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# Synthesis of spherical macroporous $WO_3$ particles and their high photocatalytic performance

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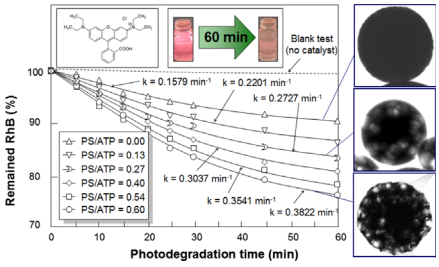
## HIGHLIGHTS

- Spherical macroporous tungsten trioxide particles by a spray-pyrolysis method.
- Control of outer diameter by changing initial precursor concentration.
- Control of pore structure by changing template-to-tungsten oxide source mass ratio.
- Excellent photocatalytic performance due to existence of porous structure.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Tungsten trioxide ($WO_3$) materials have excellent performance in transferring visible-light energy and are widely used in photocatalysis, solar cells, and hydrogen generation. However, $WO_3$ is expensive and in short supply. It is therefore important to develop efficient materials that use smaller amounts of $WO_3$. One strategy is to produce porous materials so that the entire area of the $WO_3$ material can be used and activated effectively. In this study, we synthesized macroporous $WO_3$ particles using a spray-pyrolysis method with colloidal templating. Ammonium tungsten pentahydrate (ATP) was used to produce $WO_3$ without impurities, and polystyrene (PS) spheres were used to promote spherical macropore formation. The synthesized particles were characterized using thermogravimetric analysis, X-ray diffraction, nitrogen adsorption, scanning electron microscopy, and transmission electron microscopy (TEM). Several process parameters (i.e. initial precursor concentration and mass ratio between host and template) were investigated to get highly ordered porous particles with controllable porous structure and particle outer diameter. Photocatalytic analysis results showed that the amount of PS that provided the optimum photocatalytic enhancement. Our results showed that a PS/ATP mass ratio of 0.60 provided $WO_3$ particles with a photocatalytic rate 2.5 times that of dense $WO_3$. TEM analysis showed that highly ordered macropores were produced, enabling better penetration and interaction of molecules and light in the deepest part of the active catalyst, resulting in enhancement of the photocatalytic rate. This method will be useful for large-scale synthesis of small amounts of $WO_3$ with high photocatalytic performance.



## 1. Introduction

Recently, tungsten trioxide ($WO_3$) has been widely studied because it has an affinity for visible light, and is chemically inert, thermally stable, and harmless (Liu et al., 2012; Saepurahman

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et al., 2010; Sun et al., 2010). These excellent properties make this material useful for solar-related applications such as photocatalysts, solar cells, water splitting, and hydrogen generation. However, there are several problems regarding the use of this material, particularly with regard to its availability. The material is scarce, and its use is affected by rising prices and export restrictions imposed by producer countries. Efficient materials with good performances are therefore essential in the face of increasing demand but decreasing resources (Zheng et al., 2011).

To solve the above problems, design of materials in the nanometer-sized ranges is the best. However, the use of this type of material remains problems. The application of nanoparticles is known to have greater adverse health effects than larger particles because of the possibility for them to be deposited into the alveoli and potentially be absorbed through the skin. Further, when the nanoparticles are disposed of directly, there are environmental problems to overcome. Therefore, specific processes for separating these nanomaterials (after nanoparticles are not used any longer) are crucial although the separation process is typically expensive. These difficulties and costs in the separation process are not found when using larger particles (Nandiyanto et al., 2009a).

Design of materials with porous structures has been much studied to solve this difficulty. An increase in the porous structural order improves the material performance and also reduces the amounts of raw materials used (Nandiyanto et al., 2009a). However, there is little information on porous $WO_3$ in the literature. Until recently, there were only few papers on porous $WO_3$.Baeck et al. (2003), Teoh et al. (2005), and Li et al. (2010) used surfactants as templates, and materials with mesoporous structures were successfully prepared. However, the surfactant sometimes cannot be removed completely (Huang et al., 2012), which may produce impurities and adversely affect the material performance. Instead of surfactants, Singh et al. (2008) and Chen et al. (2011a) proposed the use of gas bubbles to form pores. Although such methods are effective, the synthetic procedures are complicated and require the use of electrochemical devices, limiting scaling-up of production. Huang et al. (2012) suggested controlling particle growth to produce micro-flower particles. Control of the particle morphology has been reported, but the use of sodium tungsten can create problems, and additional purification processes are needed to remove sodium from the final product. In addition, the above methods result in the formation of mesoporous structures, which are not applicable to the photodecomposition of large molecules because of limitations in mass transfer, diffusivity, and penetration of molecules and photons into or out of the mesoporous system (Nandiyanto et al., 2009b).

To develop materials with pores larger than those in the mesoporous range, Sadakane et al. (2008), Sumida et al. (2002), and Chen et al. (2011b) proposed the use of submicron polymer spheres as templates. Macropores with spherical pore shapes were obtained. However, the process has limitations as it can only be used to produce films. Lv et al. (2011) further developed the process by using carbon spheres as the template. Porous particles were successfully produced, but because carbon could damage the catalytic performance, carbon removal is of particular concern. Leghari et al. (2011) and Amano et al. (2010) suggested using hydrothermal processes instead of templating methods. Although hydrothermal processes successfully create macroporous structures under template-free condition, these processes have limitations such as formation of pores with irregular sizes and structures, and difficulties in producing monodispersed particles.

Most reports show that the above methods have been successfully used to prepare porous $WO_3$, but the physical appearance of the product (i.e., roughness, porosity, agglomeration, and irregular shape of the prepared particles) and the mechanism of porous particle formation have not been considered. Also, these methods have the disadvantages of high costs, time-consuming processes, low throughput, and unsuitability for large-scale production. Furthermore, correlations between porous structure and material performance have not yet been discussed, while such information is crucial for optimizing the performances of porous particles.

In our previous works, we reported the synthesis of porous particles with controllable pore size and particle outer diameter using liquid-phase synthesis (Nandiyanto et al., 2009b) and spray methods (Gradoń et al., 2004; Nandiyanto et al., 2010; Nandiyanto et al., 2009a; Nandiyanto and Okuyama, 2011; Nandiyanto et al., 2013; Nandiyanto et al., 2012). Optimization of the process parameters (i.e., surface charge, size, and concentration of colloidal nanoparticles) was also investigated in detail to get highly ordered porous film and particles (Nandiyanto et al., 2013). With this optimization, control of particle morphology, porous structure, pore size, particle outer diameter are possible. This optimization is then used for developing the synthesis of particles from the smallest engineered porous silica nanoparticles (Nandiyanto et al., 2009b) to micrometer-sized particles (Nandiyanto et al., 2010; Nandiyanto and Okuyama, 2011).

Based on our previous works, the purpose of this study was to develop a method for the rapid synthesis of spherical macroporous $WO_3$ particles with controllable porous structure and particle diameter (from 0.3 to 2 μm) and to examine the correlations between the porous structure and the photocatalytic performance over non-porous $WO_3$ particles. We limited our synthesis method in preparing particles with few hundred nanometers of pores with the prospect of reducing diffusion limitation of molecules with larger size and high concentration. In general, the use of these types of pores can be possible for applications in molecules with variation of sizes and concentrations. The spherical macroporous $WO_3$ particles were prepared by a spray-pyrolysis of a precursor suspension containing ammonium tungsten pentahydrate (ATP) as a tungsten source and polystyrene (PS) spheres as a colloidal template. Unlike other methods that involve complicated and time-consuming processes, the present method enables one-step production of macroporous $WO_3$ particles with a residence time of several seconds, which is promising for industrial applications. Several process parameters (i.e. initial precursor concentration and mass ratio between host and template) were investigated to get highly ordered porous particles. In addition, although the processing time is a crucial factor in the particle formation in the spray method (i.e. providing conversion of raw material, giving more time for solvent evaporation, and offering self-assembly of components into their maximum structure), we did not focus on this parameter in the present paper because this parameter has been discussed in detail in our previous work (Gradoń et al., 2004).

Experimental results showed that the porous structure and particle diameter were controllable only by varying the PS/ATP mass ratio and the initial precursor concentration, respectively; while most previous $WO_3$ papers have not dealt with these good porous structure and outer diameter control. Due to the advantage of the template method (Nandiyanto et al., 2010; Nandiyanto et al., 2013), the present method also allows the production of particles with spherical macropores. A detailed investigation was performed to determine the optimum amount of PS needed to obtain maximum photocatalytic performance, and the photocatalytic rate was compared with that of non-porous $WO_3$ particles. As a result of the macroporous structure, the number of catalytic active site increases, resulting the particles with macroporous structure to have better performance than those with dense structure. A mechanism for porous $WO_3$ particle formation is also proposed; where this has not been covered in previous reports.

## 2. Experimental section

### 2.1. Raw materials

Macroporous $WO_3$ particles were prepared from a precursor containing ATP (Kanto Chemical Co., Inc., Japan) and 230-nm additive-free