

Terahertz driven nanosecond dynamics of oxygen defect state in anatase TiO_{2-x}

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Abstract: Oxygen deficient TiO_2 has tunable photocatalytic activity thanks to a large defect state absorption band below the ultraviolet gap. Terahertz short pulses explore the electrodynamics around the oxygen vacancies, where deeply localized charges are converted into long-lived metastable states with potential applications in electro-optic switching devices.

Ultrafast nonlinear terahertz (THz) spectroscopy is applied at the TeraFERMI beamline of the Italian FERMI Free Electron Laser (FEL), where intense (multi MV/cm peak field), broadband (up to 5 THz) and ultrashort (< ps) terahertz (THz) pulses are generated by Coherent Transition Radiation from the relativistic electron bunches of the FEL [1].

The beamline allows addressing the THz nonlinear properties of materials, ranging from quantum materials to bio-chemical samples, by measuring the single(two) color THz pump-THz(infrared) probe response.

Here, we aim at showing an example on titanium dioxide, a largely available and naturally occurring functional oxide, and a benchmark among photocatalytic materials.

Oxygen vacancies in titanium dioxide have a strong impact on its photoactivity, by introducing band-gap states and consequently extending the photoresponse from the UV to the visible light region [2].

We achieved control on the oxygen defect state in TiO_{2-x} , by modulating the infrared response associated to photoexcitation of oxygen vacancies by employing the intense terahertz short pulses delivered by TeraFERMI.

The signatures of the presence of the electronic states associated to oxygen in TiO_{2-x} have been first identified by means of a multi-technique approach, including XRD characterization and steady-state optical spectroscopy from the infrared to the ultraviolet. The time-resolved THz pump/infrared probe measurements allow to explore the polaron-like electron dynamics around these oxygen vacancies, by unveiling the conversion of deeply localized defect states into long-lived metastable states, with a lifetime in the nanosecond range [3].

This approach is completely new, being based on a pump-probe experiment where a sub-gap terahertz pump beam is used for the first time.

Our new finding impacts the exploitation of oxygen deficient titanium dioxide, a functional material largely usable for solar energy conversion, as well as in novel opto-electronic applications.

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References

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