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Preparation of Carbon Coated $FeWO_4$ and its Photocatalytic Activity Under Visible Light

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Abstract: Preparation of carbon coated $FeWO_4$ was carried out by heat treatment of $WO_{2.9}$ with iron acetate at 400^{o}C, followed by carbonization with poly(vinyl alcohol) (PVA) as carbon precursor at 800^{o}C in N_2 atmosphere. The powders mainly consist of $FeWO_4$. The photocatalytic activities of their samples were confirmed by phenol photodecomposition in its aqueous solution. Carbon coated $FeWO_4$ powders revealed photocatalytic activity under visible light. However, the photocatalytic activity of $FeWO_4$ without carbon coating could not be detected. Carbon coating to the $FeWO_4$ derived the photocatalytic activity under visible light irradiation. An addition of 10% PVA to the carbon coating derived the highest photocatalytic activity to decompose the phenol.

TiO_2 semiconductor photocatalyst has been applied in the mineralization of undesirable chemical pollutants in water and air [1, 2]. However, a large band gap (3.2 eV) having TiO_2 corresponds to the absorbance in the ultra-violet (UV) irradiation. This means that it is photocatalytic activating only under the UV. Improvement of the efficiency of photocatalytic activity becomes an important matter. Improvement of it has been examined by anion doping, cation doping and coupling with other semiconductors [3-7]. For utilizing solar light efficiently, the development of the photocatalyst which works under the visible light is a key subject. It was also reported that several compounds which showed semiconductor characteristics such as TaO_4, TaON, and $BiNO_4$ revealed the photocatalytic activity under visible light [8-10].

On the other hand, formation of reduced phases of TiO_2 which appear in Ti_nO_{2n-1} were observed through carbon coating to the TiO_2 at high temperature, and they revealed photocatalytic activity under visible light irradiation [11]. The reduced phase of tungsten oxide ($W_{18}O_{49}$) formed by the process of carbon coating also indicated the photocatalytic activity under the visible light irradiation [12, 13]. The thin carbon layer coated on the surface of $W_{18}O_{49}$ particles derived the adsorptivity and photocatalytic activity under visible light irradiation. Its photocatalytic activity of carbon coated $W_{18}O_{49}$ has been improved through iron doping [14]. Carbon coated $W_{18}O_{49}$ doped iron exhibited higher photocatalytic activity than carbon coated $W_{18}O_{49}$ without iron. In the formation of carbon coated $W_{18}O_{49}$ with iron, peaks of iron tungstate ($FeWO_4$) were observed on the XRD patterns of samples prepared. An increase of the addition of iron acetate derived the increasing of deposition of $FeWO_4$. The deposition of $FeWO_4$ is strongly related to the formation of solid solution between iron and $W_{18}O_{49}$.

Some of metal tungstates (MWO_4) such as $ZnWO_4$ and $PbWO_4$ have been reported as UV active photocatalyst [15]. Moreover Bi_2WO_6 is photoactive under visible light [16]. $FeWO_4$ might be worked as a photocatalyst similar to aforementioned metal tungstates. In this study, the preparation of carbon coated $FeWO_4$ and its photocatalytic activity under visible light will be discussed.

The preparation of $FeWO_4$ was carried out by using heat treatment of $WO_{2.9}$ and iron (II) acetate. They were mixed in 1:1 mass ratio and then heat treated at 400^{o}C in N_2 atmosphere. Carbon coating to the obtained powders was carried out according to the coating of carbon to the ceramic powders [17]. These powders were mixed with poly (vinyl alcohol) (PVA) in different mass ratios 90/10, 80/20, 70/30, 60/40 and 50/50 and then heat treated at 800^{o}C in N_2 to obtain the carbon coating to the $FeWO_4$. Heat treatment conditions were applied 5^{o}C /min and 60 ml/min in N_2 flow. The sample code was applied according to the following: 1-1FWPx, where F corresponds to the iron, W corresponds to the tungsten, P corresponds to PVA and x corresponds to amount of addition of PVA, respectively. Preparation of $FeWO_4$ without carbon coating was also carried out, where $WO_{2.9}$ and iron (II) acetate were mixed in 1:1 mass ratio and heat treated at 900^{o}C in N_2. The sample code 1-1FW900 was applied. The photocatalytic activities of the prepared samples were evaluated through the photodecomposition of phenol in its aqueous solution of concentration 5.3×10^{-4} mol/dm^3. Carbon coated powders dispersed in phenol solutions were kept under dark condition to saturate the phenol onto the thin carbon layer deposited through carbon coating process on the surface of $FeWO_4$ particles. After the saturation of this layer, the fluorescent lamp intensity of 7 W/m^2 (intensity from 400 -700 nm) was used as a visible light irradiation source. The residue concentration of phenol was determined by using high performance liquid chromatography (HPLC) with UV detector on an ODS-100S column using 50% MeOH/ 50% water as a mobile phase at 0.001 dm^3 / min of flow rate. The concentration of phenol was measured at the wavelength λ = 269 nm.

Fig. (**1**) shows the changes in XRD pattern with addition of PVA. $FeWO_4$ was confirmed as main peaks in 1-1FW900 (Fig. **1a**) and carbon coated samples (Fig. **1b-d**). The peaks of other chemical compounds were recognized. Traces of

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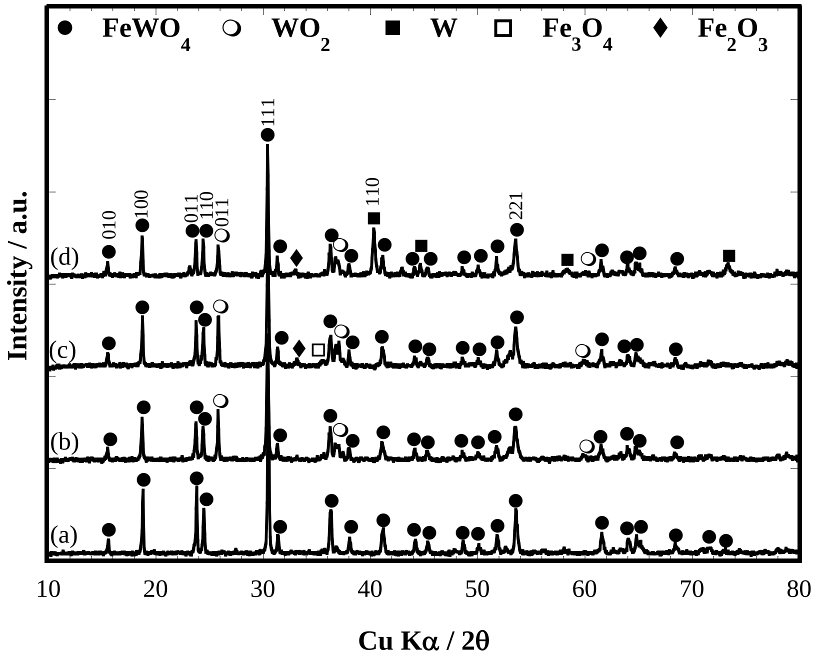

Fig. (1). XRD patterns of samples prepared, (**a**) 1-1FW900 (**b**) 1-1FWP10 (**c**) 1-1FWP30 (**d**) 1-1FWP50.

Fe_2O_3 and Fe_3O_4 obtained from the oxidation of iron acetate were also observed. WO_2 was also observed on the carbon coated samples and its deposition decreased with the increase of each addition of PVA. Increasing of amount of PVA derived the deposition of W metal in addition of 40 and 50% PVA. It has reported that the thin carbon layer was formed on the photocatalyst particle by carbon coating [18]. It seemed to carry out the formation of thinner carbon layer in this case. This carbon thin layer will be worked as an adsorption layer of pollutants.

The color of 1-1FW900 and carbon coated $FeWO_4$ powders were dark brown and black, respectively. The absorbances of their synthesized samples were measured in the wavelength range 250 -700 nm by using diffuse reflectance spectrophotometer. 1-1FW900 which mainly consists of $FeWO_4$ shows the absorbance in the whole wavelength as shown on Fig. (**2**). Carbon coated $FeWO_4$ powders also revealed absorbance in the whole range of wavelength, including visible light. Their absorbance spectra are compared to TiO_2 with anatase structure (ST-01; Ishiharasangyo Co.

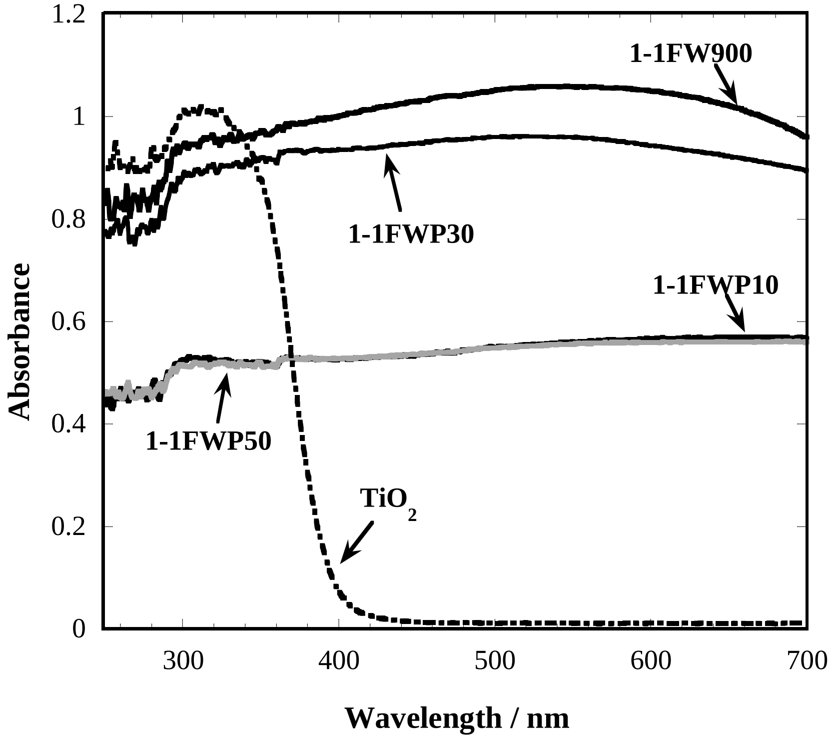

Fig. (2). UV – Vis absorption spectra of samples prepared.

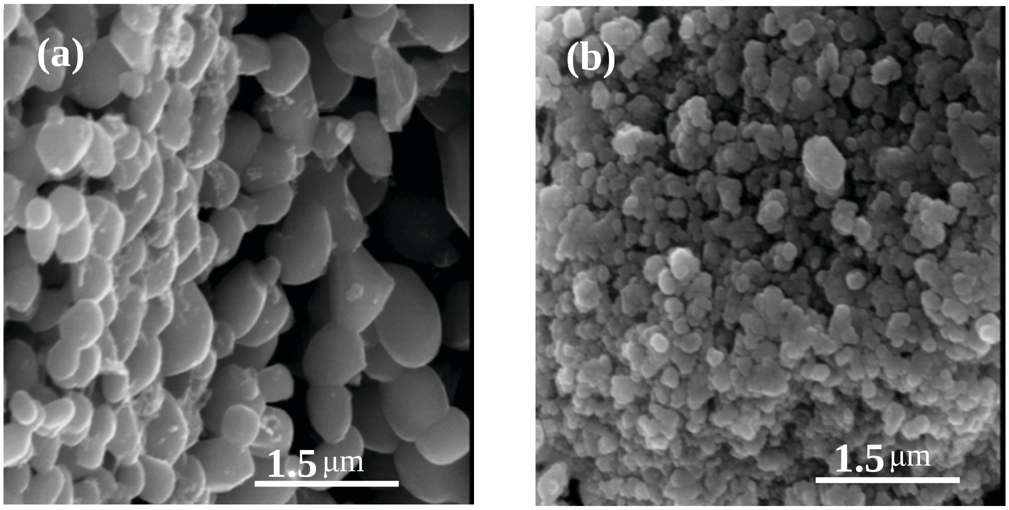

Fig. (3). SEM photographs of sample prepared, (**a**) 1-1FW900 (**b**) 1-1FWP10.

Ltd.,). ST-01 is known to be active only under UV rays and so have absorption in the wavelength range below 400 nm. The spectrum of carbon coated $FeWO_4$ is supposed to be comprised of overlapping two spectra, such as $FeWO_4$ and carbon layer coated on the surface of $FeWO_4$ particles, both can absorb visible light.

SEM photographs of 1-1FWP10 were compared with that of 1-1FW900 in Fig. (**3**). The $FeWO_4$ powders with and without carbon coating have almost round like morphology. The particle size of carbon coated $FeWO_4$ (Fig. **3b**) is small (80 – 350 nm), much smaller than $FeWO_4$ without carbon coating (Fig. **3a**). The carbon coating to $FeWO_4$ prevents the centering and growth of $FeWO_4$ crystal, smaller particle size was obtained in consequent.

Fig. (**4**) illustrates the changes in residue concentration of phenol under visible light irradiation for 1-1FW900 and carbon coated $FeWO_4$ powders. 1-1FW900 did not reveal the photocatalytic activity under visible light. On the other hand,

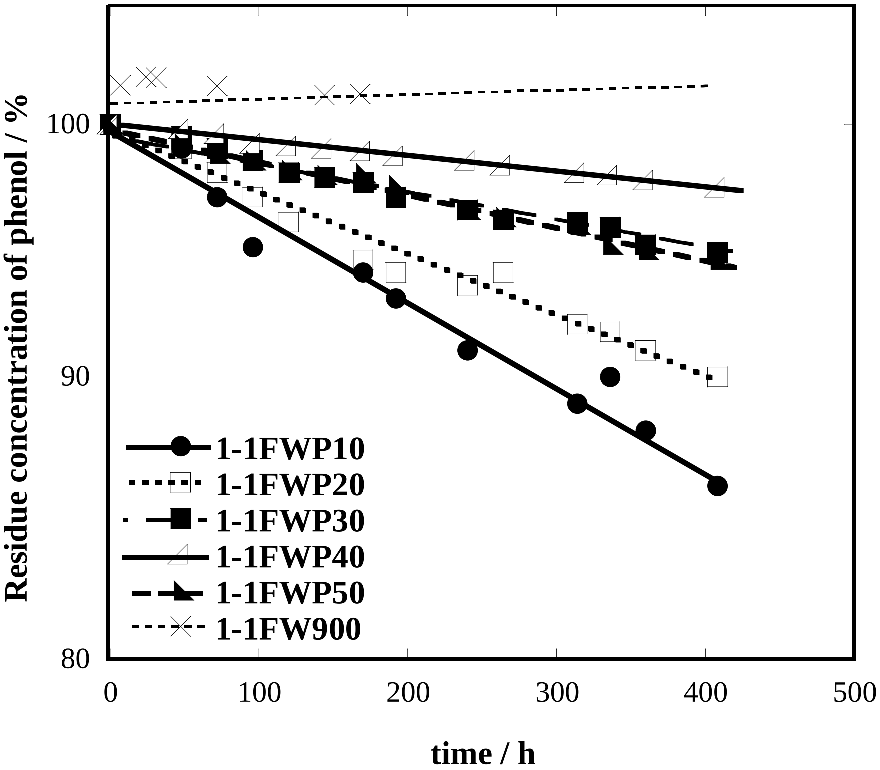

Fig. (4). Changes in residue concentration of phenol under visible light irradiation for carbon coated $FeWO_4$.

all of the carbon coated $FeWO_4$ powders exhibited photocatalytic activity under visible light. Trace concentration of intermediates through phenol decomposition (catechol and hydroquinone) have been detected. This indicates that phenol was decomposed by carbon coated $FeWO_4$ under visible light irradiation. Carbon coating to the $FeWO_4$ derived its photocatalytic activity under visible light irradiation. The two factors small size (Fig. **3b**) and carbon coating to $FeWO_4$ seems to give detectable activity under visible light. The photocatalytic activity of carbon coated $FeWO_4$ samples decreased with increasing PVA. In this case, the highest photocatalytic activity of phenol decomposition was observed on sample 1-1FWP10 prepared with 10% PVA. The high photocatalytic activity revealing 1-1FWP10 could be related to the suitable thin carbon layer for adsorption which existed in this sample.

$FeWO_4$ without carbon coating could not show photocatalytic activity under visible light irradiation. However, carbon coated $FeWO_4$ exhibited photocatalytic activity. It becomes clear that its photocatalytic activity was shown under the visible light irradiation. It is considered that the carbon coating to the $FeWO_4$ derived the photocatalytic activity under visible light, and addition of 10% PVA exhibited the highest photocatalytic activity. Preparation of the photocatalyst which worked in the visible light succeeded because of the carbon coating to the $FeWO_4$.

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