Tuning Au–TiO_2 Photocatalytic Interfaces: Impact of Oxygen Vacancies and Gold Nanoparticle Size on Electronic Structure and Carrier Dynamics

Carlos Mora Perez[1], Ernest Hermosillo[1], Drew M. Glenna[1,2], Oliver Gessner[1], Jin Qian[1]

1. Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States
2. Department of Nuclear Engineering & Industrial Management, University of Idaho, Idaho Falls, Idaho 83402, United States

Gold (Au) integrated onto titanium dioxide (TiO_2) surfaces offers a promising strategy to enhance the photocatalytic efficiency of the semiconductor system. This work investigates how oxygen vacancy defects and structural changes in the anatase TiO_2 (101) surface influence the electronic properties and carrier dynamics of the Au–TiO_2 heterojunction. To this end, we compare the pristine surface with one modified by a single surface oxygen vacancy and examine how gold nanoparticle size affects these interactions by studying Au_4, Au_{19}, and Au_{20} clusters. Ground-state density functional theory (DFT) calculations demonstrate that the oxygen vacancy dramatically modifies the interfacial electronic structure, with density of states (DOS) analysis revealing the formation of a trap state for the isolated TiO_2 slab model. Upon formation of the Au–TiO_2 heterojunction, the defect site results in a larger perturbation to the DOS of the closed-shell Au clusters (Au_4, Au_{20}) TiO_2 heterojunction compared to the open-shell Au_{19} cluster TiO_2 heterojunction. Meanwhile, ab initio molecular dynamics (AIMD) simulations at 300 K further reveal distinct differences in the atomic motion of the AuNPs and the TiO_2 surface between pristine and oxygen-vacancy-modified systems under experimentally relevant conditions. Furthermore, nonadiabatic molecular dynamics (NAMD) simulations were employed to calculate carrier lifetimes associated with electron injection and electron–hole recombination processes across the interface. These findings underscore the critical role of defect engineering and interfacial structural dynamics in tailoring the performance of Au–TiO_2 photocatalytic systems.

Keywords: Gold, Oxides, DFT, AIMD, NAMD, Injection, Recombination