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Au/BiOCl heterojunction within mesoporous silica shell as stable plasmonic photocatalyst for efficient organic pollutants decomposition under visible light

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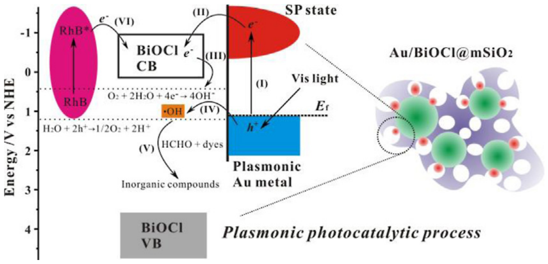
HIGHLIGHTS

- A heterojunction of Au/BiOCl was fabricated within the mesoporous silica shell.
- The compact contact between Au and BiOCl enables electrons back flow from Au to BiOCl.
- Au/BiOCl@mSiO$_2$ plasmonic photocatalyst shows efficient visible light photoactivity.
- Hydroxyl radicals are the main oxidants in formaldehyde and Rhodamine B decomposition.

GRAPHICAL ABSTRACT



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ABSTRACT

A new mesoporous silica protected plasmonic photocatalyst, Au/BiOCl@mSiO$_2$, was prepared by a modified AcHE method and a subsequent UV light induced photodeposition process. The surfactant-free heterojunction allows the electrons spontaneously flow from Au to nearby BiOCl surface, leading to the accumulation of positive charges on Au surface, and negative charges on Bi species under visible light. Au/BiOCl@mSiO$_2$ exhibits high visible light photocatalytic efficiency in complete oxidation of aqueous formaldehyde and Rhodamin B. We showed that a positive relationship exists between the LSPR effect and rate enhancements, and leads to a hypothesis that the metallic Au LSPR enhances the photocatalytic rates on nearby semiconductors by transferring energetic electrons to BiOCl and increasing the steady-state concentration of active $^{\bullet}$OH species by a multi-electron reduction of molecular oxygen. The $^{\bullet}$OH species is the main oxidant in photocatalytic transformations, whose intensity is greatly enhanced in the dye-involving systems due to the synergetic effect between LSPR and dye sensitization processes. In addition, the mesoporous SiO$_2$ shell not only inhibits the over growth of BiOCl nanocrystals within the silica frameworks, but also protects the dissolution of chloride or Au species into aqueous solution, which ultimately makes the Au/BiOCl@mSiO$_2$ catalysts rather stable during photocatalysis.

1. Introduction

Heterogeneous photocatalysis has been considered as a promising and green chemical process for the removal of organic contaminants in water [1–7]. Among the various semiconductor photocatalytic materials, bismuth oxyhalides, especially bismuth

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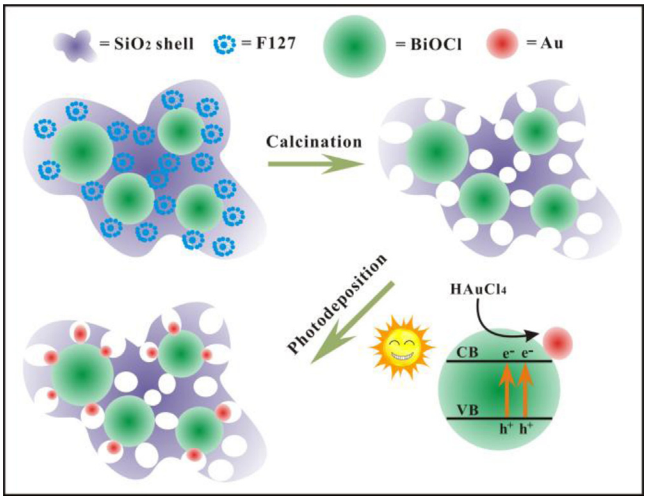
oxychloride (BiOCl), have evoked much interests owing to their novel properties and extensive applications in catalysis, pigments, nanodevices and nanosensors [8–16]. Due to its unique layered structure, facet-dependent oxygen activation property, and high photo-corrosion stability, BiOCl has been frequently demonstrated to be an excellent photocatalyst for the oxidative decomposition of many organic compounds under UV irradiation [17–19]. However, the intrinsic wide band gap ($E_g \approx 3.4$ eV) limits its further application in the visible light region ($\lambda > 400$ nm). To harvest the visible light that occupies ~43% of the solar spectrum, designing a photocatalytic system for activating molecular oxygen, the organic pollutants or both, and thus effectively promoting the surface redox reactions is indispensable. Many synthetic techniques, including metal-ion and nonmetal doping, have been developed to extend the absorption of only-UV-activated semiconductors (e.g., TiO_2) to visible spectrum [20–25]. However, the doped materials usually suffer from serious problems such as thermal instability, photo-corrosion, and fast charge recombination rates.

More recently, a new strategy for improving the efficiency of photocatalytic processes has emerged, involving the strong localized surface plasmon resonance (LSPR) of Cu, Ag and Au nanoparticles (NPs) [26–31]. Semiconductors loaded with these coinage metals exhibited visible light activity based on LSPR, which has been observed in many photochemical processes. The photoactivity enhancement might be ascribed to the charge transfer from photoexcited metal to the semiconductor and/or LSPR-induced electromagnetic fields in the vicinity of the plasmonic nanostructure. From this point of view, in any case, the improved absorption of photons by LSPR of metal NPs as well as a tight interface between metal and semiconductor is both important to promote visible light activity in plasmonic photocatalysts. The presence of an obstacle on the interface, such as surfactant, however, will impede the direct charge transfer or remarkably decrease the intensity of LSPR-induced electromagnetic field close to semiconductor, as this field decays exponentially with distance [32]. To avoid the use of surfactants and realize a compact metal/semiconductor interface, photo-reduction method is such a promising synthetic strategy that not only excludes the surfactants usage, but also enables the selective deposition of metals on semiconductors surface where *in situ*photogenerated electrons can reduce metal ions into metallic phases with the assistance of UV/vis light irradiation.

Inspired by previous studies that the construction of heterojunction is an effective way in enhancing the photocatalytic properties of certain photocatalysts [33–36], we suppose that coupling of plasmonic Au metals with BiOCl may offer new opportunities to achieve an efficient visible light photocatalytic system. Moreover, although BiOCl has been frequently employed for photocatalytic purposes, limited information on the oxygen activation pathways on such material has been obtained, especially considering its positive conduction band (CB) level that intrinsically hampers the single-electron oxygen reduction process to form reactive oxygen species.

Herein, we fabricated a mesoporous silica ($mSiO_2$) shell protected BiOCl material by our newly developed AcHE method [37–38], and subsequently deposited AuNPs onto its surface using a UV light induced photodeposition method [39], as illustrated in Scheme 1. The resulting photocatalyst is thus termed as Au/BiOCl@$mSiO_2$. It is found that AuNPs can selectively deposited on the BiOCl surface regardless of its crystal facets, and the closed contact between AuNPs and BiOCl led to the formation of positive $Au_n^{\delta+}$ clusters on Au surface and a negative charge accumulation in adjacent Bi species. This kind of surface charge balance is suggested to promote molecular oxygen activation by an LSPR-induced multi-electron reduction process to ultimately generate $^{\bullet}OH$ radicals in the heterojunction interface under visible light irradiation, resulting in the high photocatalytic efficiency of Au/BiOCl@$mSiO_2$ during oxidative decomposition of formaldehyde (FAD) and Rhodamin B (RhB) in water. In addition, the mesoporous SiO_2 shell not only serves as physical barriers to inhibit the over growth of BiOCl crystals under high temperature calcination and protect the dissolution of chloride and Au species in Au/BiOCl composite, but also provides mesochannels and straight pore configuration to the efficient adsorption and diffusion of reactant molecules [40], making Au/BiOCl@$mSiO_2$ a stable and efficient plasmonic photocatalyst.

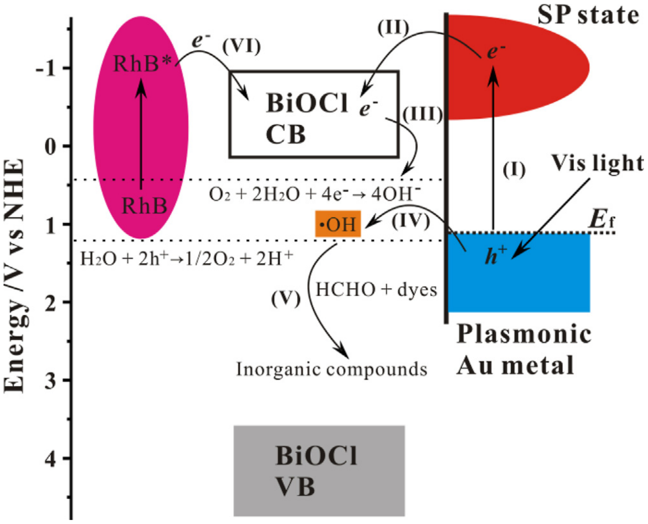


Scheme 1. Schematic illustration of the synthetic routes of Au/BiOCl@$mSiO_2$ photocatalyst involving AcHE and photodeposition methods.

2. Experimental

2.1. Materials

The surfactant triblock copolymer Pluronic F127 ($EO_{96}PO_{70}EO_{96}$, MW = 12,000 g/mol), auric chloride acid ($HAuCl_4{\cdot}4H_2O$), α-phenyl-*tert*-butyl-nitrone (PBN) and 5,5-dimethyl-pyrroline-*N*-oxide (DMPO) spin-trapping reagents were provided by Aldrich. Tetraethyl orthosilicate (TEOS), acetic acid (HOAc), hydrogen chloride (HCl), bismuth nitrate ($Bi(NO_3)_3$), FAD solution and RhB dyes supplied by Sinopharm Chemical Reagent



Scheme 2. Proposed reaction mechanisms for FAD and RhB decomposition over Au/BiOCl@$mSiO_2$ photocatalysts under visible light.