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With this wide spread of applications, earth-abundant photo-catalysts are attracting extensive interest, especially based on anatase TiO₂ due to its abundance^{6,8} and low toxicity^{5,9}.

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APPLICATION NOTE


CHARGE CARRIER RECOMBINATION DYNAMICS OF SEMI CONDUCTOR PHOTOCATALYST

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INTRODUCTION

Photocatalysis, the induction of chemical changes by absorption of light, is crucial for many environmental studies and sought for water splitting and hydrogen production^{1,2}, as well as artificial photosynthesis⁵. With this wide spread of applications, earth-abundant photo-catalysts are attracting extensive interest, especially based on anatase TiO₂ due to its abundance^{6,8} and low toxicity^{5,9}.



FluoroSpectrometer

Due to its wide bandgap at 3.2 eV, however, it is not a good absorber in the visible range. Visible routes to extend its absorption include doping with transition metals to induce defect states in the lattice and tune the bandgap towards the visible.

In this application note, by means of time-resolved photoluminescence spectroscopy, we study the dynamics of charge carriers in copper-nitrogen titanium oxide (Cu-N-TiO₂).

METHODS & MATERIALS

Time-resolved emission maps were performed in an FLS980 Fluorescence Spectrometer equipped with double excitation and emission monochromators, a photomultiplier tube detector (Hamamatsu, R928P) and a 450 W Xe lamp for steady-state spectral measurements. A Q-switched Nd:YAG laser (Continuum, Mira) directly coupled to the spectrometer in L geometry was used as excitation in time-resolved measurements. The fundamental frequency of the laser was tripled, generating 355 nm light pulses of 4 ns pulse width at a repetition rate of 10 Hz and irradiance of 18 mJ/cm². Gratings blazed at 450 nm were used in the excitation and emission arms, with higher diffraction orders being filtered by the integrated long wave pass filters in the FLS980.

Thin films of pure and Cu-N-doped TiO₂ samples were deposited on <100> silicon substrates by radio-frequency (RF) magnetron sputtering. High purity TiO₂ and copper plates were used in a vacuum deposition chamber under argon atmosphere. For PL measurements, the samples were placed on a front face sample holder utilizing 80° orientation, while a 90° nm long pass filter placed on the sample holder was used to eliminate scattering excitation light.

RESULTS - DISCUSSION

The distinctive decay kinetics of TiO₂ and Cu-N-TiO₂ are evident in the time-resolved emission maps of Figures 1 and 2, respectively. Particularly, exciton emission at 410 nm in pure TiO₂ is completely quenched in favour of the Cu-N defect states associated to the nano-columns formed at the surface of the deposited films^{10,11}.

The fit of the decays at 410 nm and 550 nm were directly extracted from the maps of Figures 1 and 2. The long-lived exciton lifetime of pure TiO₂ corresponds to a single-exponential of 93 ps, displayed in Figure 3. Although the long-lived emission fits well in an equation of the form $I(t) = I_0 e^{-t/\tau}$, the recombination kinetics at 550 nm were better fit to stretched exponentials of the form $I(t) = I_0 (t/\tau)^{-n} e^{-t/\tau}$.

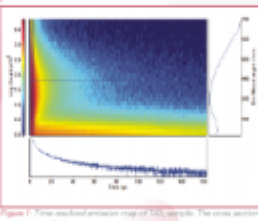
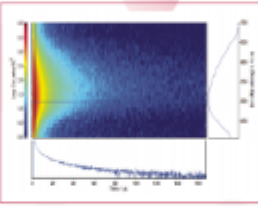



Figure 1. Time-resolved emission map of TiO₂ sample. The color section is at 320 ps and 550 nm.

Figure 2. Time-resolved emission map of sample Cu-N-TiO₂ sample. The color section is at 320 ps and 550 nm.

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