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Carbon dots-decorated $Na_2W_4O_{13}$ composite with WO_3 for highly efficient photocatalytic antibacterial activity

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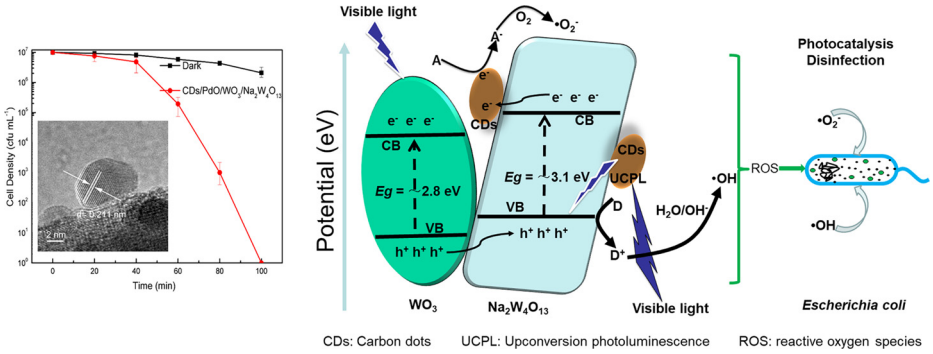
GRAPHICAL ABSTRACT



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ABSTRACT

Photodisinfection by semiconductors has been proven to be an effective method for achieving antibacterial or antifungal activity. However, the toxicity of the nanomaterial to the environment and organisms is a major concern. Herein, a highly efficient and environmentally friendly photodisinfection material of a carbon dots (CDs) decorated $Na_2W_4O_{13}$ composite with WO_3 photocatalyst was fabricated via a facile hydrothermal-calcination approach. The TEM (transmission electron microscopy) images showed that CDs decorated the surface of the $Na_2W_4O_{13}$ flakes. Compared with the samples without incorporated CDs, the as-synthesized composite of CDs/$Na_2W_4O_{13}$/WO_3 exhibited excellent antimicrobial activity against *E. coli* under visible light illumination. Electron spin resonance (ESR) spectroscopy and reactive species scavenging experiments revealed that the hydroxyl radicals and superoxide radical anions played the most important role in the photocatalytic bacterial inactivation. Furthermore, the cytotoxicity of the CDs/$Na_2W_4O_{13}$/WO_3 composite was evaluated by analyzing the viability of HepG2 and Chinese hamster lung (V79) cells using Cell Counting Kit-8 (CCK-8).

1. Introduction

Recently, pathogens have exhibited resistance to single or multiple antibiotics due to the extensive release and misuse of antibiotics in recent decades, which has created an increasing global public health threat [1,2]. However, there is a shortage of new antibiotics that can

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completely solve this problem [3]. Thus, other strategies to protect against pathogenic bacteria are urgently needed. To date, several methods have been developed to replace antibiotics, such as antibacterial nanosilver materials [4], photocatalytic disinfection [5], and photodynamic therapy. Among these methods, photocatalytic disinfection, pioneered by Matsunaga et al. and based on reactive oxygen species (ROS), is the most different from the conventional methods. Compared with widely used disinfection methods, such as antibiotic and chlorine disinfectants, the photocatalytic disinfection of microbial pathogens could reduce the formation of potentially harmful disinfection byproducts (DBPs), effectively disinfect the whole spectrum of pathogens, and utilize solar illumination as the energy input for the disinfection process. Thus, photocatalytic disinfection, an environmentally friendly and sustainable treatment technology, has attracted increasing attention and has been widely studied in recent years due to the advantages described above [6–8].

Tungsten oxide (WO_3)-based materials have been shown to be important photocatalysts with advantages of nontoxicity, abundant sources and stability in acidic media. These materials have been implemented in various applications, such as dye-sensitized solar cells, sensors, hydrogen evolution from water splitting, water and air purification, CO_2 photoreduction, and bacterial disinfection. Additionally, the experimental band gap energy of WO_3 (2.5–2.8 eV) makes it an attractive visible-light-driven photocatalyst [9]. However, two main obstacles inhibit the practical photocatalytic application of pure WO_3. One is the relatively low conduction band (CB) edge with respect to the standard H^+/H_2 redox potential [10,11]. The other significant obstacle is the rapid recombination of photogenerated charge carriers. Therefore, many strategies such as surface hybridization with graphene [12–14], noble metal deposition [15–17], and coupling with other semiconductors [18–21] have been widely studied to improve the photocatalytic activity of WO_3. On the one hand, $Na_2W_4O_{13}$, which has a band gap of ~3.1 eV, has been shown to exhibit useful properties such as luminescence, ionic conduction and water splitting [22,23]. Importantly the CB level of $Na_2W_4O_{13}$ is more negative than that of WO_3 and is suitable not only for O_2 production but also for H_2 production in photocatalytic water splitting.

Carbon dots (CDs) have attracted broad interests due to their outstanding physical and chemical properties, such as low toxicity, good chemical stability, excellent upconversion photoluminescence (UCPL) behavior, unique photoinduced electron transfer and promising electron reservoir properties [24–28]. The outstanding electronic properties of CDs as electron donors and acceptors make them promising modifiers for catalysis [29,30]. In addition, the upconversion function of CDs allows the visible and near-infrared spectrum of sunlight to be utilized, which can enhance the photocatalytic efficiency of semiconductors [31]. Therefore, CDs can be utilized as modifying materials to enhance the photocatalytic activity of traditional photocatalysts by decreasing electron-hole recombination and broadening the photoabsorption region. Very recently, CDs have been coupled with semiconductors, such as TiO_2 [31], C_3N_4 [25,29], WO_3 [32], Cu_2O [33] and others [34], to improve their photocatalytic activity.

Here, we introduced a new strategy for the synthesis of a CDs/$Na_2W_4O_{13}$/WO_3 composite by the use of a palladium-mediated hydrothermal reaction. The photodisinfection properties of the CDs/$Na_2W_4O_{13}$/WO_3 composite was evaluated by monitoring the survival rate of *E. coli* under visible light irradiation. Moreover, the dominant reactive species in photodisinfection by the CDs/$Na_2W_4O_{13}$/WO_3 composite was determined by ESR and RS scavenging experiments. Furthermore, a cell counting experiment demonstrated that the CDs/$Na_2W_4O_{13}$/WO_3 composite could be used as an environmentally friendly photodisinfection material.

2. Experimental section

2.1. Synthesis of photocatalyst

The CDs-decorated and undecorated samples were first synthesized by a solvothermal reaction and subsequently calcined in air according to the previously reported procedure [35] with proper modifications, as briefly described below. First, 6 mmol of WCl_6 and 0.006 mmol of $PdCl_2$ (0.1% molar ratio relative toWCl_6) were dissolved in 30 mL of ethanol and stirred vigorously for 1 h to obtain mixture A. Second, 30 mL of NaOH (36 mmol) ethanol solution was slowly added dropwise into mixture A at room temperature. Third, the suspension was transferred to a 100 mL Teflon-lined autoclave, maintained at 200 °C for 6 h, and then cooled to room temperature. After the solvothermal reaction, the obtained precipitate was washed once each with distilled water and ethanol and then dried at 80 °C overnight. After drying, the precipitate was crushed into a fine powder and calcined at varying temperatures of 350 °C, 450 °C and 550 °C in air for 5 h to obtain the sample, and marked as WO_3, CDs/$Na_2W_4O_{13}$/WO_3, $Na_2W_4O_{13}$. A reference sample, $Na_2W_4O_{13}$/WO_3, was prepared in the same way but without the addition of $PdCl_2$ and was calcinated at 450 °C.

2.2. Characterization

The crystal structure was characterized by powder X-ray diffraction (XRD) with Cu Kα radiation on a D8 Advance X-ray Diffractometer (Bruker, Germany).The scan range of 2θ was 10° to 80° at a scan rate of 0.5°/min. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were examined by a JEM-2100 transmission electron microscope (JEOL, Japan). Scanning electron microscopy (SEM) images were obtained on a JSM-7001 F scanning electron microscope (JEOL) at an acceleration voltage of 10 kV. The presence of C, Na, W and O in the CDs/$Na_2W_4O_{13}$/WO_3 composite was analyzed by X-ray photoelectron spectroscopy (XPS). The XPS measurements were made using an ESCALAB250 X-ray photoelectron spectrometer (Thermo Fisher Scientific Inc., MA) with an Al K anode (1486.6 eV photon energy, 300 W). Fourier transform infrared spectra (FTIR) were recorded on a Nicolet 6700 spectrometer (Thermo Fisher Scientific Inc.) to analyze the functional groups in the samples. The optical absorbance was determined from the diffuse reflectance measurements obtained on a U-3900H UV–vis spectrophotometer (Hitachi Limited, Japan) using $BaSO_4$ as the reference. Steady state photoluminescence (PL) spectra of the materials were obtained on a fluorescence spectrometer (Hitachi F-7000, Japan) with 385 nm excitation at room temperature.

2.3. Photocatalytic disinfection performance

A fixed concentration of 1 mg photocatalyst/mL *E. coli* suspension was used in the experiments. A 10 mg portion of the photocatalyst in 9.9 mL of a buffer solution was first injected into a sterile 60 mm × 15 mm Petri dish and dispersed ultrasonically for 10 min. Then, 0.1 mL of the *E. coli* suspension (ca. 10^9CFU/mL) was added to the Petri dish to give an initial *E. coli* concentration of ca. 10^7CFU/mL in the photocatalytic disinfection experiments.

A 300 W xenon lamp (MicroSolar300, Beijing Perfect Light Technology Co. Ltd., China) was used for the photocatalytic inactivation experiments and as the light source with a UV cut-off filter ($\lambda > 400$ nm). The light intensity striking the cells was ca. 10 mW/cm^2, as measured by an FZ-A optical radiometer (Photoelectric Instrument Factory of Beijing Normal University, China). A 0.1 mL aliquot of the cell suspension was withdrawn at regular time intervals. Following appropriate dilution with PBS buffer solution (pH 7), the 0.1 mL aliquots were spread onto an agar medium plate and incubated at 37 °C for 24 h. Then, the number of viable cells in terms of colony-forming units was counted. Control experiments were also carried out