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Plasmon-exciton coupling at Ag nanocluster decorated TiO_2(110) surface studied by time-resolved two-photon photoemission spectroscopy
SHIJING TAN, ADAM ARGONDIZZO, HRVOJE PETEK, Department of Physics and Astronomy, University of Pittsburgh — We study the spectroscopy and electron dynamics at Ag nanocluster decorated TiO_2(110) surface upon photoexcitation of plasmonic modes by two-photon photoemission spectroscopy (2PP). Depositing Ag onto a reduced rutile TiO_2(110) surface at room temperature forms pancake-like Ag particles with an average diameter of 4 nm and height of 1.5 nm. Measurements of the 2PP yield from Ag/TiO_2 surface with tunable femtosecond laser excitation show enhancement at plasmonic resonances. Exciting with s-polarization ($\vec{S}$) the plasmonic resonance enhancement has a single peak at 3.1 eV, whereas with p-polarization ($\vec{P}$) there is an additional more intense resonance at 3.8 eV. We attribute the 3.1 and 3.8 eV peaks to the in-plane and the surface-normal plasmon modes respectively. Crystal azimuth orientation dependent excitation with ($\vec{S}$) shows an anisotropy in the 2PP spectra for the 3.1 eV in-plane plasmon mode when the laser electric field is aligned in the [001] vs. [1$\bar{1}$0] directions. The existence of two plasmon modes and the in-plane plasmon anisotropy imply that the plasmon modes are perturbed by coherent coupling with excitons in the rutile TiO_2 substrate. We speculate that plasmon-exciton resonant energy transfer could play an important role in the plasmonically enhanced photocatalysis at the Ag/TiO_2 surface.

Hrvoje Petek
Department of Physics and Astronomy, University of Pittsburgh

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