Original Research Paper

Strongly-coupled silver chloride–tungsten oxide hybrid nanocomposite with excellent antibacterial effect

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A B S T R A C T

A novel hybrid nanocomposite composed of AgCl nanoparticles and $W_{18}O_{49}$ nanorods was fabricated through a facile, clean, efficient deposition route. The AgCl–$W_{18}O_{49}$ nanocomposite has been found to exhibit excellent antibacterial activity, which may arise from the high-density loading of the AgCl nanoparticles on the $W_{18}O_{49}$ nanorods and the strongly-coupled interaction between the two components. Under light irradiation, partially photoreduction of the AgCl nanoparticles could convert the AgCl–$W_{18}O_{49}$ nanocomposite to the plasmonic Ag–AgCl–$W_{18}O_{49}$ nanophotocatalyst with enhanced antibacterial activity. The AgCl–$W_{18}O_{49}$ nanocomposite is promising candidate for potential application in the field of marine antifouling coatings.

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1. Introduction

Biofouling corrosions cause serious damages to the marine bodies including shipping vessels, marine platforms, marine buildings, sea probes and so on [1–3]. Microbiologically-influenced corrosion (MIC) accounts for the overwhelming majority of all forms of biofouling corrosions. At present, the widely-adopted solution to cope with the biofouling corrosions is to utilize antifouling coatings, especially those with antibacterial activity [4–7]. However, the existing marine antifouling coatings commonly contain toxic components such as cuprous oxide (Cu_2O) and zinc chloride ($ZnCl_2$), the leakage of which could inevitably lead to unrecoverable destruction of ocean's ecological balance. Therefore, synthesis of novel, efficient, stable, and environmentally friendly antifouling materials are required for marine industry.

In the past few decades, a large number of antifouling materials have been prepared, among which semiconductor photocatalysts have gained tremendous attentions because they could not only decompose organic pollutants but also inhibit bacterial growth under light irradiation. Besides oxide semiconductors such as TiO_2 [8], ZnO [9], Bi_2O_3 [10], Fe_2O_3 [11], and WO_{3-x} ($0x < 1$) [12], other types of photocatalysts including sulfide (e.g., CdS) [13], phosphide (e.g., GaP) [14], bimetallic structure [15], ternary

compounds (e.g., Bi_2WO_6, $BiVO_4$, BiOCl, Ag_3PO_4) [16–19], and carbon-based materials (e.g., C_3N_4) [20–22] have also been reported. Recently, hybrid composites, which are usually composed of two or more phases, compounds, or constituents with strongly-coupled interaction between them, are attracting more and more attention due to their significantly-improved photocatalytic properties [23]. As a novel class of hybrid photocatalysts, plasmonic photocatalysts, usually described as Ag@AgX (X = Cl, Br, I, etc), have been widely proved to exhibit excellent photocatalytic properties and high durability due to the surface plasmon resonance (SPR) effect of Ag metal [24–26]. Particularly, the Ag@AgX (X = Cl, Br, I) composites are promising antibacterial materials since the Ag metal or Ag^+ ions could effectively inhibit bacterial growth. At present, the fabrication of the Ag@AgX (X = Cl, Br, I) plasmonic photocatalysts usually involves two steps: the first step is the formation of AgX (X = Cl, Br, I) particles and the second is their photochemical reduction. This makes the synthesis procedure complicated and difficult to control. In addition, research work so far on the Ag@AgX (X = Cl, Br, I) plasmonic photocatalysts has been mainly focused on their applications for decomposition of toxic pollutants, water splitting toward H_2 production, and destruction of bacteria [27–32]. Little emphasis has been devoted to controlling the continuous release of Ag^+ ions by regulating the structure of the Ag@AgX (X = Cl, Br, I) composites. Indeed, excessive exposure of Ag and its compound directly to external environment could promote the release of Ag^+ ions significantly, thereby

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depressing its long-term antibacterial activity [33–35]. For practical application, it is highly important to design novel plamonic photocatalysts that could maintain the sustained consumption of the Ag^+ ions.

In this paper, following the successful synthesis of bundled $W_{18}O_{49}$ nanorods (NRs) via a solvothermal route, we fabricated a novel hybrid $AgCl–W_{18}O_{49}$ nanocomposite (NC) for the first time based on the loading of AgCl nanoparticles (NPs) on the bundled $W_{18}O_{49}$ nanorods (NRs) through a simple, clean, efficient deposition route without photochemical processing. The high-density decoration of the AgCl NPs and their strong coupling with the $W_{18}O_{49}$ NRs account for the excellent antibacterial of the $AgCl–W_{18}O_{49}$ NC. Under light irradiation, the $AgCl–W_{18}O_{49}$ NC can be converted to the plasmonic $Ag–AgCl–W_{18}O_{49}$ nanophotocatalyst with enhanced antibacterial activity. The mutual encapsulating structure of the $AgCl–W_{18}O_{49}$ nanocomposite could not only improve its stability but also guarantee the sustained release of Ag^+ ions, enhancing its prolonged antibacterial effect.

2. Experimental

2.1. Chemicals

Tungsten hexachloride (WCl_6, 99.9%) was purchased from Aladdin Industrial Inc. Silver nitrate ($AgNO_3$, >99.8%), cyclohexanol, ethanol, sodium chloride (NaCl), and distilled water were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as-purchased without further purification.

2.2. Preparation of $W_{18}O_{49}$ NRs

The $W_{18}O_{49}$ NRs were prepared by using a solvothermal method, similarly to our previous report [36]. Typically, 30 mg of WCl_6 was dissolved in 2 ml of ethanol in a beaker to obtain a solution, which was then transferred into a Teflon-lined high-pressure reaction vessel of 50 ml capacity. Subsequently, 30 ml of cyclohexanol was added to the vessel. The vessel was then sealed and heated at 200 °C in a Muffle furnace for 5 h. The as-synthesized product was finally obtained by centrifugation, washed with distilled water three times, and dried naturally for further use.

2.3. Preparation of $AgCl–W_{18}O_{49}$ NC

The $AgCl–W_{18}O_{49}$ NC was prepared by using the solvothermally-synthesized $W_{18}O_{49}$ NRs as supports through a direct deposition route. NaCl aqueous solution is selected as the Cl^- source for the production of AgCl NPs, referring to the related literatures [24,26,37]. The as-prepared $W_{18}O_{49}$ NRs was firstly dispersed in 30 ml of ethanol in a glass tube that was placed in an ultrasonic oscillator. After ultrasonic dispersion for 30 min, the $W_{18}O_{49}$ NRs solution was transferred to a beaker that was placed on the object table of a magnetic stirrer. 5 ml of saturated NaCl aqueous solution was then added to the above $W_{18}O_{49}$ NRs solution. Subsequently, 10 ml of ethanol solutions of silver nitrate at a concentrations of 0.5 M were slowly dropped into the $W_{18}O_{49}$ NRs solution under magnetic stirring. Stopped stirring when the solution color started to change from blue to white gray, and collected the final powders by centrifugation.

2.4. Characterization

Phase compositions of the as-synthesized samples were characterized by X-ray diffraction (XRD, D/MAX-2500, Cu radiation). Morphology and microstructure of the as-synthesized samples were analyzed by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) using a JEOL 2000FX microscope. For the TEM/HRTEM analysis, ethanol solutions of the samples were dropped onto carbon-coated copper grids and left to dry naturally. X-ray photoelectron spectrometry (XPS, PHI 5300, Mg kR X-ray source, 1253.6 eV) was utilized to analyze the surface chemical composition of the as-prepared products.

2.5. Antibacterial test

The antibacterial property of the $AgCl–W_{18}O_{49}$ NC was investigated via an inhibition zone method. As one of the commonly existing anaerobic species in marine environment, the gram negative bacterium of *Vibrio natriegens* was selected as an indicator. The filter paper disk was dispersed in the distilled water with the $AgCl–W_{18}O_{49}$ NC at concentrations varying from 1 to 10 g/L for 5 min and then dried. 200 μL of activated *V. natriegens* was uniformly spread in solid medium in the agar plates by using spread plate method with a triangular spreader. The filter paper disks with the $AgCl–W_{18}O_{49}$ NC were placed in the plates with *V. natriegens*, which were finally incubated at 37 °C for 48 h to examine the inhibition zones in dark and under full spectrum light in a light incubator, respectively. Empty paper disks were also placed in the agar plates as references.

3. Results and discussions

The solvolthermal process with WCl_6 as precursor and ethanol as solvent led to the formation of pure $W_{18}O_{49}$ with monoclinic structure (JCPDs. 71-2450), as revealed by the XRD result (Fig. 1a). Obviously, there is an intensive and narrow peaks at $2\theta = 23.4°$, which can be indexed to the (0 1 0) plane of the monoclinic $W_{18}O_{49}$. This suggests that the [0 1 0] orientation is the dominant growth direction of the $W_{18}O_{49}$ crystal. The survey XPS spectrum of the $W_{18}O_{49}$ evidences the existence of only W and O elements, verifying its high purity, as shown in Fig. 1b. TEM image provides direct information of the microstructure of the as-prepared $W_{18}O_{49}$ crystal. From Fig. 1c and S1 (see Supplementary material), we observe uniform $W_{18}O_{49}$ NRs with diameters of 10–15 nm and lengths of 150–300 nm. The $W_{18}O_{49}$ NRs also have been found to exhibit bundled feature, probably due to their high aspect ratio. Fig. S2 (see Supplementary material) provides a high magnification TEM image of the $W_{18}O_{49}$ NRs, it is clear that at least three NRs well aligned in one direction were stacked together to form the bundle, as marked by dotted lines. HRTEM image (Fig. 1d) shows that the $W_{18}O_{49}$ NR is single crystalline with high crystallinity. The lattice spacing of the $W_{18}O_{49}$ NR is measured to be ~0.378 nm, corresponding to the (0 1 0) plane of monoclinic phase of $W_{18}O_{49}$. Thus, it could be determined that the $W_{18}O_{49}$ NRs grew along the [0 1 0] direction during the solvothermal reaction, in good conformity with the XRD result.

After the direct deposition process, the main XRD diffraction peaks of the final sample can be well indexed with monoclinic $W_{18}O_{49}$ and cubic AgCl (JCPDs. 31-1238), suggesting the successful formation of AgCl, as indicated in Fig. 2a. Fig. 2b shows the survey XPS spectrum for the final sample, which contains the elements of W, O, Ag and Cl, in agreement with the XRD result. As displayed in Fig. 2c, the Ag 3d spectrum consists of two peaks with binding energies of 374.43 and 368.44 eV, which can be attributed to Ag $3d_{3/2}$ and Ag $3d_{5/2}$ of Ag^+, respectively [38–40]. TEM images indicate that high-density AgCl NPs with uniform size of ~15 nm in diameter were decorated on the surfaces of the $W_{18}O_{49}$ NRs after the deposition process, as clearly shown in Fig. 2d and e. Combined with the XRD results, it could be confirmed that the deposition process successfully lead to the formation of the $AgCl–W_{18}O_{49}$ NC.