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RAPID COMMUNICATION

Heteroepitaxial approach to explore charge dynamics across Au/$BiVO_4$ interface for photoactivity enhancement

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Abstract
Heterostructure provides a powerful route in manipulating electrical transport, optical response, electrolytic water splitting and water treatment of complex oxides. As a model for noble metal/complex oxide heterostructures, we have successfully prepared Au/$BiVO_4$ (BVO) heterostructures in which the Au nanoparticles (NPs) with various sizes and densities were uniformly deposited on the {001} facets of epitaxial BVO thin films. The heterostructures exhibit significantly enhanced photoactivities in both dye degradation and electrolytic water splitting. By employing X-ray photoelectron spectroscopy, the energy band alignment of Au/BVO heterojunction suggests a charge separation at their interfaces, that can manipulate the photoexcited electron–hole pairs and photocatalytic efficiency of the heterostructures. Photogenerated carrier injection, which mainly affects the photoactivity of photocatalysis, was detected across Au/BVO interfaces by ultrafast

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dynamics spectroscopy. This study delivers a general approach to probe and understand the photochemistry of noble metal-complex oxide heterostructures for photoconversion applications.

Introduction

The harvesting of solar power for useful purposes is always a splendid gold for human beings. Photo-assisted electrochemical (PEC) water splitting can become more competitive as the cost continues to decrease with the development of nanotechnology. Current research directions focus on acquiring higher efficiency, visible light absorption, and cost-less scale up process. Although a lot of potential materials and prototype devices are developed along these research directions, the remaining key issue is the material stability in water. Hydro-compounds are formed on the surface when the materials are placed into water, this strongly reduces the efficiency of PEC. The reliability issue is yet to be addressed before practical applications come out. Complex oxides are an emergent class of next-generation design-driven, multi-scale renewable materials with tremendous potential to lead to the development of new functionalities, tailored properties, and sustainability across the whole life-cycle [1-3]. In order to tailor the functionalities, complex oxide heterostructures have been demonstrated as an effective approaches [4-6]. One of the most important factors in photocatalytic reaction and photoelectric conversion is to separate photoexcited charge carriers and to ensure direct charge transfer across the heterojunctions. Hence, an in-depth understanding of charge separation inner the oxides and charge transfer at the heterojunction is essential to design high efficient photocatalyst structures. Recently, researchers have demonstrated that the charge separation and photoactivity properties are closely related to the exposed crystal facet of photocatalysts [7-10], and the charge transfer between metal/oxide interfaces depends on the shape, size and concentration of metal nanoparticles (NPs) [11-13]. The major approach is a decoration of metal NPs with hybrid structure or polycrystalline material, which consists of multiple crystal facets as show in Figure 1a. The multiple crystal facets and defects in conventional systems set challenge for fundamental understanding the nature interactions of metal/oxide and photoactivity behavior. Thus, a designed high quality metal/oxide heterostructure, in which the metal NPs with well-controlled the shape, size, and density are deposited on a particular facet of the single crystal oxide for studying the correlation between photoactivity behaviors and natural metal/oxide interactions, remains elusive.

$BiVO_4$ (BVO) has a direct band gap of ~2.5 eV, hence it is considered as a good example material for photocatalytic applications in the visible light range. Indeed, it has demonstrated as one of the most promising photocatalysts for the evolution of O_2 and photoelectrochemical water splitting under the visible light irradiation owing to the favorably positioned band edges and good stability [14-17]. In addition, the theoretical solar-to-hydrogen conversion efficiency of the BVO reached 9.2% with a maximum photocurrent of 7.5 mA cm^{-2} under standard AM 1.5 solar light irradiation [18]. Therefore, in this study, BVO has been chosen as a model system to demonstrate an approach to understand the physics of PEC on the heterostructures of complex oxide and noble metal based on epitaxial growth, which can eliminate other factors such as grain boundaries, structure defects, and impurity phases. We establish a combination of heteroepitaxy with high quality interface consisting single crystal monoclinic BVO thin films and Au NPs, as illustrated in Figure 1b. Au NPs of various sizes and densities was uniformly grown on {001} facets of BVO by using dewetting technique [19]. The Au NPs size and density dependences of band alignment and the dynamic relaxation processes of Au/BVO were examined by a combination of X-ray photoelectron spectroscopy and ultrafast dynamics as well as the correlation between them and the photoactivity behaviors are discussed. In addition, the contribution of surface plasmon resonance (SPR) excitation on enhanced photoactivity of Au/BVO was explored based on the 3D finite-difference time domain simulation. Our study suggests that the heteroepitaxial approach can serve as a fundamental platform to study and understand the fundamental photochemistry of metal/complex oxide heterostructures.

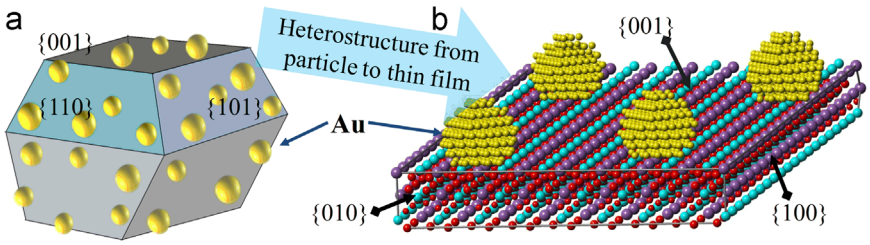

Figure 1 Conventional photocatalytic nanoparticle conjugation without clear interfacial atomic structures. The present work is to construct an effective interfacial charge transfer by heteroepitaxial approach.