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Plasmonically enhanced multiphoton photoemission at metal nanoparticle decorated surfaces

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Excitation of plasmon resonances in metallic nanoparticles can enhance a variety of electromagnetic phenomena ranging from surface enhanced Raman scattering to photocatalysis. The topic of plasmonically enhanced photocatalysis is very popular, yet the mechanisms for the observed effects are difficult to establish because they involve complex chemical, electromagnetic, and electronic interactions between disparate materials. We employ multiphoton photoemission spectroscopy (mPP) with broadly tunable femtosecond excitation to investigate the photoemission mechanisms for the clean and metal nanoparticle (Ag and Au) decorated TiO_2 and graphite surfaces. On reduced TiO_2 surfaces, 2PP proceeds from t2g symmetry Ti-3d defect states via a resonance with unoccupied eg states.1 In the case of graphite, mPP is predominantly of thermionic nature due to ineffectively screened Coulomb interactions, which are responsible for extremely efficient electron-electron scattering. In the presence of metal nanoparticles, the mPP processes are significantly enhanced, and provide clues to plasmon-substrate coupling that could be responsible for photocatalysis.

1 Argondizzo, A., Cui, X., Wang, C., Sun, H., Shang, H., Zhao, J., & Petek, H. Ultrafast multiphoton pump-probe photoemission excitation pathways in rutile TiO_2. Phys. Rev. B 91, 155429 (2015).