungated, fast (0-10 ns) and slow (10-150 ns) window excited at (a) 1840.5 eV and (b) 1847 eV. The fast luminescence was scaled to that of the slow window and shifted up for clarity. The inset in (a) shows the slow and fast decays at 1.97 eV (top) and 2.65 eV (bottom), respectively.

The Si and O K-edge XANES recorded with total electron yield (TEY) and photoluminescence yield (PLY) at selected wavelengths are shown in Fig.3. Results from Figs. 2 and 3 were obtained at the XOR-4idc beamline of APS.

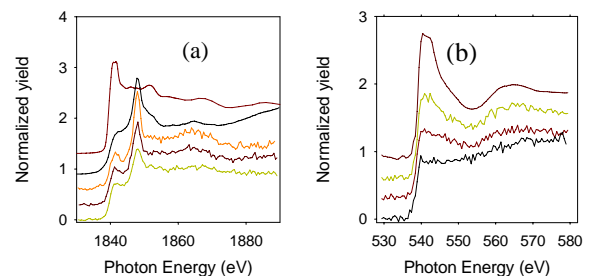


Fig.3 (a) From top to bottom, Si K-edge XANES for Si(100), SiNW in TEY, SiNW in PLY with emission at 1.97 eV (649 nm), 2.36 eV (535 nm) and 2.65 eV (468 nm); (b) From top to bottom, O K-edge of SiNW in TEY and PLY at the same emission wavelengths as shown in (a).

The XEOL, and the Ir M₃ - edge XANES in TEY, FLY and PLY (zero order) for Ir(ppy)₃ are shown in Fig.4

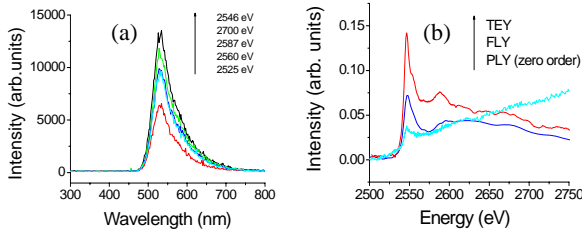


Fig.4 (a) XEOL and (b) Ir M_3 – edge XANES in TEY, FLY and PLY (zero order). Data were obtained at the CSRF DCM beamline at SRC.

The XEOL from Tb^{3+} ion in aqueous solution excited at 2115 eV is shown in Fig. 5 (a). It was collected in vacuum with a liquid cell equipped with a $3\mu m$ Mylar window [8]. The study of XEOL from liquid with soft x-rays opens up new research opportunities. The spectrum exhibits a series of peaks of which the pattern varies little compared with the XEOL from solid $TbCl_3$ at excitation energies near the $N_{5,4}$, $M_{3,2}$ and $L_{3,2}$ -edges [7], and a peak in the UV attributable to emission from the window [8]. Fig. 5(b) shows the 4d - 4f giant resonance of solid $TbCl_3$ at the $Tb N_{5,4}$ -edge. The TEY is compared with the PLY recorded at 484 nm and 546 nm.

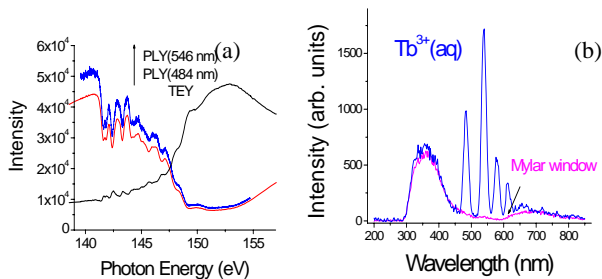


Fig. 5 (a) XEOL from Tb^{3+} (aq) and the Mylar window (Data from the DCM at CSRF). (b) $Tb N_{5,4}$ – edge XANES of $TbCl_3$ (solid): PLY compared with TEY (Data from the PGM at CLS)

Discussion

Si NANOWIRE: The TRXEOL from SiNW (Fig.2) shows that the luminescence spectrum exhibits an intense peak at 1.97 eV (649 nm) accompanied by weak features at 2.36 eV (535 nm) and 2.56 eV (486 nm). The decay of the 1.97 peak is notably slower than that of the shoulder peak (inset). This observation is consistent with recent results that both the Si and the surface oxide encapsulating SiNW contribute to the luminescence [6]. In terms of excitation photon energy, the maximum luminescence occurs at 1847.5 eV, which is the Si 1s to t_2 transition (SiO_2 resonance) with Si in a tetrahedral oxygen environment. While the fast-gated XEOL (0-10 ns) shows a dramatic drop in the branching ratio of the intense peak (1.97 eV) versus the high-energy shoulder, the slow window (10-150 ns) only shows a small reduction in intensity. This observation suggests that the 1.97 eV and 2.65 eV emissions are of different origin, attributable to SiO_2 and elemental nanocrystalline Si, respectively. This is supported by the PLY spectra in Fig. 3(a) where the intensity ratio of Si (1840.5 eV) to SiO_2 (1847 eV) resonance increases from the PLY at 1.97 eV to the PLY at 2.65 eV. This is further confirmed by the observation that the O K-edge PLY (2.65 eV, mainly Si) bears little resemblance to the TEY of SiO_2 while the PLY (1.97 eV, mainly oxide) is the same as the TEY.

Ir(ppy)₃: The luminescence from $Ir(ppy)_3$ excited in the vicinity of the Ir M_3 -edge ($3p_{3/2}$) (Fig.4) shows a green emission band with a shoulder at longer wavelength. The intensity increases across the absorption edge in the PLY as shown in Fig. 4(b). This observation is in contrast to the inverted PLY observed at the C and N K-edge [4] and is attributed to a more effective energy transfer to the triplet state via spin-orbit coupling at the Ir site. The origin of the luminescence is primarily from the triplet states [4]. This is also confirmed by TRXEOL at the Ir L_3 -edge (not shown). Similar behavior is also observed in Ru(II) complexes [9].

Tb^{3+} ION: Another system of considerable interest is the XEOL from 4f elements of the rare earths. Here we select XEOL from Tb^{3+} ($4f^8$) because Tb^{3+} has a nearly invariant emission pattern in most chemical environments since the metal ion is stable and the f orbitals are atomic like. The XEOL shown in Fig.5 (a) is from a 0.5 M Tb^{3+} (aq) solution excited with 2115 eV photon energy. The luminescence shows a characteristic pattern with four strong peaks in green and accompanying weak features originated from 5D_4 - $^7F_{0-6}$, f - f transitions [10]. More details will be discussed elsewhere [7, 8]. XEOL from solid $TbCl_3$ excited with UV and hard x-rays shows nearly the same luminescence pattern. Fig.5 (b) displays the PLY for the 4d - 4f giant resonance at the $Tb N_{5,4}$ -edge. It shows two interesting features: (i) the PLY spectra are inverted; and (ii) the PLY enhances the details of the pre-edge resonance considerably. The details of these results will be reported elsewhere [7]. It is anticipated that this technique combined with high-energy resolution monochromators and cryogenic control will have useful applications in materials analysis from optomagnetic devices to fluorescent proteins.

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