Guided-mode Resonance Enhanced Near-infrared-to-visible Upconversion Fluorescence in a Resonant Waveguide Grating

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Abstract— Guided mode resonance (GMR) enhanced near-infrared (near-IR)-to-visible upconversion fluorescence (UCF) from a rare-earth doped polymer resonant waveguide grating (RWG), comprised of a $NaYF_4$:Yb/Tm nanocrystals doped poly-methyl-methacrylate ($NaYF_4$:Yb/Tm-PMMA) thin layer on top of a textured SU8 substrate with a thin intervening layer of TiO_2. Strong UCF is observed by matching either incoming near-IR excitation or out-going UCF extraction to the GMR wavelengths of the rare-earth doped polymer RWG. The intensity of the UCF can be enhanced up to 10^4 times in visible range and 10^3 times in near-IR range compared with that from a flat area. According to the rigorous coupled-wave analysis calculations, high enhancement of UCF is attributed to the strong local field generated at the TiO_2 waveguide layer due to the resonance between the near-IR excitation light and the GMR. The extraction of the UPF is further promoted when the wavelengths of the UPF resonate with the GMRs.

1. INTRODUCTION

Recently, upconversion (UC) nanocrystals have attracted much attention due to their great potential applications, such as biodetection, bioimaging, solid-state lasers, three-dimensional displays, and solar cells [1–6]. The high efficient yield of UC nanocrystals are typically codoped with lanthanide, including ytterbium (Yb^{3+}) sensitizer ions and activator ions such as erbium (Er^{3+}), thulium (Tm^{3+}) or holmium (Ho^{3+}). The sensitizer of Yb^{3+} ions absorb infrared radiation and then transfer their photon energy to activator ions via multi-photon transition process. Several distinct and narrow emission bands over ultraviolet, visible, and near-infrared wavelengths can be produced from activator ions. Until now, the use of lanthanide-doped UC nanocrytals show considerable advantages [7], for example low toxicity, high chemical stability, and high signal-to-noise ratio, compared with the conventional luminescent labels, such as organic dye molecules, quantum dots, and dye-doped silica/gold nanomaterials.

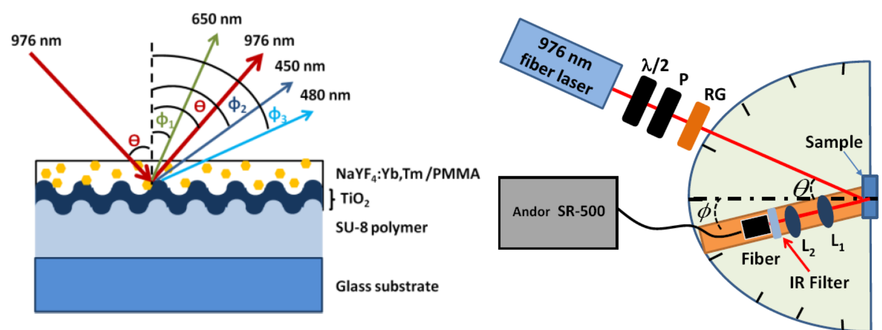
Resonant waveguide grating (RWG) [8–15], that can more efficiently excite and extract the light emitted by fluorescent or nonlinear materials, are widely used in the enhancement of the traditional fluorescence and nonlinear harmonic generation. A RWG typically consists of a high refractive-index grating-waveguide layer and a low refractive-index supporting layer, which can produce very sharp reflection and near zero transmission anomalies that signature the guided mode resonance (GMR). It is very useful for enhancing excitation or extraction of fluorescence signal by aligning either the excitation wavelength or the emission fluorescent spectrum with GMR. Indeed, when the GMR occurs in the RWG, the excitation can be enhanced as a result of the strong local field generated at the surface of grating. If fluorescent molecules are in direct contact with the grating, the fluorescence signal can be improved with this strong local field. When the wavelength of the fluorescence signal overlaps with resonant mode, the extraction of fluorescence signal can be further promoted due to its high reflection.

In this work, we demonstrate an all-dielectric TiO_2 RWG covered with a $NaYF_4$:Yb/Tm nanocrystals doped PMMA ($NaYF_4$:Yb/Tm-PMMA) thin layer to enhance near-infrared (near-IR)-to-visible upconversion fluorescence (UCF). A simple and low cost two-beam interference technique and electron-beam deposition system were used to fabricate the TiO_2 RWG on the scale of mm's. Giant multiplicative enhancement in UCF, combining enhanced excitation and enhanced extraction effects, can be observed up to 10^4 times in visible range and 10^3 times in near-IR range compared with that from a flat area.

2. SAMPLE PREPARATION AND MEASUREMENT SETUP

2.1. Design and Fabrication of RWG

Figure 1(a) shows the schematic design of a 1D RWG with a $NaYF_4$:Yb/Tm-PMMA thin layer. The structure consists of, from top to bottom, a $NaYF_4$:Yb/Tm-PMMA layer, a 1D sinusoidal waveguide-grating (TiO_2), a bottom cladding layer (SU8), and a glass substrate. In order to obtain a TE GMR mode at normal incidence at around 750 nm, the TiO_2 layer was designed to be 60 nm thick (T_{TiO_2}) with periodicity (Λ) of 470 nm. A 1D SU8 grating was first fabricated by a two-beam interference technique [16, 17], and then a TiO_2 layer was deposited on top of SU8 grating by an electron-beam deposition technique. The thickness of SU8 (T_{SU8}) and TiO_2 (T_{TiO_2}) were 1400 nm $\pm$ 100 nm and 60 nm $\pm$ 5 nm by SEM measurement. Total area of the RWG is $6 \times 6\,mm^2$. From AFM measurement, the period (Λ) and depth (d) of grating were determined to be 466 nm and 60 nm $\pm$ 5 nm, respectively.



(a) (b)

Figure 1: (a) Schematic of a 1D RWG covered with a $NaYF_4$:Yb,Tm doped with PMMA layer. (b) UPL measurement setup. RG: long-pass filter, P: polarizer, $\lambda/2$: half-wave plate, L_1-L_2: lenses, θ: incident angle of excitation beam, ϕ: collected angle of UPL signal, and IR Filter: short-pass filter.

The $NaYF_4$:20% Yb, 2% Tm nanocrystalline phosphor was chosen as the upconversion fluorescent material, which was synthesized using a co-precipitation method. The mean sizes of nanoparticles were 30 nm by transmission electron microscopy (TEM) measurement. The $NaYF_4$:Yb/Tm-PMMA with 20 wt% was first dissolved in toluene then spin-coated on the top of the TiO_2 RWG. The RWG with a $NaYF_4$:Yb/TmPMMA layer was then baked for 1 hour at 70°C on a hotplate before use. The thickness (T_N) of the $NaYF_4$:Yb/Tm-PMMA thin layer was 250 nm $\pm$ 50 nm by SEM measurement. The refractive indices of $NaYF_4$:Yb/TmPMMA (n_N), SU8 (n_{SU8}) and TiO_2 (n_{TiO_2}) are 1.485, 2.066 and 1.581 at 0.75 µm obtained by ellipsometry measurements. The refractive index of glass substrate is 1.512 at 0.75 µm. Typical distinct emission bands of a $NaYF_4$:Yb/Tm-PMMA thin film are centered around 450, 480 and 650 excited by 976 nm. The emission bands at 450, 480, and 660 could be assigned to ${}^1D_2 \rightarrow {}^3F_4$, ${}^1G_4 \rightarrow {}^3H_6$, ${}^1G_4 \rightarrow {}^3F_4$ and ${}^1G_4 \rightarrow {}^3H^5$ transitions of Tm^{3+} ion [18], respectively.

2.2. Experimental Setup

In the experiment, a 0.5-W solid-state diode laser at 976 nm was employed as an excitation beam to generate upconversion signal from sample. The collimated beam with a beam size of 0.7 mm diameter was used, and its excitation power was adjusted with the combination of a half-wave plate and a polarizer. A grating spectrometer (Andor Shamrock SR-500i) adopted with one fiber detector was used to collect and analyze the upconversion signal. Before the signal reached the detector, one IR filter was used to block the excitation beam. The transmission spectra of the RWG sample were measured with a halogen white light source and a grating spectrometer (Andor Shamrock SR-500i), the sample was rotated with respect to the incident beam.

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

3.1. Angle-resolved Transmission Spectra of GMR

Figure 2(a) shows the measured transmission spectra of the GMR mode in the RGW, which the transmission spectra as a function of incident angle for TE incidence. In experiment, the normal-incident GMR mode locates at 740 nm, which is closed to the prediction. As the angle increases from the normal incidence, the GMR mode at normal incidence splits into two separate modes, by reason of first order diffraction from the grating: one red-shifts with the incident angle, and the other blue-shifts. Red-shifted dispersion can use to enhance the excitation field, which the excitation wavelength (λ_{ex}) of 976 nm falls into GMR mode when the incident angle (θ) sets 31.5° (highlight in Figure 2). Blue-shifted dispersion can use to enhance the extraction intensity, which the emission wavelength (λ_{em}) of 480 nm matches with the resonance mode at the collection angle (ϕ) of 39° (highlight in Figure 2).

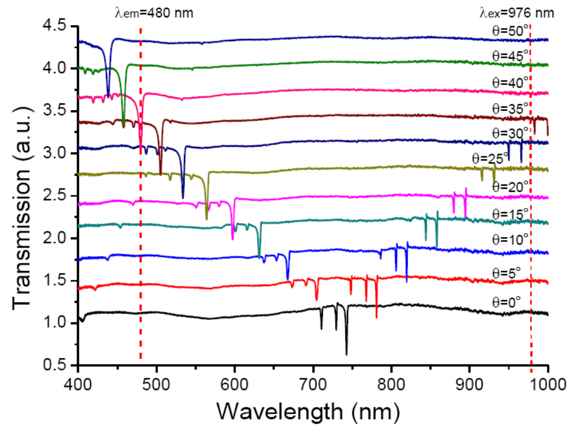


Figure 2: (a) Angle-resolved transmission spectra of the RWG covered with a $NaYF_4$:Yb/Tm-PMMA at the different incident angle (θ) for transverse-electric (TE) mode. **Enhanced excitation:** the excitation wavelength (λ_{ex}) of 976 nm falls into GMR mode when the incident angle (θ) sets 31.5° (highlight). **Enhanced extraction:** the emission wavelength (λ_{em}) of 480 nm matches with the resonance mode at the collection angle (ϕ) of 39° (highlight).

3.2. Enhanced Excitation and Extraction

The resonant excitation for enhancing the UCF signal of the RWG was first investigated. The power of the excitation laser beam was used at 300 mW, and the collection angles (ϕ) of fiber detector set at 0°. The incident angle of illumination beam was scanned from 0° to 35° in 0.25° steps. When the incident angle of excitation beam matches with the GMR ($\theta = 31.5°$), the PL intensity of upconversion spectrum has dramatically increase. Figure 3(a) shows the UCF spectra of the RWG with a $NaYF_4$:Yb/Tm-PMMA thin layer under illuminating the excitation laser beam at the resonant angle ($\theta = 31.5°$). This enhanced UCF causes from the effect of enhancement of the excitation light due to its resonant coupling to GMR mode. The UCF spectra emitted from a flat

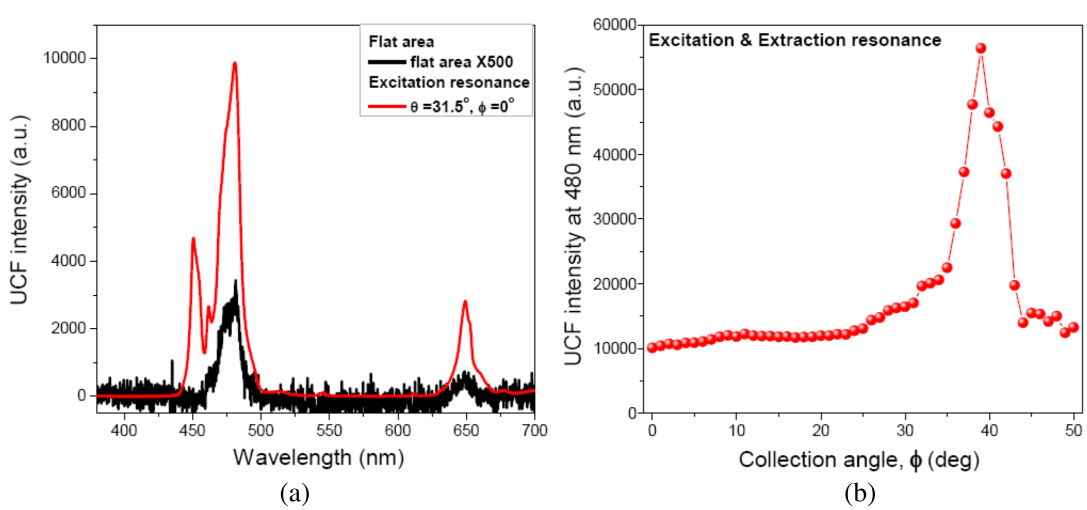


Figure 3: (a) UCF spectra emitted from the RWG with a $NaYF_4$:Yb/Tm-PMMA thin layer under resonance on ($\theta = 31.5°$) and a flat sample. (b) UCF intensity at 480 nm as a function of collecting angle.

sample, which is no grating structure, also plots in Figure 3(a) for comparison. The UCF intensity from the RWG with a $NaYF_4$:Yb/Tm-PMMA thin layer was enhanced by a factor of 2×10^3 compared with that from the flat sample. To further enhance the UCF signal with the RWG with a $NaYF_4$:Yb/Tm-PMMA, we next investigate the effect of enhanced extraction of the fluorescent emission. The RWG sample was illuminated with 976 nm wavelength laser beam at $\theta = 31.5°$, and the collection angle of detector was varied from 0° to 50° in one-degree steps. Figure 3(b) plots UCF intensity at 480 nm as a function of collecting angle. When the collected angle was set at 39°, the UCF intensity reaches a maximum. This is the orientation where 480 nm wavelength light resonant with the RWG, as indicated by one of modes that blue shifts with incident angle in Figure 2. At this resonant condition the UCF intensity at 480 nm was enhanced nearly 6-fold enhancement compared with that collected at 0°. Compared with the UCF intensity from the flat sample, the UCF signal enhanced with both the excitation and extraction at resonance with GMR modes of the RWG produces a total enhancement factor of 10^4 times in visible range. A total enhancement in near-IR range ($\lambda_{em} = 650$ nm) can be obtained to be nearly 10^3 times.

4. CONCLUSIONS

We demonstrated that the UCF signal can be enhanced up to 10^4 times in visible range and 10^3 times in near-IR range by aligning the GMR modes with the incident excitation light and the peak emission wavelengths of a $NaYF_4$:Yb/Tm-PMMA layer in the RWG structure. By setting the incident angle of the 976 nm wavelength laser beam at 31.5°, incident light resonates with the grating wave structure and produced strongly enhanced E-field near the TiO_2 and $NaYF_4$:Yb/Tm-PMMA layer interface, leading to enhance excitation field and a 2×10^3 times enhancement. Furthermore, by setting the collection angle of the detection system at 39° away from the normal direction of the RWG, another 6-fold enhancement of the fluorescent signal at 480 nm wavelength was obtained due to the high reflection of the GMR mode.

ACKNOWLEDGMENT

The authors gratefully acknowledge financial support from the National Science Council, Taiwan, under grant Nos. NSC 98-2112-M194-008-MY3, NSC 99-2112-M194-008-MY3 and NSC 98-2811-M194-007.

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