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Visible light photoinactivation of bacteria by tungsten oxide nanostructures formed on a tungsten foil

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ABSTRACT

Antibacterial activity of tungsten oxide nanorods/microrods were studied against *Escherichia coli* bacteria under visible light irradiation and in dark. A two-step annealing process at temperatures up to 390 °C and 400–800 °C was applied to synthesize the tungsten oxide nanorods/microrods on tungsten foils using KOH as a catalyst. Annealing the foils at 400 °C in the presence of catalyst resulted in formation of tungsten oxide nanorods (with diameters of 50–90 nm and crystalline phase of WO_3) on surface of tungsten foils. By increasing the annealing temperature up to 800 °C, tungsten oxide microrods with $K_2W_6O_{19}$ crystalline phase were formed on the foils. The WO_3 nanorods showed a strong antibacterial property under visible light irradiation, corresponding to >92% bacterial inactivation within 24 h irradiation at room temperature, while the $K_2W_6O_{19}$ microrods formed at 800 °C could inactivate only ~45% of the bacteria at the same conditions.

1. Introduction

Various metal-oxide materials have recently been developed for photocatalytic activities [1–5]. For instance, the semiconductor titanium dioxide (TiO_2) has shown a good chemical stability and high reactivity under UV (ultraviolet) light irradiation [6]. TiO_2 has a wide band gap of 3.2 eV and absorbs light with wavelengths ≤387 nm, and thus like many other metal-oxides, it can only absorb a small fraction of the UV solar light [7]. This undesirable property necessitates the development of new visible light photocatalysts to extend the absorption wavelength range into the visible light region. As such, among the transition metal oxide groups, the tungsten oxide family has shown to be an appropriate semiconductor with many applications in sensors [8] and photocatalytic devices [9]. From this group, tungsten trioxide (WO_3) with different nanostructures is considered as an active catalytic material with a small band gap in the range of 2.4–2.8 eV. This alloy can be used as a visible-light-driven photocatalysis due to its strong absorption of the solar spectrum as well as its stable physico-chemical properties [9–11]. In addition to these findings, a recent study by the authors has newly found that tungsten oxide possesses an interesting biophotocatalytic property [10]. With this feature and the non-hazardousness of tungsten oxide [11], the compound can have a great potential for applications in nano-bio-technology with a strong photocatalytic tracking characteristic.

In order to investigate the properties of tungsten oxide at an extremely small scale, many synthetic methodologies have been utilized to grow 1D and 2D nano-scaled structures of tungsten oxides [12]. For instance, for growing 1D nanostructure of tungsten oxides, vapor–liquid–solid (VLS) and vapor–solid (VS) methods have been proposed [13,14]. Most of these growth methods need high processing temperatures; nevertheless, with a proper catalyst, tungsten oxide nanostructures can be synthesized at a much lower temperature [9].

In this paper, we first proposed a simple method to synthesize tungsten oxide using potassium hydroxide as a catalyst on a tungsten foil substrate through a two-step heating process at a low temperature. Then, we reported the antibacterial property of the 1D synthesized tungsten oxide nanorods (TON) and tungsten oxide microrods (TOM). While considering the annealing temperature effect, the antibacterial activity of the prepared nanorods was evaluated by examining the photoinactivation of *Escherichia coli* (*E. coli*) bacteria in an aqueous solution.

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2. Experimental

Tungsten foils with 99.95% purity and dimensions of 1 cm × 1 cm × 1 mm were cleaned with ethanol and acetone before the experiments. Then, 0.1 mL (milli-liter) of 0.7 M (5 wt%) KOH (potassium hydroxide) solution was dropped on the foil. When the solvent vaporized, tiny KOH seeds precipitated on the surface of the foil. The foil was put in a horizontal quartz boat that was placed in the uniform temperature zone of a conventional high-temperature furnace. Under the atmospheric pressure, the temperature of the furnace was raised from the room temperature up to 390 °C at a ramping rate of 30 °C min^{-1} (step 1). This temperature was maintained for 30 min, and then raised to 400, 500, 600, 700 and 800 °C at a similar ramping rate (step 2). After 2 h, the furnace was gradually cooled down to room temperature. The cooled samples were rinsed with de-ionized water gently and then dried at 50 °C in air for 5 min.

The surface morphology of the samples was examined using field emission-scanning electron microscopy (FE-SEM, Hitachi S-4160 at 30 kV). Before FE-SEM, the surfaces of the samples were coated by a gold thin film using the desktop sputtering (Nanostructured Coating Co.). X-ray diffraction (XRD) patterns of the samples were obtained using a Stoe Stadimp system equipped with a Cu-Kα radiation source with a step size of 0.05°. The surface chemical composition of the films was investigated using X-ray photoelectron spectroscopy (XPS, Specs-EA 10 Plus). A concentric hemispherical analyzer was used to analyze the binding energy of the surface photoelectrons excited by an Al-Kα X-ray source at the energy of 1486.6 eV. All binding energy values were determined by calibration of a fixed core level line of C(1s) at 285.0 eV as a reference point.

Antibacterial activity of the films was investigated against *E. coli* bacteria (ATCC 25922, USA) by using a method called drop-test. The *E. coli* was selected as a model for the Gram-negative bacteria, because it is one of the most common bacteria causing many serious infections such as bacteremia, urinary tract infection and food poisoning [15]. Before any microbiological experiment, the glassware and samples were sterilized by autoclaving at temperature of 120 °C and pressure of 15 lbs for a period of 15 min, as also mentioned in literatures (see, e.g., [16]). The bacteria were cultured on a nutrient agar plate at 37 °C for 24 h. The cultured bacteria were added to 10 mL of saline solution to obtain the bacterial concentration of ~10^8 colony forming units (CFU)/mL. Then, a portion of the saline solution containing the bacteria was diluted to ~10^6 CFU/mL. To carry out the antibacterial drop-test, each film was put in a sterilized Petri dish, and 100 μL of the diluted saline solution containing the bacteria were spread on surface of each film. The films were exposed to irradiation of a 110 mW/cm^2 Hg lamp (using a cut-off filter to remove the irradiation wavelengths below 400 nm) at room

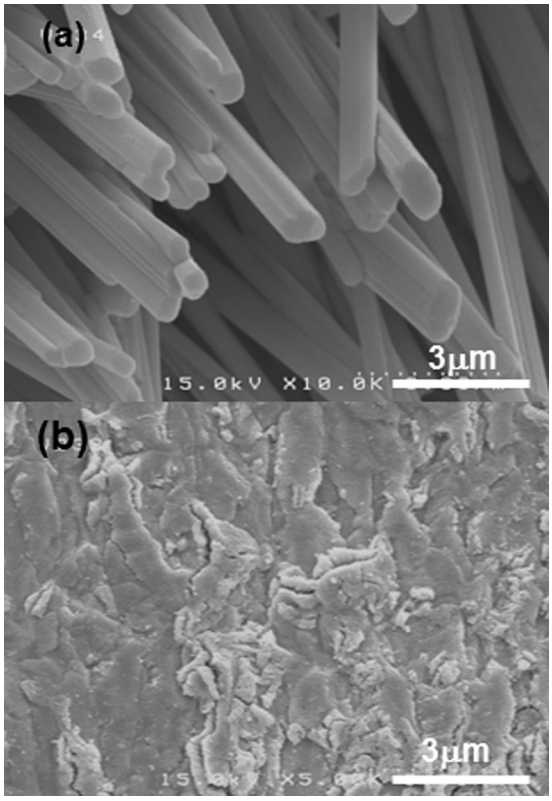

Fig. 1. SEM images of the tungsten oxide films prepared at 700 °C (in step 2) (a) in the presence and (b) in the absence of KOH as a catalyst.

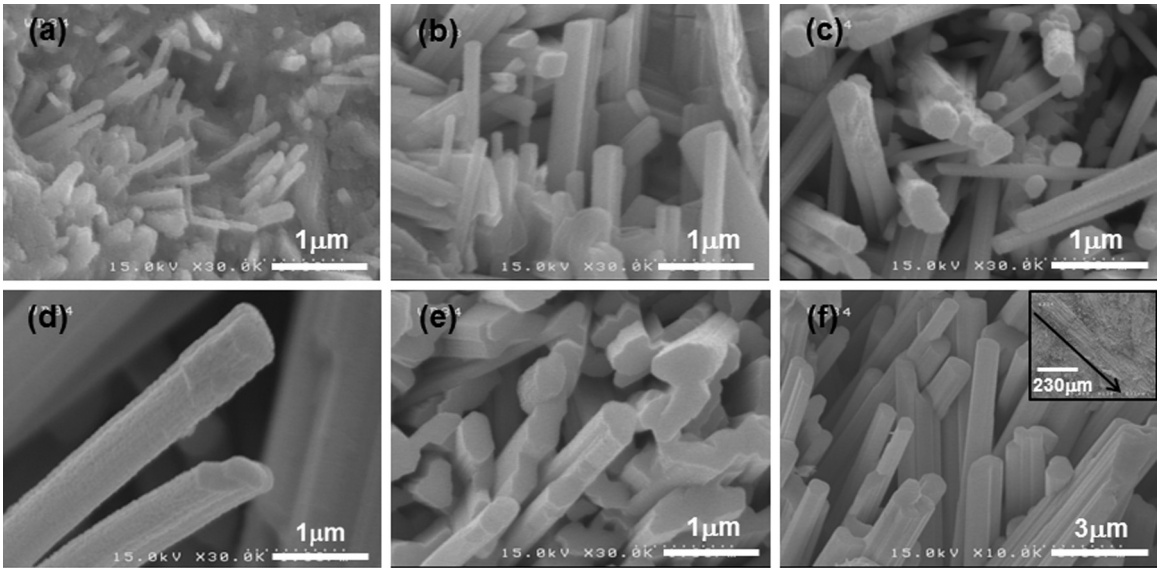

Fig. 2. SEM images of the tungsten oxide films after annealing at (a) 400, (b) 500, (c) 600, (d) 700 and (e, f) 800 °C, inset figure (f) shows long nanostructures synthesized at 800 °C.