

## Synthesis, Structure and Photocatalytic Activity of Titanium Containing Anderson-Type Polyoxometalate

Hye Ran Noh<sup>a, b</sup>, Jong-Yun Kim<sup>a, b</sup>, Tae-Hyeong Kim<sup>b</sup>, Jeongmook Lee<sup>a, b</sup>, Jung Hwan Park<sup>c</sup>, Sang Ho Lim<sup>a, b\*</sup>  
<sup>a</sup>Radiochemistry and Nuclear Nonproliferation, University of Science and Technology, Daejeon 34113, Republic of Korea

<sup>b</sup>Korea Atomic Energy Research Institute, Daejeon 34057, Republic of Korea

<sup>c</sup>Department of Nuclear & Quantum Engineering, Korea Advanced Institute of Science and Technology

\*Corresponding author: slim@kaeri.re.kr

### 1. Introduction

Polyoxometalates (POMs) are cluster compounds composed of transition metals with high oxidation state and oxygens. Owing to many outstanding properties including redox activity and structural diversity, POMs have been applied to broad fields, such as materials, catalysis, bio- and nanotechnology and radiochemistry [1-3].

Out of the most prominent POM structures, Anderson-type POMs with a general formula of  $[H_y(XO_6)_M O_{18}]^n$  ( $y=0-6$ ,  $n=2-8$ ,  $M$ =addenda atom,  $X$ =heteroatom) represent one of the basic topological structures of the POM family. Anderson-type POMs have a planar arrangement and two terminal O atoms attached to each metal atom unlike other types, which can have high reactivity and various coordination modes. Thus, it is used as an ideal inorganic building block that can be modified by combining with various multifunctional hybrid materials [4].

Another important feature of Anderson type POMs is incorporating various heteroatoms with different size and oxidation states, which can lead to change their photocatalytic performance. The photocatalytic performance is governed by their HOMO-LUMO energy gap, which are greatly affected by the central heteroatom [5]. Therefore, the synthesis research on incorporating various heteroatoms into Anderson-type POMs have been conducted in order to find the excellent photocatalyst candidates.

Herein, we discovered that the Anderson POM,  $Na_2K_6Ti_{10.92}W_{6.08}O_{24} \cdot 12H_2O$  (Ti-POM), which consists of pure inorganic framework built from a central Ti core supported by six  $WO_6$  inorganic scaffold, and the crystal structure was confirmed and refined using single-crystal X-ray diffraction (SC-XRD). In addition, we calculated its bandgap energy by applying the Kubelka-Munk conversion to UV-visible diffuse reflectance spectra, in order to evaluate whether Ti-POM can be used as a photocatalyst.

### 2. Methods and Results

#### 2.1 Synthesis

$TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$  (Alfa Aesar) and  $Na_2WO_4 \cdot 2H_2O$  (Sigma-Aldrich) were used as purchased.

Hydrothermal reaction was used to synthesize the Anderson-type Ti-POM.  $TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$  (0.1599 g,  $5.79 \times 10^{-4}$  mol) and  $Na_2WO_4 \cdot 2H_2O$  (0.8814 g,  $2.67 \times 10^{-3}$  mol) were mixed with 10 mL of deionized water. The mixture was placed into a 23 mL Teflon-lined stainless-steel autoclave. The autoclave was sealed and heated at 230 °C for 2 days, and then cooled down to room temperature. After cooling, the autoclave was opened, and the mother liquor was collected via a filtration. Excess KCl (2.5 g,  $3.35 \times 10^{-2}$  mol) was added to the mother liquor and stirred for 1 day. Finally, the precipitate was filtered off and dried at room temperature.

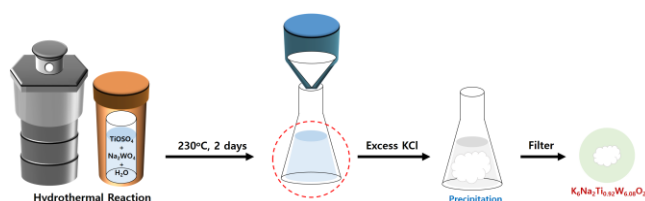


Fig. 1. Synthesis schematic of Ti-POM.

#### 2.2 Single crystal X-ray diffraction

Diffraction data were collected at 173 K using a Bruker PHOTON II X-ray diffractometer with graphite monochromated  $Mo K\alpha$  radiation. The collected data were then integrated using the SAINT program, with the intensities corrected for the Lorentz factor, polarization, air absorption, and the absorption attributable to the variation in the path length through the detector faceplate. The structures were solved by direct methods using SHELXS-13 and refined using SHELXL-13. All the calculations were performed using the WinGX-14 crystallographic software package.

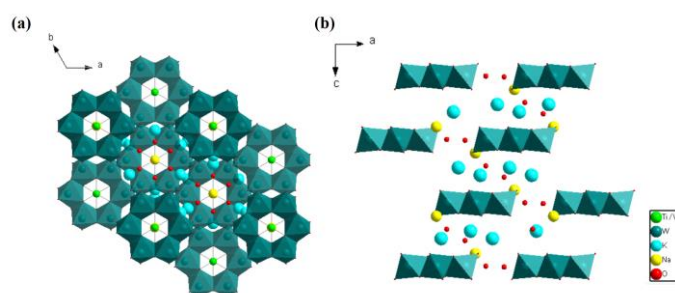


Fig. 2. Ball-and-stick representations of (a) a framework of Ti-POM in ab-plane and (b) ac-plane.

Ti-POM crystallizes in the Rhombohedral space group R-3m (No. 166) with 0-D framework structure. In detail, Ti-POM is composed of six edge sharing  $\text{WO}_6$  octahedra surrounding a central, edge sharing Ti atom of octahedral geometry ( $\text{TiO}_6$ ) leading to a planar arrangement and  $D_{3d}$  symmetry. Fig. 2(a) and 2(b) shows ball-and-stick representations of a framework of Ti-POM in (a) ab-plane and (b) ac-plane. Unlike the case of general Anderson-POMs with X/M ratio = 6,  $\text{Ti}^{4+}$  and  $\text{W}^{4+}$  are statistically disordered with 92:8% occupancy at heteroatom sites.

### 2.3 UV-vis diffuse reflectance spectroscopy

UV-visible (UV-vis) diffuse reflectance spectra for Ti-POM was obtained on a Perkin Elmer Lambda 1050 UV-vis-NUR spectrophotometer at room temperature over the 200-2700 nm spectral range. The reflectance spectra were transformed into the absorbance using the Kubelka-Munk function [6]. The Kubelka-Munk function (eq. (1)) was used to calculate absorption (K/S) data, where S is the scattering coefficient, K is the absorption coefficient, and R is the reflectance obtained in the DRS data.

$$F(R) = (1-R)^2/2R = K/S \quad (1)$$

In the  $[F(R)E]^{1/2}$ -versus-E plot (Fig. 3), extrapolating the linear region of the rising curve to zero suggested the onset of absorption at approximately 3.60 eV, which is the optical band gap energies for Ti-POM.

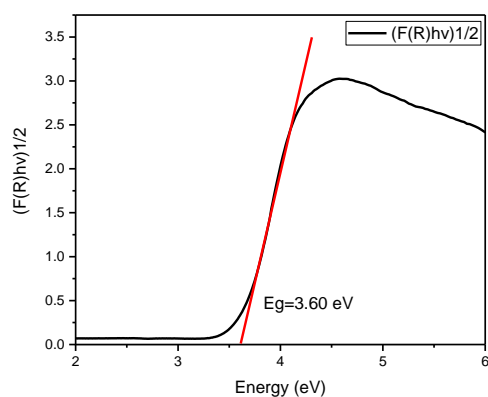


Fig. 3. UV-visible diffuse reflectance spectra of Ti-POM.

### 3. Conclusions

We discovered that the Anderson-type Polyoxometalate  $\text{Na}_2\text{K}_6\text{Ti}_{0.92}\text{W}_{6.08}\text{O}_{24} \cdot 12\text{H}_2\text{O}$ , which consists of pure inorganic framework built from a central Ti core supported by six  $\text{WO}_6$  inorganic scaffold, and the crystal structure was confirmed and refined

using SC-XRD.

Synthesized Ti-POM and  $\text{TiO}_2$ , which is a well-known as a prominent photocatalyst, both have similar chemical composition and electronic properties, because they both contain transition metal elements with  $d^0$  electron configuration and oxygen atoms. Therefore, we propose our POM as a potential candidate for water splitting photocatalyst. Optical characterization result showed that the light absorption range is from 200 to 400 nm, and the band gap is 3.60 eV, which is sufficiently larger than the theoretical minimum band gap (1.23 eV) for water splitting.

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