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Visible Light Photocatalytic Degradation of Methylene Blue Using V_2O_5 Nanoparticles

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Abstract: *Flame spray pyrolysis (FSP) was employed to synthesize vanadium pentoxide (V_2O_5). The crystalline phase, morphology and size of the nanoparticles were characterized by XRD, FE-SEM, HR-TEM and EDXS. The specific surface area of the nanoparticles was measured by nitrogen adsorption (BET analysis). The XRD patterns showed that the nanoparticles had the orthorhombic phase of V_2O_5 with the JCPDS file No. 41-1426. The SEM image showed nanoparticles have clear spherical morphologies. The crystallite size of V_2O_5 spherical particles was in the range of 20-30 nm. The photocatalytic activities of V_2O_5 NPs were determined by studying the degradation of methylene blue under visible light irradiation.*

Keywords: *V_2O_5, nanoparticles, flame spray pyrolysis, methylene blue, visible light*

1. Introduction

Vanadium pentoxide (V_2O_5) nanoparticles (NPs) is an one kind of the important photocatalysts material because of its unique advantages, such as its low price, easy synthesis, availability, good optical and electrical properties. V_2O_5 NPs can be synthesized by different methods including sol-gel [1-2], electrospinning [3], hydrothermal [4], chemical vapour deposition [5] flame spray pyrolysis [6] and precipitation [7]. Flame spray pyrolysis (FSP) is a versatile process for synthesis of nanoparticles materials with high surface area [8].

Methylene blue (MB) is a commonly dye that finds enormous applications in dyeing industry. In order to treat the dye effluents photocatalysis is one of the feasible methodologies that can be effectively exploited for the complete degradation of various dye pollutants [9-11].

In this research, V_2O_5 NPs were synthesized by a one-step of flame spray pyrolysis (FSP) process. The crystalline phase, morphologies and particles size of the NPs were characterized by XRD, FE-SEM, HR-TEM and EDXS. The specific surface area of the nanoparticles (SSA_{BET}) was measured by nitrogen adsorption method and the effects of V_2O_5 catalyst on the photocatalytic decomposition behavior of methylene blue were investigated.

2. Experimental

2.1 Preparation and characterization of the catalyst

The V_2O_5 NPs were synthesized by FSP technique [7] by using vanadium (V) oxytripropoxide (Aldrich, 98%) diluted in diethylene glycol/toluene/tetrahydrofuran (30/30/20 vol%) as the precursor solution. The solutions were fed into a FSP reactor by a syringe pump with a constant feed rate of 5 mL/min while 5 l/min O_2

is being dispersed (5/5 flame). After evaporation and combustion of precursor solution, particles are formed by nucleation, condensation, coagulation and coalescence. Finally, the nanopowders were collected on glass microfiber filters with the aid of a vacuum pump. The crystalline phase, morphologies and particles size of flame-made NPs were analyzed by X-ray diffraction spectroscopy (XRD) using CuK_α radiation at 2θ = 20-80° with a step size of 0.06° and a scanning speed of 0.72º/min, field emission-scanning electron microscopy (FE-SEM) and high resolution- transmission electron microscopy (HR-TEM) and and energy dispersive X-ray spectrometry (EDXS). The specific surface area of V_2O_5 NPs was measured by nitrogen adsorption (BET) analysis. The optical properties of V_2O_5 NPs were evaluated in term of UV-Vis absorption spectra at room temperature.

2.2 Photocatalytic measurement

0.05 g V_2O_5 NPs were suspended into a 500 mL beaker containing 250 ml of 10 g/L methylene blue (MB, $C_{16}H_{18}ClN_3S$, Merck, Germany). After V_2O_5 NPs suspension was continuously stirred for 30 min under dark condition, 5 mL of sample was withdrawn from suspension. Then it was centrifuged in order to separate V_2O_5 NPs from MB solution. The initial concentration (C_0) of MB in the solution was measured with an UV-VIS Spectrophotometer (U-2900, Hitachi, Japan). Subsequently, the remain suspension was illuminated with visible light using halogen lamp (Philips 50W, 12V). The distance between suspension and halogen lamp was 15 cm. The photodegradation was carried out under magnetic stirring for 2 h. At each interval of 10 min, 5 mL of the irradiated suspension was withdrawn and centrifuged. The residual concentration of MB in the solution was determined with an UV-VIS Spectrophotometer (U-2900, Hitachi, Japan). The photodegradation experiment was also conducted only in the presence of visible light without V_2O_5 NPs for the comparison purpose.

3. Results and discussion

3.1 Structure and morphology of V_2O_5 NPs

The phase and crystallinity structures of V_2O_5 NPs were carried out by XRD analysis as shown in Fig. 1. The typical XRD patterns of V_2O_5 NPs was highly crystalline, and all the diffraction peaks can be confirmed to be orthorhombic crystalline phase of vanadium pentoxide match well with the JCPDS file no. 41–1426 (Space group: Pmmn, a = 11.51 Å, b = 3.565 Å, c = 4.372 Å). The crystallite size of V_2O_5 NPs was calculated using Sherrer's equation to be ~22 nm. The specific surface area (SSA_{BET}) of V_2O_5 NPs was measured by nitrogen adsorption and the results clearly showed that SSA_{BET} of V_2O_5 NPs was ~56 m^2/g. Accurate particle size and morphology of V_2O_5 NPs were further confirmed by TEM images.

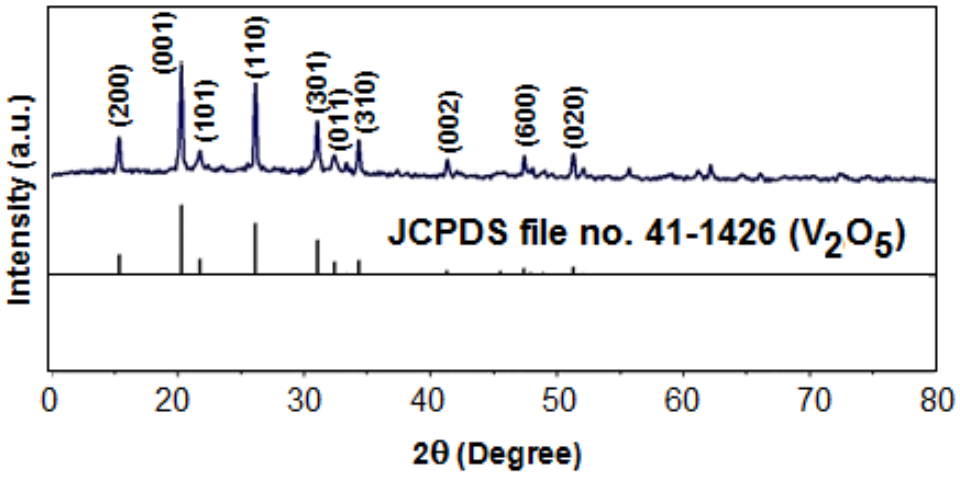

Fig. 1: XRD patterns of the flame-synthesis V_2O_5 NPs.

Figure 2 (a) and (b) show the SEM micrographs and EDXS analysis of V_2O_5. The NPs had agglomerated nanosphere morphology with an average diameter of 20–40 nm. The chemical elements of V_2O_5 NPs were analyzed from EDXS spectra. The signal of EDXS spectra corresponded to V and O elements.

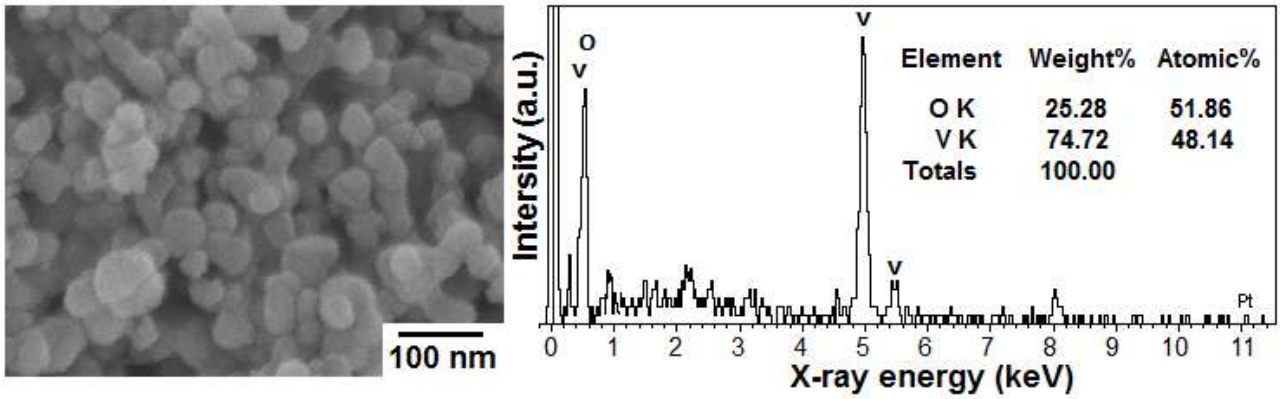

Fig. 2: (a) SEM image (b) EDXS spectra of V_2O_5 NPs

HR-TEM image of V_2O_5 is shown in Fig. 3a,b. Spherical V_2O_5 NPs (20-40nm) were found according to the TEM results. Figure 7b indicates that the *d*-spacing was about 0.33 nm consistent with the (010) plane of the orthorhombic structure, indicating that these NPs grew along the [010] direction.

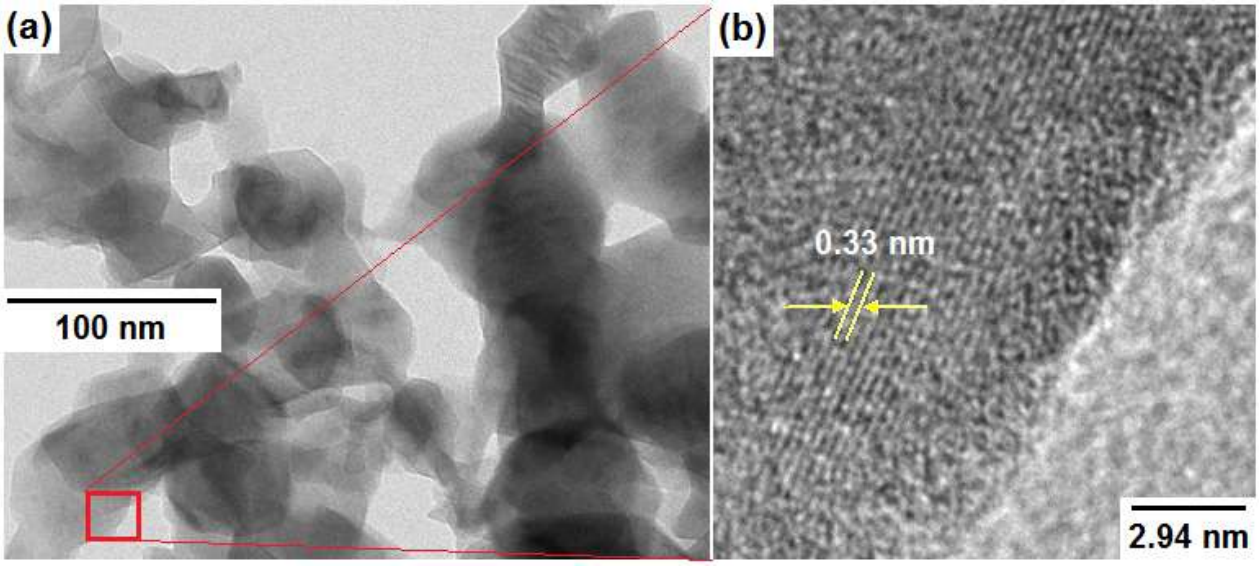

Fig. 3: (a) and (b) HR-TEM image of V_2O_5 NPs

Figure 4(a) shows UV–vis diffuse reflectance spectra analysis of V_2O_5 NPs. The direct band gap energy can be estimated from a plot of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) as shown in Fig. 4(b). The intercept of the tangent to the plot will give a good approximation of the band gap energy for the V_2O_5 [12]. The estimated band gap energies were 2.03 eV for V_2O_5.

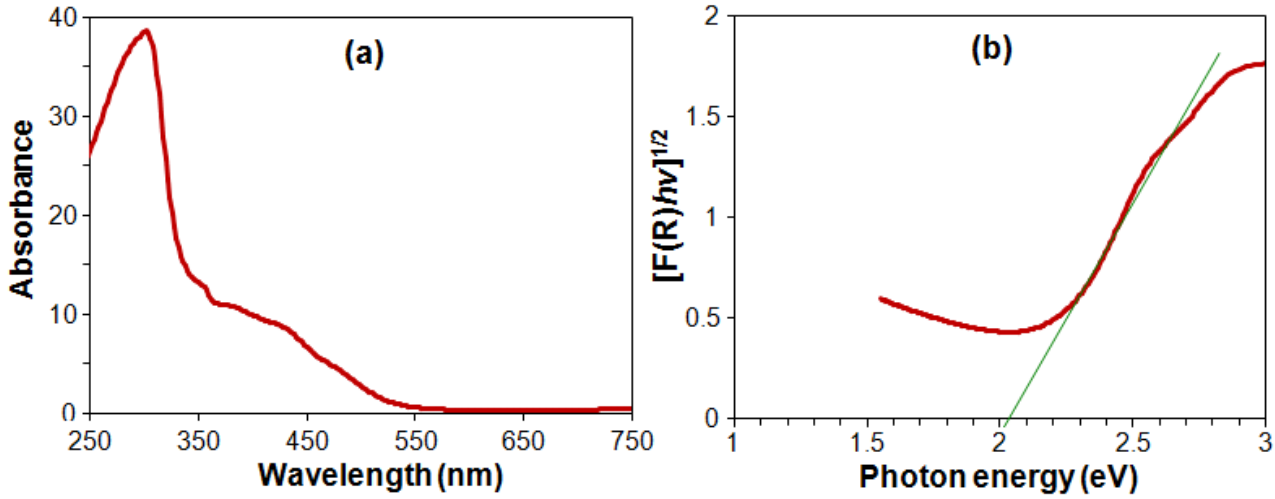

Fig. 4: (a) UV–vis diffuse reflectance spectra and (b) plots of $(\alpha h\nu)^{1/2}$ vs. photon energy ($h\nu$) for V_2O_5 samples.

3.2 Photocatalytic activity and mechanism

Photodegradation of MB in the presence of V_2O_5 NPs synthesized via the flame spray pyrolysis method is shown in Figure 5(a). The results showed that ca. 81% MB was degraded. For comparison purposes, the photodegradation experiment was also conducted only in the presence of visible light without V_2O_5 NPs. Without V_2O_5 NPs, only ca. 1% MB was degraded. For the kinetic study, Figure 5(b) shows pseudo-first-order plot for MB degradation in the presence of V_2O_5 NPs synthesized via the flame spray pyrolysis method. The pseudo first-order model was explained by $\ln(C_0/C) = kt$ where k is the apparent pseudo first-order rate constant (min^{-1}), C_0 is the initial concentration of MB, and C is the concentration of MB at each interval of irradiation times (t). It was found that a pseudo first-order rate constant (k) for MB degradation in the presence of V_2O_5 NPs was 0.0135 min^{-1}.

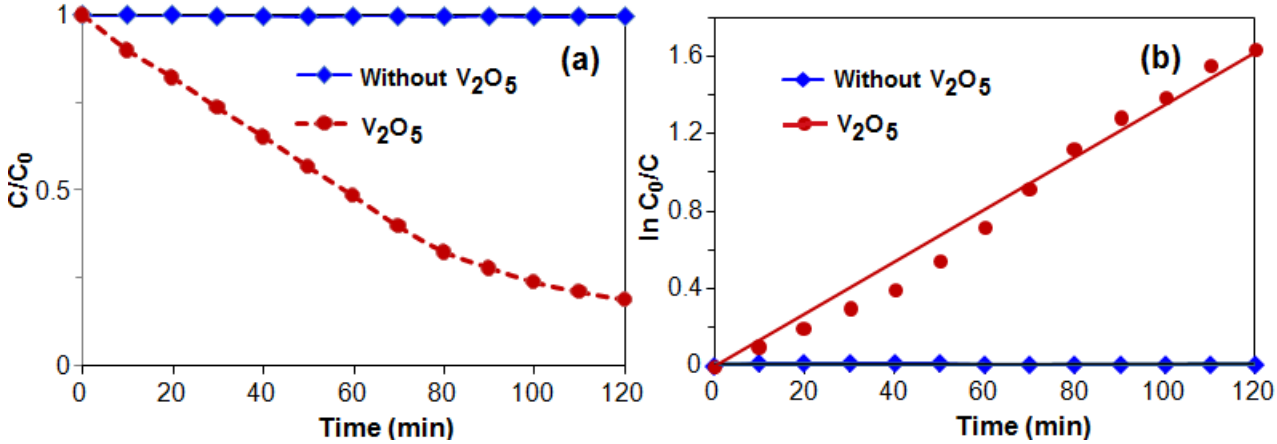

Fig. 5: (a) Photodegradation and (b) Pseudo-first-order plot for methylene blue degradation in the presence of V_2O_5 NPs synthesized via the flame spray pyrolysis method.

4. Conclusions

In this research, V_2O_5 NPs were successfully synthesized by a one-step of flame spray pyrolysis (FSP) process. The XRD patterns showed that the nanoparticles had the orthorhombic phase of V_2O_5. The SEM image revealed nanoparticles have clear spherical morphologies. The crystallite size of V_2O_5 spherical particles was in the range of 20-30 nm. The SSA_{BET} of V_2O_5 NPs was ~56 m^2/g. The estimated band gap energies were 2.03 eV for V_2O_5. Finally, the photocatalytic activities of V_2O_5 NPs were determined by studying the degradation of MB under visible light irradiation. The results showed that ca. 81% MB was degraded. MB degradation in the presence of V_2O_5 NPs was found to be pseudo-first-order reaction with the rate constant (k) of 0.0135 min^{-1}.

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