Cellulose-Based WO₃ Nanocomposites Prepared by a Sol–Gel Method at Low Temperature

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Abstract. A facile method was developed to prepare cellulose-based WO₃ nanocomposites. The preparation was carried out by a sol-gel method by involving treatment of tungsten hexachloride and tri-block nonionic polymer at the temperature as low as 100 °C. The morphology, surface chemical composition, functional groups, and crystal phase of the as-prepared cellulose-based WO₃ nanocomposites were investigated by scanning electron microscopy, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, and X-ray powder diffraction, respectively.

1. Introduction
Heterogeneous photocatalysis with inorganic semiconductors offers clean, solar driven process for the treatment of all kinds of contaminants, especially for the removal of organic dyes from wastewaters [1]. Among semiconductors, tungsten trioxide (WO₃) is promising for photocatalysis due to its strong adsorption within the solar spectrum (≤480 nm) and high thermal and physicochemical stability [2–4]. Efforts have been done on photocatalytic degradation of dyes in solutions involving suspensions of WO₃ particles [5, 6]. However, from a practical viewpoint, recycling the photocatalytic powders in the aqueous purification is a challenging task [7].

In an effort to solve this problem, immobilization of the catalyst on some substrates with large surface areas has received much attention. A variety of substrates such as glass, graphene, and textile fibers have been investigated [8–10]. Among these different substrates, cellulose is very promising candidate for high performance photocatalyst because of its stretchability, flexibility, biodegradability, and lightweight. Immobilization of the catalyst on cellulose surface leads to the formation of inorganic–organic hybrid composites which by the synergistic combination of the components’ characteristics can exhibit additional functionalities such as pollutants decomposition, self-cleaning and antibacterial properties [11].

In this article, we firstly described a facile route to prepare the cellulose-based WO₃ nanocomposites at a temperature of 100 °C. The prepared cellulose-based WO₃ hybrid material was characterized by using a variety of measurements.

2. Experimental
The cellulose fibers were bleached plain weave 100% cotton fabric which was obtained from a local market. The cellulose fibers were immerged into the nonionic detergent solution at 80 °C for 20 min to
remove the impurities, and then washed three times by deionized water and dried at 60 °C for 5 h. All chemicals were of analytical grade.

The preparation of cellulose-based WO₃ nanocomposites was carried out by a sol-gel method. The tri-block nonionic polymer, poly (ethylene oxide)₂₀–poly (propylene oxide)₇₀–poly (ethylene oxide)₂₀ (PI23) was used as a precursor. 5.0 mmol tungsten hexachloride (WCl₆) was dissolved in 50 mL ethanol and stirred at room temperature for 5 h. Subsequently the solution was stirred for 24 h at 40 °C. The cellulose fibers were added to the solution, followed by dropwise addition of 10 mL of 0.025 M PI23 ethanol solutions under moderate stirring. The mixture was then kept under constant stirring at 100 °C for 4 h. The fibers were collected by filtering, then heated at 60 °C for 5 min in preheated oven and cured at 100 °C for 5 min. To remove unattached particles, it was rinsed with deionized water and dried at 40 °C for 8 h.

The morphology of pristine cellulose fibers and cellulose-based WO₃ nanocomposites were characterized by scanning electron microscope (SEM, JSM-5600, operating at 15 keV) and field emission scanning electron microscopy (FE-SEM, Hitachi S-4800, operating at 5 keV). The surface chemical composition of the sample was performed on a Kratos XSAM–800 (UK) spectrometer with an AlKα (hv=1486.6 eV) radiation X-ray source. The functional groups of the samples were carried on a Nicolet 4700 spectrometer. The crystal phase was characterized by a powder X-ray diffraction (XRD) using D/max-2550 PC (Rigaku) for Cu Kα (λ=1.54056 Å) radiation at 40 kV and 200 Ma.

3. Results and Discussion
The surface morphologies of the samples are shown in figure 1. The surface of the pristine fibers is smooth, clean with convolution (figure 1a). According to figure 1b-1d, it can be found that the sample surface is covered by the WO₃ nanoparticles. However, the WO₃ nanoparticles distribution on the fiber surface is not quite uniform at a microscopic level. It is indicated that the loading of WO₃ particles on cellulose fibers was a deposit owing to the fact the fact that the scraggly surface of cellulose fibers makes it against forming of homogeneous film. The EDS spectrum of sample (figure 1e) reveals the presence of element W.

The surface characteristic of cellulose-based WO₃ nanocomposites also was characterized by X-ray photoelectron spectroscopy (XPS), as shown in the figure 2. Figure 2a shows the total XPS spectrum, in which W peak can be seen clearly and the W content is 3.6%. Figure 2b shows the results of W 4f XPS spectrum. The two peaks at 35.85 and 37.96 eV in the spectrum can be assigned to W 4f7/2 and W 4f5/2, respectively [12, 13]. It is indicated that the surface of cellulose fibers is formed only of W⁶⁺-states of WO₃-phase.

The interaction between the WO₃ and cellulose fibers was also confirmed by FT-IR spectroscopy as shown in figure 3a. After WO₃ loading, some relatively strong and weak bands at 818, 895 and 950 cm⁻¹ are observed in the infrared regions of 1100–650 cm⁻¹, which correspond to tungsten-oxygen stretching, bending and lattice modes. The peak at 818 cm⁻¹ is assigned to ν (W–O–W). The weak peak at 895 cm⁻¹ is attributed to W–O–W bridging mode [14]. The bands at 950 cm⁻¹ is attributed to ν (W–O) of W=O group. It is to be noted that the position of W=O vibration peak of cellulose-based WO₃ nanocomposites is different from that of WO₃ nanoparticles in the literature (962 cm⁻¹) [15]. This may be due to the interaction of the WO₃ particles with the functional groups on the surface of cellulose fibers. Moreover, the intensity of the peak at 1079 cm⁻¹ clearly increased for cellulose-based WO₃ nanocomposites, which could be explained by the influence of the formation of C–O–W bond. Figure 3(b) illustrates the XRD patterns of samples. It is found that sample of cellulose-based WO₃ nanocomposites presents almost all the diffraction peaks corresponding to pristine cellulose fibers. Moreover, a strong diffraction peak at 25.66° and a weak diffraction peak at 30.04° appear. Further, the intensity of the peak at 16.56° increases obviously. These three peaks are attributed to orthorhombic WO₃·H₂O phase (JCPDS No. 43–0679).
Figure 1. SEM images of (a) pristine cellulose fibers, (b) low and (c) high magnification views of cellulose-based WO₃ nanocomposites; (d) FE-SEM image of cellulose-based WO₃ nanocomposites; (e) EDS spectrum of cellulose-based WO₃ nanocomposites.
4. Conclusions
In summary, we successfully synthesized cellulose-based \( \text{WO}_3 \) nanocomposites through a facile sol-gel method using the tri-block nonionic polymer P123 as a precursor. The hybrid nanocomposites were characterized by series techniques. The loading of \( \text{WO}_3 \) nanoparticles on cellulose fibers surface exhibits great potential for degrading organic pollutants in wastewater treatment and other functional applications.

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6. References
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