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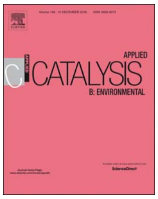

Research Paper

Plasmonic molybdenum oxide nanosheets supported silver nanocubes for enhanced near-infrared antibacterial activity: Synergism of photothermal effect, silver release and photocatalytic reactions

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ABSTRACT

Plasmonic MoO_{3-x} nanosheets supported Ag nanocubes were designed as high-efficient Near-infrared (NIR) light driven antibacterial agent. The as-designed MoO_{3-x}-Ag not only significantly reduces the cost and toxicity of Ag, but also greatly enhances the antibacterial activity towards *E. coli* and *S. aureus* in comparison with bare MoO_{3-x} and Ag upon NIR laser irradiation. Three effects are believed to contribute to this enhancement: (1) the plasmonic MoO_{3-x}-Ag exhibits excellent NIR light absorption and photothermal conversion abilities, which help to kill bacteria; (2) NIR light induced heat in MoO_{3-x} also diffuses to Ag nanocubes and triggers the release of more Ag^+, leading to bacterial cell death; (3) under NIR light irradiation, hot electrons and holes are generated and separated through MoO_{3-x}-Ag interface, which produces reactive species for the oxidation of out membrane of bacteria. The synergism of NIR light driven photothermal effect, silver release and photocatalytic reaction makes the designed plasmonic MoO_{3-x}-Ag a promising antibacterial agent for cleaning the microbial contaminated water environment.

1. Introduction

Utilization of solar energy for wastewater treatment and pathogenic bacteria killing represents an economic and clean approach to alleviating steadily worsening environmental issues and improving the public health [1–4]. Recently, various semiconductor-based photocatalysts have been developed to kill inactive bacteria under light irradiation [5–7]. However, one big limitation of the semiconductor-based photocatalysts is the contradiction between light absorption range and redox ability of photo-induced charge carriers [8,9]. Generally, wide bandgap semiconductors only absorb ultraviolet (UV) light (wavelength (λ) < 400 nm), which accounts for a very small fraction (≈ 5%) of solar spectrum. While for semiconductor with narrower bandgap, the light absorption extends to visible ($400 < \lambda < 780$ nm, ≈ 43%) range, but the higher valence band maximum (VBM) or lower conductive band minimum (CBM) reduces the redox ability of the photogenerated charge carriers and decreases the photocatalytic antibacterial activity. In comparison with UV and visible light, near-infrared (NIR) light ($780 < \lambda < 2500$ nm) not only accounts for a large proportion (≈ 52%) of the solar spectrum, but also penetrates into biological tissues more deeperly with lower photo-damage to living bodies [10]. Thus the development of NIR responsive photocatalysts is a promising route to improving the solar energy conversion efficiency in bacteria killing with no observable damage to the exposed tissue [11].

Considering the bandgap of NIR light excitable semiconductor is too narrow to meet the energy requirement in driving the necessary redox reactions, alternative approaches have been utilized in the development of NIR light driven antibacterial photocatalysts. For one thing, upconversion nanocrystals can absorb low-energy NIR lights and emit high-energy UV or visible light in realizing the higher redox abilities [12,13]. However, upconversion nanocrystals can only absorb NIR light in a specific wavelength, greatly decreasing the utilization of solar photons. For another, noble metal nanocrystals with plasmonic absorption in NIR

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region generate hot charge carriers in driving the photocatalytic process for antibacterial application [14,15]. In comparison with upcoversion nanocrystals, the plasmonic photocatalysts apparently enlarge the NIR light absorption range. Furthermore, the plasmonic photothermal effect can also help to kill the bacteria [16,17]. However, bare noble metal is uncompetitive for the future development of antibacterial agent considering the high cost and earth rarity of them. In addition, most of plasmonic noble metal absorb photons in the visible region, which can only be extended to the NIR range through precise shape control [8,15]. Moreover, noble metal also induces significant toxic effects to human health and environment [18]. Therefore, reducing the use of noble metals is a key issue in the future development of NIR responsive plasmonic photocatalytic antibacterial agents.

Recently, it was reported that plasmonic absorption has also been found on heavily doped semiconductor with an appreciable free carrier concentration, such as MoO_{3-x} and WO_{3-x} [19,20]. In comparison with plasmonic metal, plasmonic semiconductor greatly reduces the consumption of noble metal and decreases the toxicity to the organism [21]. Moreover, the plasmonic semiconductors show much stronger light absorption in the NIR region. In this paper, plasmonic MoO_{3-x} nanosheets were designed in combination with Ag nanocubes for effectively killing pathogenic bacteria under NIR light irradiaiton. MoO_{3-x} efficiently absorbs plasmonic light in NIR region, which not only converts to heat and kills the bacteria through photothermal lysis, but also transfers the heat to Ag and triggers the release of Ag^+ for an enhanced antibacterial activity. Furthermore, the hot electrons and holes can be generated and separated through MoO_{3-x}-Ag interface, which also generate free radicals and lead to the destruction of the outer membrane of the bacterial cell. Resulted from the synergistic effect of plasmonic heating, Ag^+ release and generated reactive species, both Gram-negative and Gram-positive bacteria were effectively killed by the designed MoO_{3-x}-Ag photocatalyst under NIR light irradiation. As far as we known, it is the first report on the development of plasmonic semiconductor based photocatalyst for NIR antibacterial application.

2. Experimental

2.1. Chemicals

Molybdenum powder (Aladdin, M109124), poly(vinyl pyrrolidone) (PVP, M.W. ≈ 55000, Aldrich, 856568), NaSH (Sigma-Aldrich, 161527), ethylene glycol (EG, Sigma-Aldrich, 324558) and silver trifluoroacetate (Aladdin, S109509) were used in our synthesis. All other chemicals were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. The water used in all experiments was de-ionized. All chemicals were used as received without further purification.

2.2. Synthesis of MoO_{3-x} nanosheets

In a typical synthesis [19], 2 mmol of molybdenum powder was added to 24 mL of ethanol in a 40 mL Teflon vessel. Then 3 mL of H_2O_2 was introduced and magnetically stirred for 1 h to obtain transparent yellow solution, which was then transferred to a Teflon-lined stainless-steel autoclave and heated at 150 °C for 12 h. After the autoclave had cooled down to room temperature, the resultant product was separated by centrifugation and washed with ethanol several times. The final product was then dried at 45 °C for 12 h.

2.3. Synthesis of Ag nanocubes

In a typical synthesis [22], 10 mL EG was added into a 50 mL three-neck flask and pre-heated under magnetic stirring at 150 °C. 0.12 mL NaSH (3 mM in EG) was quickly injected into the heated solution. After 2 min, 1 mL HCl solution (4 mM in EG) was introduced into the reaction solution, followed by the addition of 2.5 mL PVP solution (20 mg/mL in EG) after another 2 min. Next, after the third 2 min, 0.8 mL solution of silver trifluoroacetate (282 mM in EG) was added. The reaction was allowed to proceed at 150 °C for 40 min. The product was collected by centrifugation, and washed with acetone and water several times to remove excess PVP. The as-obtained Ag nanocubes were redispersed in water for further use.

2.4. Preparation of MoO_{3-x}-Ag hybrid structures

In the synthesis of MoO_{3-x}-Ag structure, 10 mg MoO_{3-x} nanosheets were dispersed in 40 mL ethanol through sonication. Then 1.0 mL of Ag nanocubes (0.5 mg mL^{-1} in water) was added into the dispersion. The mixture was further sonicated for 5 min, and then transferred to a Teflon-lined stainless-steel autoclave, and heated at 100 °C for 1 h. After the autoclave had cooled down to room temperature, the resultant product was separated by centrifugation and washed with water several times. The final product was then dried at 45 °C for 12 h. Ag nanospheres were also assembled on the MoO_{3-x} nanosheets through the same method, which were obtained through etching Ag nanocubes with $Fe(NO_3)_3$ according to previous report [23].

2.5. Sample characterizations

Prior to electron microscopy characterizations, a drop of the aqueous suspension of particles was placed on a piece of carbon-coated copper grid and dried under ambient conditions. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken on a JEOL JEM-2100F field-emission high-resolution transmission electron microscope operated at 200 kV. Scanning electron microscopy (SEM) was performed with a Hitachi S-4800 scanning electron microanalyzer with an accelerating voltage of 15 kV. Powder X-ray powder diffraction (XRD) patterns were recorded by using a Philips X'Pert Pro Super X-ray diffractometer with Cu-Kα radiation ($\lambda = 1.5418$ Å). X-ray photoelectron spectra (XPS) were collected on an ESCALab 250 X-ray photoelectron spectrometer, using non-monochromatized Al-Kα X-ray as the excitation source. UV-vis-NIR diffuse reflectance data were recorded in the spectral region of 240–1600 nm with a Shimadzu SolidSpec-3700 spectrophotometer. Photoluminescence (PL) spectra were recorded on a Jobin Yvon Horiba Fluorolog-3-Tau Spectrofluorometer. The concentrations of metal elements were measured as follows: the samples were dissolved with a mixture of HCl and HNO_3 (3:1, volume ratio) which was then diluted with 1% HNO_3. The concentrations of metals were then measured with a Thermo Scientific PlasmaQuad 3 inductively-coupled plasma mass spectrometry (ICP-MS).

2.6. Cell cytotoxicity test

Cytotoxicity of the samples to human umbilical vein endothelial cells (HUVEC) was evaluated by a standard 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide (MTT) assay. HUVEC were seeded in 96-well U-bottom plates at a density of 5.0×10^4–1.0×10^5 cells per milliliter (90.0 μL per well) and cultured for 12 h in an incubator (37 °C, 5% CO_2), prior to the addition of the sample suspension at a range of concentrations (0 ~ 200 μg mL^{-1}). After being cultured for a further 24 h with samples, 20.0 μL of MTT solution (normal saline or 5.0 mg mL^{-1} phosphate buffer solution) was added into each sample, and incubated at 37 °C for 4 h. The culture media were discarded and then 150.0 μL of dimethylsulfoxide (DMSO) was added to each sample in order to dissolve the formazan, with shaking for at least 15 min. The corresponding spectra were recorded with a microplate reader at 595 nm. The cell viability rate (VR) was calculated based on the below equation:

$$VR\ (\%) = A/A_0 \times 100\%$$