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Two-Photon Poly(phenylenevinylene) DFB Laser†

Francesco Scotognella,[‡,∥] Daniel P. Puzzo,[§,∥] Margherita Zavelani-Rossi,[‡] Jenny Clark,[⊥] Maria Sebastian,[§] Geoffrey A. Ozin,*[,§] and Guglielmo Lanzani[#]

[‡]*Dipartimento di Fisica, Istituto di Fotonica e Nanotecnologie CNR, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy,* [§]*Department of Chemistry, University of Toronto, 80 St. George Street, Toronto M5S 3H6, Canada,,* [⊥]*Cavendish Laboratory, University of Cambridge, J.J. Thomson Avenue, Cambridge CB3 OHE, United Kingdom, and* [#]*CNST of IIT@polimi, Department of Physics, Politecnico di Milano, Piazza Leonardo Da Vinci 32, 20127 Milano, Italy.* [∥]*F. S. and D. P. P. equally contributed to this work.*

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Two-photon pumped lasing of a poly(phenylenevinylene)-titania-silica (PPV-TiO_2-SiO_2) nanocomposite comprised of PPV synthesized within the void spaces of a multilayer nanoparticle TiO_2 and SiO_2 1D photonic crystal is reported for the first time. With this distributed feedback (DFB) device, we have discovered the surprising result that two photon lasing requires only a factor of 2 higher intensity than one photon lasing thereby allowing laser excitation densities far below those that cause material degradation. The lower excitation density makes possible laser operation in the high-repetition rate regime and the use of compact and cheap NIR pump sources. All this makes our device rather interesting for optical telecommunication applications.

Introduction

Conjugated polymers are well suited for ultrafast photonics, because they have large cross-sections for optical transitions, work like four level systems, and have short excited-state lifetimes.[1] Planar or vertical distributed feedback DFB lasers based on polymers as active material behave well under optical pumping with short laser pulses and have been demonstrated for a variety of materials.[2−5] Under ultrafast optical excitation, polymer DFB lasers work in the gain switching regime and emit laser pulses with duration in the order of a few hundreds femtoseconds.[6,7] This suggests they could be used as ultrafast light converters, or all optical logic gates in optical networks.[8,9] Their application is however hampered by the problem of power dissipation and material damage. At a high-repetition rate, the total power deposited into the organic layer far exceeds the damage threshold, limiting expected applications to disappointing sub-GHz rates. It seems that the beneficial intrinsic properties of high optical non linearity and ultrafast response are nullified by deleterious thermal degradation.[1]

Here we report the first study of two-photon pumped lasing in a hybrid organic/inorganic vertical cavity. The active material is poly(phenylenevinylene), PPV, dispersed in a composite of PPV-TiO_2/SiO_2 in which the TiO_2 and SiO_2 nanoparticles are organized into a one-dimensional photonic crystal (1D PC). The chose of PPV is due to the fact that PPV has been extensively studied in the previous for its interesting properties in two-photon absorption.[10,11] Previous reports of amplified spontaneous emission small molecule crystals and of two-photon pumped polymer lasers were for conjugated polymers other than PPV and using spin-coated films onto 1D and 2D photonic crystal substrates.[12−14] In this study we compare laser pumping by single photon excitation with that of two photon excitation.. We find the unexpected and exciting result that two photon pumping requires only a factor of 2 higher intensity

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*Corresponding author. E-mail: gozin@chem.utoronto.ca.

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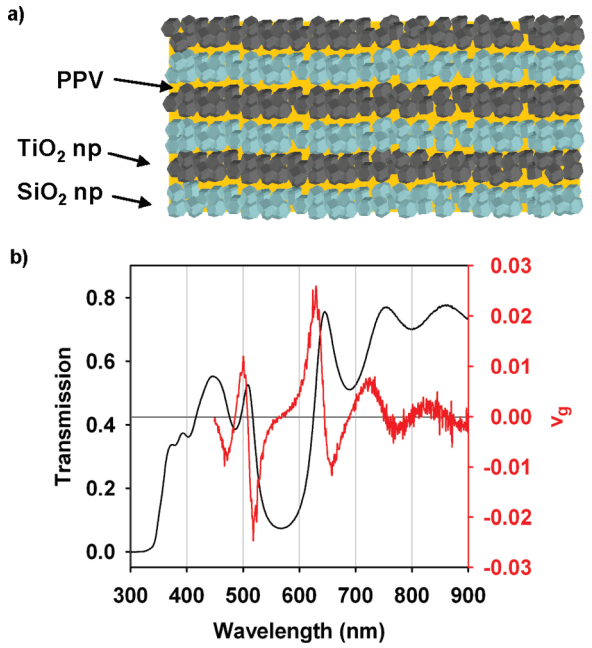

Figure 1. (a) Scheme of the PPV-nanoparticle 1D PC. (b) Transmission optical spectrum and group velocity of the 1D PC, which is highest at the stopband edges.

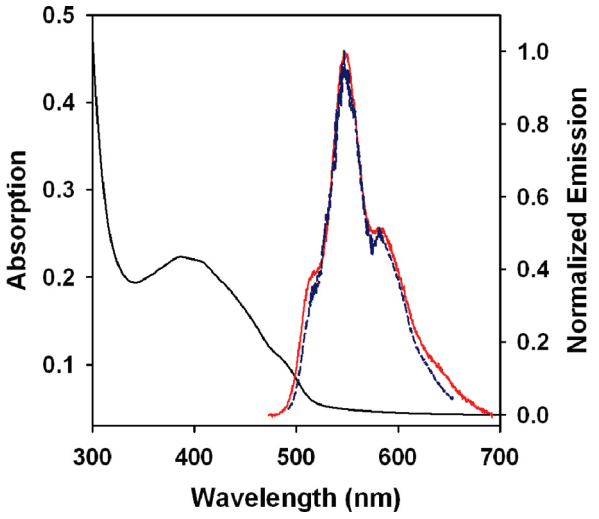

Figure 2. One-photon absorption spectrum of PPV (black line) and emission of PPV by one-photon (red line) and two-photon (blue line) laser excitation.

than one-photon pumping. This allows lasing under much milder pumping condition, far below material degradation.

Experimental Section

The 1D PC sample employed in this study consists of eleven periodically alternating layers of SiO_2 and TiO_2 nanoparticles fabricated by spin coating, obtained through a method already described in the literature.[15−17] The effective refractive indexes of the SiO_2 and TiO_2 layers, determined by ellipsometric porisimetry, are 1.21 and 1.80 at 598 nm, respectively. The nanoparticle layers show significant porosity of 38 and 34% for SiO_2 and TiO_2 layers respectively. The thicknesses of the layers are 140 and 63 nm for SiO_2 and TiO_2, respectively, with a structure total height of about 2 μm. After the 1D PC fabrication, the PPV polymer precursor has been infiltrated in the nanoparticle photonic crystal and the desired composite has been obtained via a reported thermal treatment (Figure 1a).[4,18]

To measure the laser emission of the sample we pumped the device with the fundamental and the second harmonic of an amplified Ti:Sapphire tunable laser (Clark-MXR, Inc.). The selected wavelengths were 780 nm and its second harmonic at 390 nm obtained by frequency doubling in a beta barium borate crystal (pulse duration of 180 fs, repletion rate of 1 kHz). The sample has been excited obliquely by the pump laser focused by a 500 mm lens, whereas the laser emission was collected normal to the substrate by an optical multichannel analyzer (OMA) (1.2 nm resolution).

Discussion

In Figure 2, the absorption spectrum of the PPV is depicted (black line). We have excited the PPV film by single-photon (second harmonic at 390 nm) and two-photon (fundamental at 780 nm) pumping and we have recorded the emission spectra. The emission spectra are identical for single and two-photon pumping (see Figure 2). According to the Kasha rule,[19] in both cases the emission state is the same.

In Figure 3, the laser emission and the laser characteristics for the two types of pumping are shown. Laser emission appears as a narrow line (Figure 3a,c) at the blue-edge of the photonic stopband, according to the theory of the distributed feedback laser.[20−22] The peaks are centered at 520 and 530 nm for one-photon and two-photon pumping, respectively. The red shift of the two-photon pumped laser emission is discussed later. In panels b and d in Figure 3, we plot the input-output (i.e., excitation energy − output intensity) characteristics of the emission (for single- and two-photon pumping). They show the typical signatures of laser action, namely a clear threshold at approximately 180 μJ/cm^2 and 150 μJ/cm^2 for single0 and two-photon pumping, respectively, with concomitant line narrowing (from ~40 nm to ~3 nm) and a linear increase for higher excitation energies. It is remarkable that we have not observed amplified spontaneous emission in a PPV sample out of the cavity.[4,23] In terms of photon/cm^2, the laser thresholds are $T_{1ph} = 3.5 \times 10^{14}$ photon/cm^2 and $T_{2ph} = 5.9 \times 10^{14}$ photon/cm^2.

It is remarkable that the two-photon threshold is of a magnitude comparable to the one for single photon pumping. We can provide some comments on this observation.

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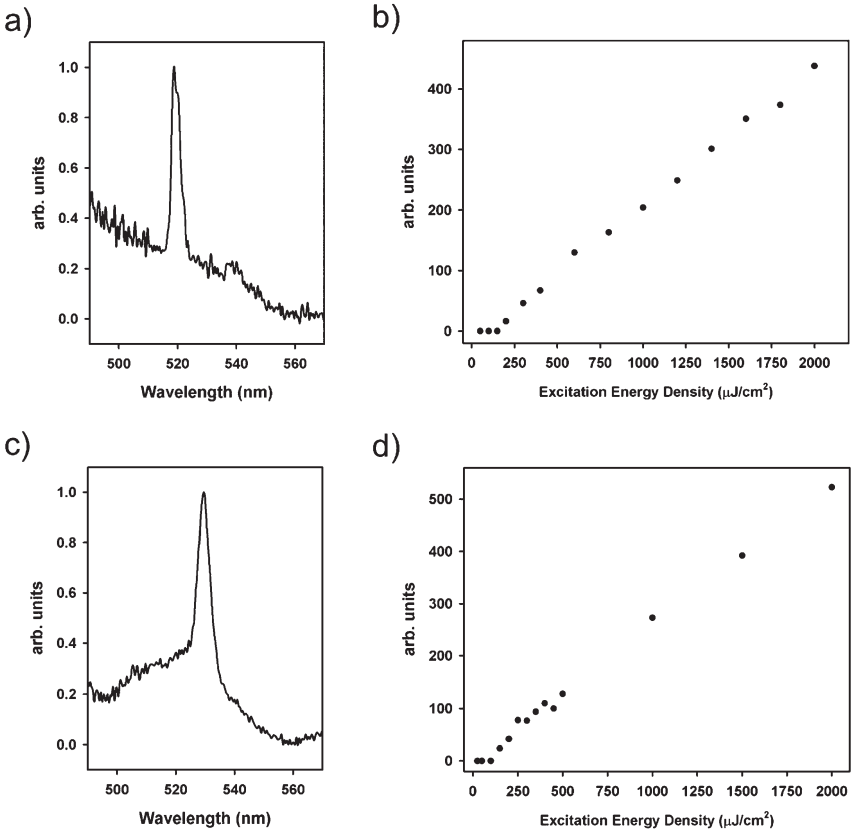

Figure 3. (a) Laser emission spectrum using 390 nm excitation; (b) laser input−output characteristics for 390 nm excitation; (c) laser emission spectrum using 780 nm excitation; (d) laser input−output characteristics for 780 nm excitation.

According to the non linear Lambert−Beer law

$$\frac{dI}{dz} = -N_0\sigma I - N_0\gamma I^2 \qquad (1)$$

where σ and γ are first- and second-order absorption cross-sections, I the light intensity, z the direction of propagation, and N_0 the ground-state population. For polymers, a typical value of σ is 1×10^5 cm^{-1}, whereas γ has a value that is between 1×10^{-48} and 1×10^{-45} cm^4 s/photon.[24] Considering that the spot sizes for single-photon and two-photon pumping are 5×10^{-4} cm^2 and 2×10^{-3} cm^2, respectively the number of photons at threshold are

$$N_{\mathrm{th}}{}^{(I)} = 1.7 \times 10^{11}\text{photon}$$

$$^{N_{\mathrm{th}}(2)} = 2.8 \times 10^{11}\text{ photon for } \gamma = 1$$
$$\times 10^{-45}\text{ cm}^4\text{ s/photon, corresponding to maximum } \gamma \text{ value}$$

$$N_{\mathrm{th}}{}^{(2)} = 1 \times 10^8\text{ photon for } \gamma = 1$$
$$\times 10^{-48}\text{ cm}^4\text{ s/photon, corresponding to minimum } \gamma \text{ value}$$

To get a deeper insight in the physical process we have to take into account the density per volume. As a matter of fact, we have to consider two different volumes for the different types of pumping (Figure 4). For the single photon, the penetration depth is a few hundreds of nanometers into the sample, due to the high absorption cross-section. On the contrary, for the two-photon pumping, because of the much-lower-absorption cross-section, the penetration depth is the entire depth of the sample, that is about 2 μm thickness. Note for the two-photon process we also consider the fact that at 780 nm wavelength there is an increase in the photon density of states due to the photonic structure (Figure 1b), so we assume that the 780 nm excitation goes back and forth at least two times in the device, and thus the effective sample length is about 4 μm. Thus, we have volumes of 1×10^{-8} cm^3 and 8×10^{-7} cm^3 for single- and two-photon absorption, respectively giving a volume density of absorbed photons of

$$N_{\mathrm{th}}{}^{(1)}/V = 1.7 \times 10^{19}\text{ photon/cm}^3$$

$$N_{\mathrm{th}}{}^{(2)}/V = 7$$
$$\times 10^{17}\text{photon/cm}^3\ (\gamma = 1 \times 10^{-45}\text{ cm}^4\text{ s/photon})$$

$$N_{\mathrm{th}}{}^{(2)}/V = 1.25$$
$$\times 10^{14}\text{ photon/cm}^3\ (\gamma = 1 \times 10^{-48}\text{ cm}^4\text{ s/photon})$$

From these results, it appears that lasing under two-photon pumping involves a much lower density of excited

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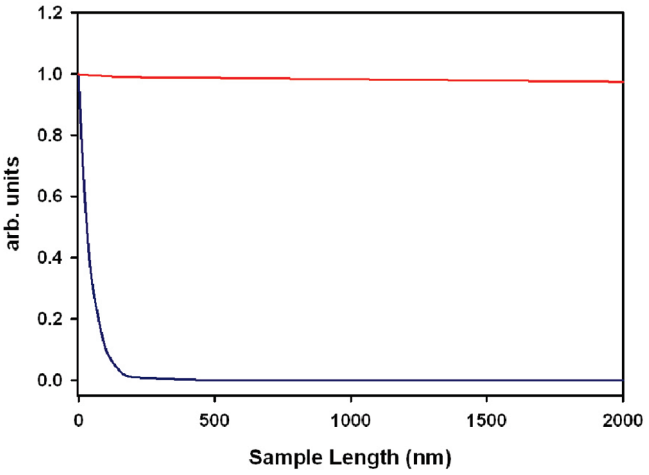

Figure 4. Simulation of the absorption depth for one- (red) and two-photon (blue) pumping, according to eq 1 with values given in the text.

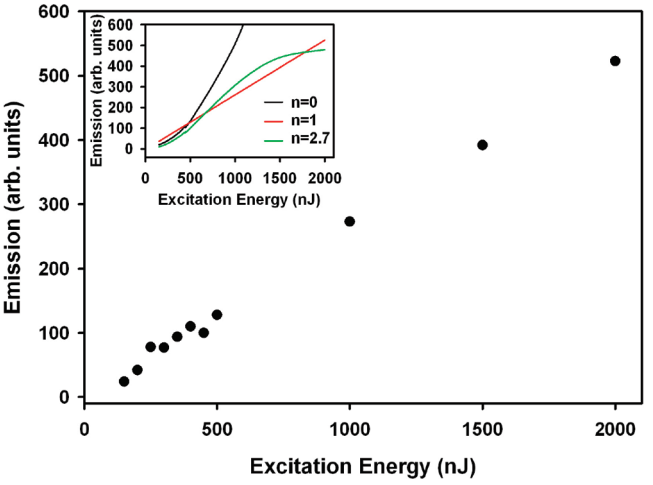

Figure 5. Experimental data of the two-photon pumping characteristics above threshold and simulation according to eq 2b with intensity-dependent losses proportional to $I^{2.7}$ (black line) and I (red line).

states, with advantages for nonlinear loss mechanisms such as singlet annihilation and charge separation.

Moreover, by converting the measured threshold per pulse in W/cm^3 (using for the optical gap of PPV a value of 2.5 eV) and assuming a repetition rate of 1 THz we obtain a total excitation power density for two-photon pumping of about 50 MW/cm^3 (with $\gamma = 1 \times 10^{-48}$ cm^4 s/photon), whereas that for one photon pumping is 6.8 TW/cm^3. Considering that the damage threshold power density P_{th}^{D} of a polymer slab under cw excitation has been estimated at about 100 MW/cm^3, we arrive at the striking conclusion that in our DFB laser, two-photon pumping allows for higher-repetition-rate excitation than by using one-photon pumping. In fact, using two-photon pumping, it would be possible to operate in the THz regime, without causing material degradation, whereas one-photon pumping would at most support a 100 MHz repetition rate. This is a crucial observation for developing new polymer-based telecommunication laser systems.

Finally, we can ascribe the red shift of the two-photon pumping laser emission (from 520 to 530 nm) to the larger optical path of the 780 nm excitation inside the sample. In fact, 390 nm excitation is absorbed by the gain material in the first layers of the photonic crystal (that provides the distributed feedback), whereas the 780 nm excitation is absorbed throughout the thickness of the whole device. It is known that the more unit cells of a photonic crystal below the infinite crystal limit the narrower is the Bragg peak. So, with two-photon pumping, the Bragg peak is narrower than for one-photon pumping, whereas the Bragg central wavelength remains the same for both cases, hence the blue edge of the stopband is red-shifted and concomitantly the two-photon wavelength, relative to the one-photon lasing wavelength, is also red-shifted.

Another interesting and unexpected observation is that the laser input-output characteristic is fairly linear under both pumping conditions, whereas photoluminescence is quadratic for two-photon pumping. To understand this behavior at a qualitative level we write the density of photons Φ in the cavity in the steady-state regime (assuming that the pulse duration and cavity photon lifetime are comparable), taking into account the intensity-dependent losses. The latter come from the conjecture that high-intensity excitation may cause charge-carrier generation by multi photon excitations to higher lying auto ionizing states. The density of photons in the DFB can be written as follows for single- and two-photon pumping, respectively

$$\phi = \frac{\rho I}{\gamma_0 + \gamma_1 I^2} \tag{2a}$$

$$\phi = \frac{\rho I^2}{\gamma_0 + \gamma_1 I^n} \tag{2b}$$

where ρ is a coefficient proportional to the pumping rate, and γ_0 and γ_1 are coefficients for linear and nonlinear loss rates, respectively. Using eqs 2a and 2b, we obtain a numerical simulation of the input-output characteristics suggesting that the quasi-linear dependence found for two-photon pumping might result from a balance between intensity dependent absorption and intensity-dependent losses. In Figure 5, the experimental data of the two-photon pumped laser emission above threshold are reported, whereas in the inset, different simulations according to eq 2b are depicted (for $n = 0$, 1, and 2.7). For $n = 0$ (black line), the simulation shows a behavior without intensity-dependent losses, very far from the behavior of the experimental data. For $n = 2.7$, the intensity-dependent losses are caused by charge induced absorption, i.e. the intensity is high enough to give rise also to higher order transitions such as two-photon-one-step (as observed experimentally[25]), leading to autoionizing states. This simulation (red line in the inset of Figure 5) does not properly fit the experimental data, becaise unknown additional losses that need further investigation are not taken into account in this model. It is remarkable that a simulation where the intensity dependent losses in eq 2b are proportional to I ($n = 1$, green line) very well fits the linear behavior of the data, but also these linearly

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intensity-dependent losses have to be convalited via further experimental investigations.

Conclusion

In conclusion, we demonstrated lasing by two-photon pumping in nanoparticle-based 1D PC DFB geometry using PPV as active material. Our results show that two-photon pumping in vertical cavity has considerable advantages compared to single-photon pumping. In particular, the excitation density at the laser threshold is much lower with two photon compared to one photon pumping due to the lower absorption coefficient, which leads to lower nonlinear losses and larger mode volume. This has important technological impact, because the lower excitation density allows laser operation at higher repetition rate, as appropriate for information and communication technology (ICT) applications. Moreover, it allows using NIR solid-state pump sources, which are cheaper and more compact compared to the UV versions. So, the two-photon pumped vertical cavity device we introduced appears to be a potential breakthrough in the organic ICT technology.

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