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Abstract

Recent Improvements on Double-Parametric Optical Sensing of O_2 Exploiting Near-Infrared Luminescence of Mixed-Phase Anatase/Rutile TiO_2 Nanoparticles †

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Abstract: Mixed-phase titanium dioxide (TiO_2) can be effectively employed as photoluminescence (PL) based ratiometric optical sensor of O_2, thanks to its peculiar "anti-correlated" PL responses to O_2 of anatase and rutile TiO_2 polymorphs. We discuss how to exploit the simultaneous detection of luminescence arising from anatase and rutile TiO_2 nanoparticles to obtain a responsivity which is, by construction, larger than the one obtainable through other gas-responsive oxides via the same PL-based approach. Furthermore, we illustrate our recent improvements on sensor sensitivity and stability for O_2 concentrations ranging in the 10–100 ppm interval.

Keywords: oxygen sensing; optical sensing; dynamic/static photoluminescence quenching; titanium dioxide; anatase; rutile; defects; electron–hole recombination

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Introduction

Different applications in the field of environmental and biomedical sciences involve measuring the concentration of molecular oxygen (O_2) in aqueous and/or gaseous environments. To mention a few examples, we can cite the monitoring of the O_2 concentration in the exhaust stream of internal combustion engines, the correlation between the state of health of marine habitats, and the concentration values of dissolved oxygen (DO), or the behavior of cancer cells based on their hypoxia/re-oxygenation state.

Technical approaches to this issue based on photoluminescence (PL) intensity measurements receive great attention, due to a number of advantageous characteristics of optical approaches, including fast response times, no need of electrical contacts, possibility to perform sensitive measurements at room temperature, and multi-parametric responses involving the different degrees of freedom (e.g., intensity, luminescence lifetime, refractive index, polarization, etc.) that characterize the light.

Most of the optical sensors developed for O_2 detection are based on the dynamic quenching of the PL intensity of a sensitive material, related to the local O_2 concentration via the well-known Stern–Volmer formula. In most cases, organic dyes are employed as O_2-sensitive luminescent materials, although a number of inorganic semiconductor

nanomaterials, such as porous silicon and different metal oxides, also exhibit environment-dependent PL emission.

The simplest approach to PL-based optochemical sensing is based on intensity measurement of the PL emission. Unfortunately, this approach is quite prone to errors: fluctuations in the excitation light intensity can hinder the understanding of the experimental data when real-time monitoring is performed and small integration times in the PL measurement have to be used. Therefore, a great deal of technical improvements rely on using an internal PL reference: such methods, known as "ratiometric", are based on the acquisition of the ratio between the PL intensity of an O_2-sensitive species ("indicator") and the PL intensity of an O_2-insensitive species. As far as the two PL intensities are both linearly proportional to the excitation light intensity, the mentioned fluctuations are canceled out in the ratio, thus improving the experimental precision.

Here, we show how TiO_2 nanoparticles both in rutile and anatase phases can be employed to develop a ratiometric optical sensor of O_2. This sensor offers a peculiar ratiometric-enhanced responsivity, thanks to a peculiar "anti-correlated" PL response of the two polymorphs which, currently, is known to occur only in TiO_2. An example of anti-correlated PL intensity of rutile and anatase response to different O_2 concentrations is reported in Figure 1. Furthermore, we illustrate our recent results on how tailoring the near-infrared (rutile) PL emission leads to improve sensor sensitivity and stability for O_2 concentrations in the 10–100 ppm range.

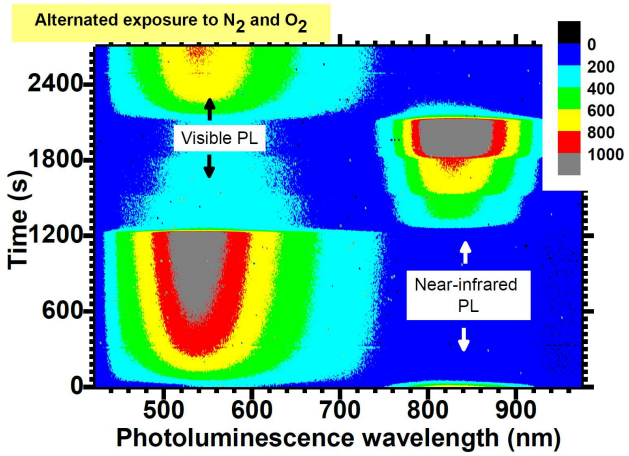

Figure 1. Example of anti-correlated PL intensity of rutile (near-infrared PL) and anatase (visible PL) response to different O_2 concentrations (time t = 1200 s, 1500 s, and 1800 s), alternated with O_2 desorption in N_2 flow.

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