

Excitation density dependence of the sensitivity enhancement of oxygen optical sensing by Amplified Spontaneous Emission in poly(9,9-dioctylfluorene) waveguides

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In this work we describe our recent results on optical gas sensors based on light emission quenching in active conjugated polymers. The complete work can be found in [1].

The development of novel active systems for gas sensing is receiving increasing attention due to the very wide range of possible applications. In particular the oxygen detection is particularly interesting in the medical field for the monitoring of oxygen content in both air and blood, as well as in the environmental monitoring field. Among the different proposed techniques optical sensors, based on the oxygen induced photoluminescence quenching, are characterized by fast response time and high sensitivity. The typical active systems are blends between an inert matrix and a phosphorescent molecule, while reversible oxygen induced fluorescent quenching in poly(9,9-dioctylfluorene) (PF8) neat films was recently demonstrated by our group [2]. A recent breakthrough in the sensitivity enhancement was represented by the demonstration that in neat active films showing optical gain, the Amplified Spontaneous Emission (ASE) and the laser intensity show a stronger relative quenching with respect to the Spontaneous Emission (SE) [3], exploited in efficient explosive vapors detection. This first results was followed by similar demonstration of explosive detection in PF8 and in the few evidences of oxygen detection.

In this work we demonstrate reversible oxygen induced emission quenching of both the Spontaneous Emission (SE) and the Amplified Spontaneous Emission (ASE) in a PF8 waveguide. We demonstrate that the ASE quenching allows us to reach a detection sensitivity up to 6.2 times larger than the SE one. We observe that the sensitivity enhancement clearly decreases as the excitation density increases discussing, for the first time, the origin of this effect, already observed in other active systems but, to date, without explanation.

The PF8 film, with a thickness of about 650 nm, was realized by spin coating on a glass substrate of a $3 \cdot 10^{-4}$ M solution in toluene. The

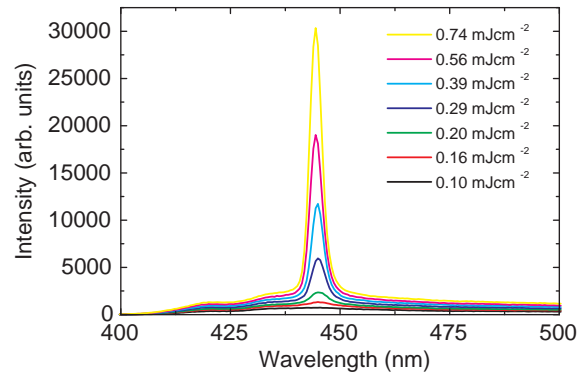


Figure 1. Excitation density dependence of the PL spectra measured in vacuum. A clear ASE band is observed in the spectra for excitation density higher than about $125 \mu Jcm^{-2}$.

sample was pumped by a Nitrogen laser (337 nm) delivering 3 ns pulses with a repetition rate of 10 Hz, focused in a $6.6 \text{ mm} \times 100 \mu\text{m}$ rectangular stripe by a cylindrical lens. The PL was collected from the sample edge, dispersed by a TRIAX 320 monochromator with a 150 l/mm diffraction grating and detected by a Peltier cooled Si-Charge Coupled Device (CCD). The spectral resolution was about 2 nm. The spectral effect of the oxygen were investigated by comparing the PL spectra measured in air with the ones measured in vacuum (about 10^{-3} mbar), as a function of the excitation density.

The PL spectra in vacuum (see Fig.1), at low excitation density, show the typical features of the Spontaneous Emission (SE) of the PF8 glassy phase, with a first peak at about 420 nm, followed by the vibronic replica. As the excitation density increases above about $120 \mu Jcm^{-2}$ a clear band due to Amplified Spontaneous Emission (ASE) is observed at about 445 nm, with an intensity strongly increasing with the excitation density.

Qualitatively similar results are obtained when

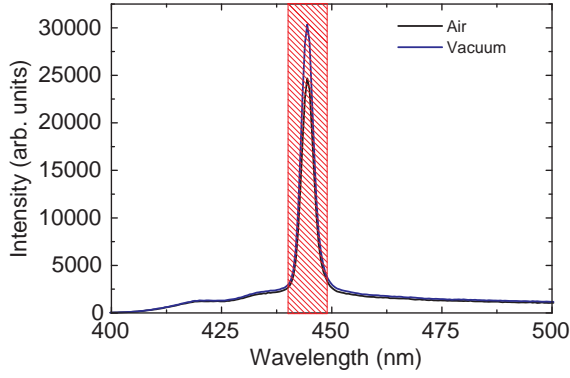


Figure 2. Emission spectra at 0.79 mJcm^{-2} in vacuum and in air, evidencing the clearly stronger intensity quenching of the ASE band (dashed area) with respect to the spontaneous emission one.

the measurement are performed in air, but the minimum excitation density to observe ASE increases up to about $150 \mu\text{Jcm}^{-2}$, and a clear intensity reduction is observed both for the SE and the ASE, clearly stronger for ASE than for SE (see Fig.2).

In order to quantitatively investigate the intensity quenching of SE and ASE, due to oxygen induced reversible quenching, we determined the emission intensities in vacuum (I_{vac}) and in air (I_{air}), by integrating the spectra in the range 410-430 nm for SE and 441-449 nm for ASE, thus determining the relative intensity quenching defined as:

$$\frac{\Delta I}{I} = \frac{I_{vac} - I_{air}}{I_{vac}} \quad (1)$$

The main results are (see Fig. 3):

1. Comparable relative quenching around 10% are observed in the two spectral bands below the ASE threshold, consistently with a general emission spectra intensity reduction without lineshape variations;
2. The ASE relative quenching rapidly increases above the ASE threshold, reaches a maximum of 23% at about 0.2 mJ cm^{-2} and then progressively decreases for higher densities, down to 18% at 0.74 mJ cm^{-2} ;
3. The SE relative quenching progressively decreases with the excitation density, down to about 6% at 0.74 mJ cm^{-2} .

These results clearly show that the detection of the emission intensity of the ASE band allows

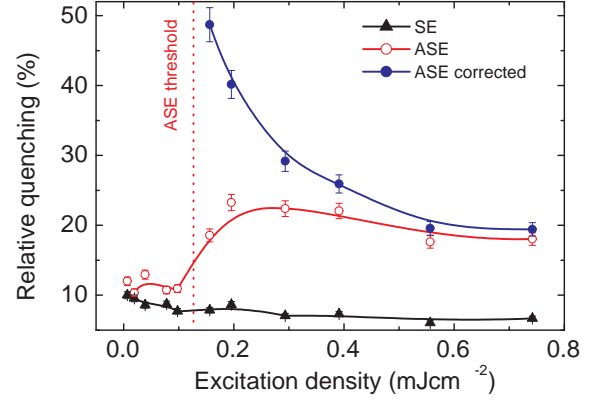


Figure 3. Excitation density dependence of the SE, ASE, and corrected ASE relative intensity quenching.

to increase the oxygen detection sensitivity with respect to the use of SE, up to more than 3 times. It is also interesting to observe that the observed oxygen sensitivity improvement is much higher than the one observed in PF8 based explosive vapors sensors suggesting a stronger reversible interaction of PF8 with oxygen with respect to nitroaromatic vapors. Moreover the maximum ASE relative quenching is observed just above the ASE threshold, when the relative contribution of the background SE in the ASE intensity detection band is maximum. When the SE quenching contribution is subtracted a maximum *corrected* ASE relative quenching of about 49% is observed just above threshold, again with a clear progressive decrease down to about 19% at 0.74 mJ cm^{-2} .

Our results clearly show that both SE and ASE relative quenching are clearly excitation density dependent, with a clear decrease as the excitation density increases, stronger for the ASE than for the SE relative quenching. A similar ASE quenching decrease at high excitation density has been to date often observed in similar optical sensing experiments, but rather surprisingly it has never been discussed at any detail level.

Generally speaking the emission quenching depends both on two independent factors, namely the number of excitons quenched by the PF8-oxygen interaction, and the strength of the intensity dependence on the exciton density.

Concerning the strength of the intensity dependence on the exciton density, the SE intensity is directly proportional to the exciton density, while the ASE intensity superlinearly increases almost exponentially with the exciton population

(far from saturation).

Moreover the ability of any analyte to quench the active material emission is related to the relative value of the molecule-analyte interaction rate (k_0) with respect to the exciton relaxation rate (k), thus the fraction of quenched excitons increases with the k_0/k ratio.

Considering that in our case the intrinsic exciton relaxation pathways are the spontaneous emission and the stimulated emission, the intrinsic exciton relaxation rate is given by $k = k_{SE} + k_{ASE}$, where k_{SE} and k_{ASE} are the decay rate of SE and ASE, respectively.

Below the ASE threshold k_{SE} does not depend on the excitation density and $k_{ASE} = 0$, thus the fraction of quenched exciton is independent on the excitation density, resulting in a constant relative intensity quenching, as observed. In this regime the relative intensity quenching directly measures the fraction of quenched excitons, which in our case is then about 10%.

Above the ASE threshold, ASE progressively becomes the main relaxation process due to the progressive increase of k_{ASE} , resulting in a decrease of the fraction of excitons decaying by SE, and of the fraction of quenched exciton, thus proportionally reducing the SE relative quenching, as observed.

Concerning the ASE relative quenching, just above threshold the fraction of quenched excitons can be expected to be close to the just below threshold value (thus still of the order of 10%), and the exponential ASE intensity dependence on the exciton number leads to a much stronger intensity decrease of the ASE band with respect to the SE one, leading to the observed higher ASE relative quenching with respect to the SE one.

As the excitation density increases the ASE intensity superlinearly increases, indicating an increase of the strength of the intensity dependence on the excitation density, which should lead to a progressive increase of the ASE relative quenching, which is instead not present. This indicates that the reduction of the fraction of quenched excitons, that is also due to the k_{ASE} increase, is the dominating factor in determining the sensitivity, resulting in a progressive sensitivity decrease as the excitation density increases.

In conclusion we observed a reversible oxygen induced quenching of the PF8 SE and ASE, demonstrating that the ASE quenching can allow a higher sensitivity of an oxygen optical sensor. We also suggest that the strong excitation density dependence of k_{ASE} has a stronger effect on the reduction of the fraction of quenched excitons than in the intensity increase, thus limiting the potentiality of sensitivity improvement

of ASE with respect to SE.

This conclusion is expected to be of general validity, as an ASE sensitivity decrease with the excitation density is always reported in similar experiments, and suggest that, rather counter-intuitively, the superlinear dependence of the ASE on the exciton density is both the factor determining the sensitivity improvement and the factor limiting the maximum value of the sensitivity.

REFERENCES

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