Exciton recombination dynamics in type II CdTe-Cu_{2-x}Te nano-heterostructures with excitonic and plasmonic properties

Ilka Kriegel,^{a, b⊥*} Andreas Wisnet,^d Ajay Ram Srimath Kandada,^e Francesco Scotognella,^{c, e} Francesco Tassone,^e Christina Scheu,^d Hui Zhang,^f Alexander O. Govorov,^f Jessica Rodríguez-Fernández,^{a, b} and Jochen Feldmann^{a, b}

^{*a*} Photonics and Optoelectronics Group, Department of Physics and CeNS, Ludwig-Maximilians-Universität München, Munich, Germany. ^{*b*} Nanosystems Initiative Munich (NIM), Munich, Germany

^c Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

^d Department of Chemistry and CeNS, Ludwig-Maximilians-Universität München, Munich, Germany

^e CNST of IIT@POLIMI, Via Pascoli 70/3, 20133 Milano, Italy

^f Department of Physics and Astronomy, Ohio University, Athens, Ohio 45701, USA

[⊥] Current address: Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano,

Italy

E-mail: ilka.kriegel@polimi.it

Abstract: A faster exciton recombination dynamics in type II CdTe- Cu_{2-x} Te nano-heterostructures occurs with increasing the size of the Cu_{2-x} Te subdomain. We suggest that an Auger mediated recombination pathway due to the free carriers in the vacancy-doped Cu_{2-x} Te subunit is the main reason for the faster dynamics. **OCIS codes:** (300.6530) Spectroscopy, ultrafast; (320.7150) Ultrafast spectroscopy; (160.4236) Nanomaterials.



Fig.1 Left column from top to bottom: Absorption spectra of pristine CdTe nanorods (upper panel) dominated by excitonic resonances, and Cu_{2-x}Te nanorods (bottom panel) with a pronounced plasmon resonance. The type II CdTe-Cu_{2-x}Te nano-heterostructures (centre) show both features. Right column: transient absorption spectra for pristine CdTe (upper panel), and two heterostructures with increasing Cu_{2-x}Te subunit, together with the dynamics at the excitonic bleach (695nm). I. Kriegel, A. Wisnet, A.R. Srimath Kandada, F. Scotognella, F. Tassone, C. Scheu, H. Zhang, A.O. Govorov, J. Rodríguez-Fernández, J. Feldmann J. Mater. Chem. C, in DOI:10.1039/C3TC32049A, press, Reproduced by permission of The Royal Society of Chemistry

Type II nanorod heterostructures based on cadmium (Cd) and copper (Cu) chalcogenides have been receiving an increasing attention due to their potential for photoenergy conversion applications.^{1, 2} Synthesis via cation-exchange enables a precise regulation of the size of the respective subunit,^{1, 2} thus delivering a tool to control the optical properties of the entire system. The optical characteristics of such heterostructures are dominated by strong excitonic features, present due to the quantum confined CdTe, and plasmonic features, as a result of the high carrier density in the vacancy-doped Cu_{2-x}Te counterpart.³⁻⁶

In this proceeding we present a domain-size dependent investigation of the optical characteristics of CdTe-Cu_{2-x}Te nanoheterostructures. We demonstrate a strong control over the contribution of the excitonic and plasmonic features to the optical response of the entire system.⁶ A theoretical investigation demonstrates a negligible groundstate interaction between the exciton and the plasmon, likely resulting from localization effects of the carriers in the Cu_{2-x}Te sub-domain⁵ and the low spectral overlap.

However, the recombination dynamics of the CdTe exciton bleach, as measured by transient absorption spectroscopy, demonstrates a strong dependence on the subunit dimensions. We ascribe the faster exciton decay with increasing $Cu_{2-x}Te$ subdomain to an Auger-mediated recombination mechanism of the exciton with the high number of carriers in the $Cu_{2-x}Te$ subunit. This assignment is testified by results obtained through bandstructure calculations that suggest an increased wavefunction leakage of the excited state electron from the CdTe subdomain into the $Cu_{2-x}Te$ subunit. Wavefunction overlap is a prerequisite for an Auger type recombination and supports our time resolved data. Taken altogether our results suggest that for photoenergy conversion a shorter copper-based subunit and the suppression of carrier density are beneficial. Furthermore, we also foresee the potential of this type of nano-heterostructures for the investigation of exciton-plasmon interactions upon an appropriate choice of materials, and thus increased spectral overlap.

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