

Synthesis, characterization and photocatalytic performance of brannerite-type LiVMoO_6

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Crystalline LiVMoO_6 with brannerite structure was synthesized by mechanochemically assisted solid-state synthesis. A mixture of Li_2CO_3 , V_2O_5 , and MoO_3 of oxide 1:1:2 molar ratio was subjected to intense mechanical treatment for 10 min in air using a planetary ball mill (Fritsch-Premium line-Pulversette No 7) and zirconia vials and balls (5 mm in diameter). The mechanically treated mixture of the metal oxides was subsequently heated for 1 hour at 450 °C. XRD, Raman spectroscopy, and SEM investigations were performed to examine phase formation, local structure, and morphology of the obtained product. Preliminary mechanical activation of the reagents led to the formation of highly reactive precursor and annealing of the latter formed submicron-sized particles of LiVMoO_6 with irregular shape, which were highly agglomerated. Photocatalytic results showed that adsorption of Malachite Green dye (MG) on the LiVMoO_6 surface is a prerequisite for its photodegradation. Degradation percentage of Malachite Green in the presence of LiVMoO_6 photocatalyst was about 70% after 210 min of UV irradiation time.

Key words: mechanochemistry, Raman spectroscopy, photocatalysis.

INTRODUCTION

Over the last decades, photocatalysis has been extensively explored as a process to efficiently conduct oxidation of organic compounds, mainly pollutants. In this sense, TiO_2 has been preferred by far over other materials as photocatalyst. Despite the proven efficiency of titania, some issues still challenge the scientific community dedicated to photo-catalysis. Recently, scientific efforts have been directed to design titania-free visible-light active photocatalysts. For example, monoclinic and perovskite materials, such as InMO_4 ($M = \text{V}, \text{Nb}, \text{Ta}$), BiVO_4 , AgTaO_3 , AgNbO_3 , and Ag_3VO_4 , have been confirmed to be active visible-light responsive photocatalysts [1–4]. In this context, some other monoclinic systems may deserve special attention. Among them, brannerite-type LiMoVO_6 compound calls the attention due to its electrochemical properties and recognised application as a positive electrode material for lithium secondary batteries [5–7]. The aim of the present study was to obtain LiMoVO_6 compound by mechanochemically assisted solid-state synthesis and to explore its structural and photocatalytic properties.

EXPERIMENTAL

Crystalline LiVMoO_6 with brannerite structure

was prepared by mechanochemically assisted solid-state synthesis. A mixture of Li_2CO_3 , V_2O_5 , and MoO_3 of oxide 1:1:2 molar ratio was subjected to intense mechanical treatment for 10 min in air using a planetary ball mill (Fritsch-Premium line-Pulversette No 7) and zirconia vials and balls (5 mm in diameter). Balls to powder weight ratio was 10:1. The mechanically treated mixture of the reagents was subsequently heated for 1 hour at 450 °C. Phase formation was checked by XRD ($\text{CuK}\alpha$, Ultima IV; Rigaku Corp.). Room temperature Raman spectroscopy measurements of LiVMoO_6 were performed in the range of 200–1200 cm^{-1} on a micro-Raman system of Jobin-Yvon Horiba (LABRAM HR-800) spectrometer with green laser (wavelength of 532 nm). LiVMoO_6 morphology and microstructure were investigated by JEOL JSM-5300 scanning electron microscope. The photocatalytic activity of the obtained LiVMoO_6 was evaluated toward the degradation of a model aqueous solution of Malachite Green (MG) oxalate (Sigma-Aldrich) under UV irradiation at room temperature. A MG solution (150 ml, 5 ppm, pH = 7) containing 0.1 g of as-prepared powder was placed into a glass beaker. Before turning on the light, the solution was ultrasonicated for 10 min and after that stirred for 10 min to ensure adsorption-desorption equilibrium in the solid/solution system. A solution of 3 ml volume was taken at regular time intervals and separated through centrifugation (5000 rpm, 5 min). Then MG

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concentration in the centrifugate was measured by an Evolution 300 UV-VIS (Thermo Scientific, 50–60 Hz, 150 VA) spectrophotometer. The photo-degradation percentage of MG was calculated by Eq. (1).

$$R = (1 - C_t/C_0) \times 100, \% \quad (1)$$

Where C_0 and C_t are MG initial concentration and concentration after certain period of irradiation time (ppm), respectively.

RESULTS AND DISCUSSION

Figure 1 presents X-ray diffraction patterns of Li₂CO₃ + V₂O₅ + MoO₃ mixture before mechanical treatment (Fig. 1a), initial mixture after mechanical treatment for 10 minutes (Fig. 1b), and mixture of mechanically treated precursors for 10 min, and subsequently calcined for 1 h at 450 °C (Fig. 1c).

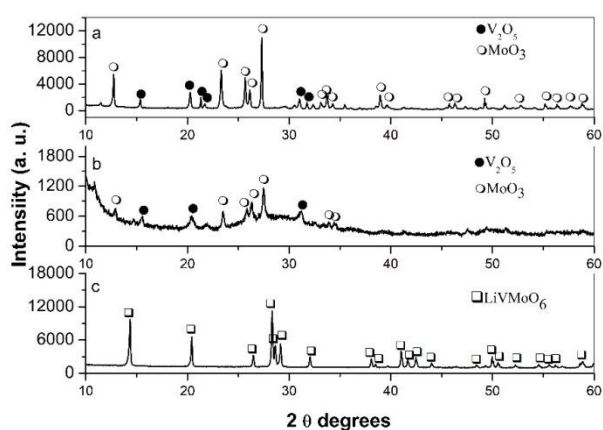


Fig. 1. XRD patterns of Li₂CO₃ + V₂O₅ + MoO₃ mixture: a) before mechanical treatment; b) after 10 min mechanical treatment under rotation speed of 500 rpm; c) after 10 min mechanical treatment and calcination at 450 °C for 1 hour.

The initial XRD pattern (Fig. 1a) shows all peaks corresponding to MoO₃ (JCPDS No 47-01320) and V₂O₅ (JCPDS No 75-0457), while the reflections of the initial Li-containing compounds are present at the background level due to weak scattering ability of the lithium atoms. The diffraction peaks of the reactants gradually decreased with milling. Moreover, partial amorphisation of the initial oxides was observed during the milling process (Fig. 1b). XRD data indicate the formation of single phase LiVMoO₆ with brannerite-type structure by mechanochemical treatment of the precursor for 10 min followed by heat treatment for 1 h at 450 °C (Fig. 1c). The diffraction pattern of the obtained LiVMoO₆ was indexed using ‘Index’ software assuming a C2/m symmetry that corresponds to the monoclinic citing of the brannerite structure and shows no traces of

impurity phases [8]. The diffraction peaks are intense and symmetrical evidencing the formation of a well crystallized LiVMoO₆ product.

The obtained material was characterized by applying Raman spectroscopy and SEM. Raman features show (Fig. 2) vibrational modes of the various MeO₆ (Me = V, Mo, Li) octahedral units building the lattice. The assignment of the observed Raman bands is shown in Table 1.

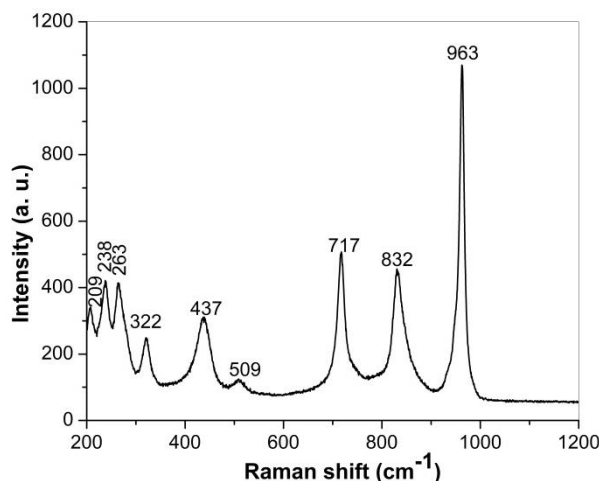


Fig. 2. Raman spectra of LiVMoO₆ obtained after mechanical activation of Li₂CO₃ + V₂O₅ + MoO₃ mixture for 10 min and subsequent heat treatment for 1 hour at 450 °C.

Table 1. Observed Raman bands and their assignment for LiVMoO₆, obtained by mechanochemically assisted solid state synthesis.

Raman band position, cm ⁻¹	Assignments	Refs.
963	$\nu(\text{Me}=\text{O}; \text{Me}=\text{V}, \text{Mo})$	9–11
832	$\nu_{\text{as}}(\text{Me}-\text{O}-\text{Me})$	9–11
717	$\nu_{\text{as}}(\text{Me}-\text{O}-\text{Me})$	9–11
437	$\nu_{\text{as}}(\text{Me}-\text{O}-\text{Me})$	9–11
322	$\delta(\text{Me}-\text{O}-\text{Me})$	9, 10
263	$\delta(\text{Me}-\text{O}-\text{Me}) + \nu(\text{LiO}_6)$	9–11

SEM images of LiVMoO₆ of different magnification are displayed in figure 3. SEM photographs evidenced that the sample consists of dense agglomerates formed from irregular shaped and small submicron-size particles.

The MG dye was used as a model pollutant to investigate the photocatalytic activity of the prepared sample. The strongest absorption peak of MG dye at 615 nm was selected to monitor the photocatalytic degradation process (Fig. 4). After UV illumination, the absorption band at 615 nm decreased rapidly and new absorption bands in the ultraviolet and visible range were not registered. This observation is in marked contrast with the data

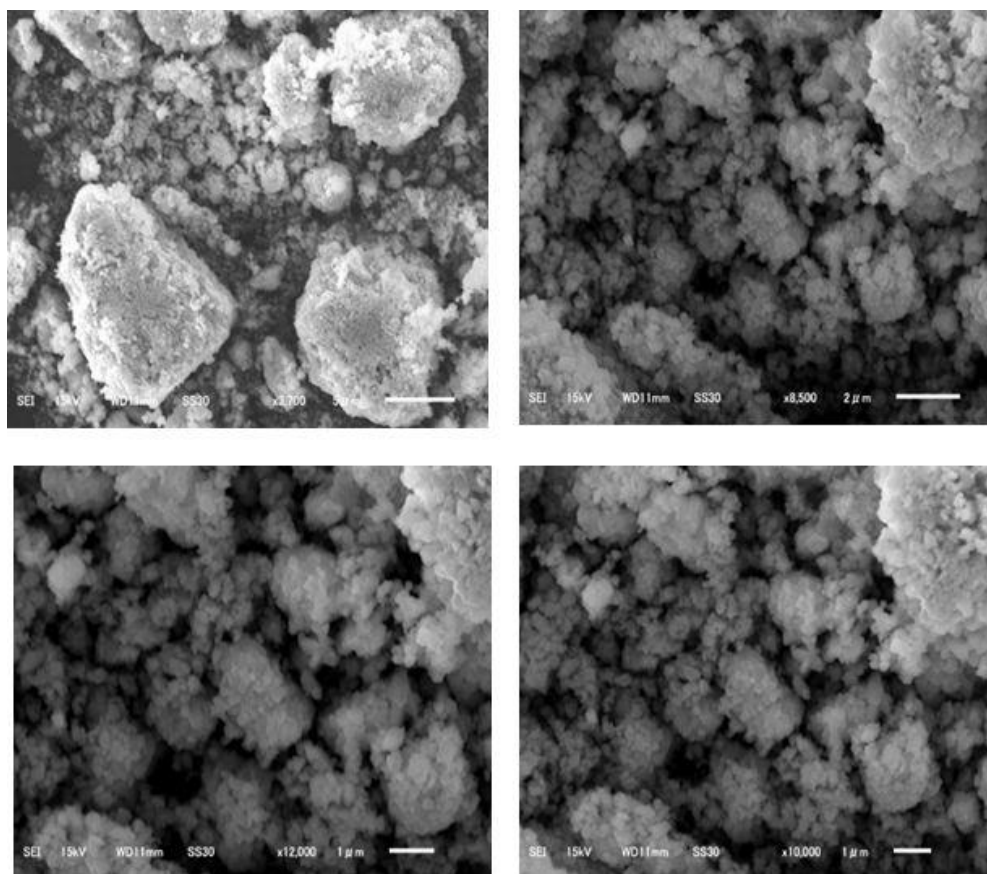


Fig. 3. SEM images of LiVMoO_6 at different magnification obtained after mechanical activation of $\text{Li}_2\text{CO}_3 + \text{V}_2\text{O}_5 + \text{MoO}_3$ mixture for 10 min and subsequent heat treatment for 1 hour at 450°C .

reported in the literature concerned with photocatalyzed degradation of many organic compounds in the presence of TiO_2 under UV irradiation, in which intermediates are easily detected by absorption spectra [12]. These photocatalytic results also show that MG is firstly adsorbed on the LiVMoO_6 surface and then photodegraded. MG degradation percentage in the presence of LiVMoO_6 photocatalyst was about 70% after 210 min of irradiation time.

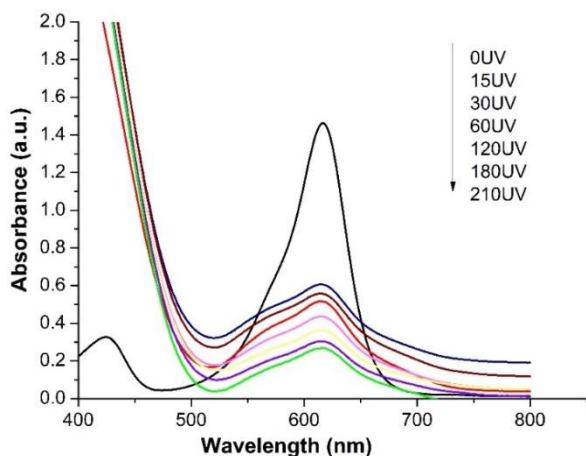


Fig. 4. Evolution of absorption spectra of MG dye solution over LiVMoO_6 powder under UV-vis irradiation.

CONCLUSIONS

Single phase LiVMoO_6 was successfully prepared by applying mechanochemically assisted solid-state synthesis. Preliminary mechanical activation of a mixture of metal oxides in a planetary ball mill led to the formation of highly reactive precursors. Annealing of the latter caused formation of submicron-sized highly agglomerated particles of LiVMoO_6 with irregular shape. Photocatalytic results show that adsorption of Malachite Green is a prerequisite for LiVMoO_6 -assisted photodegradation of MG under UV light irradiation. MG degradation percentage in the presence of LiVMoO_6 photocatalyst was about 70% after 210 min of irradiation time.

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REFERENCES

1. J. Ye, Z. Zou, H. Arakawa, M. Oshikiri, M. Shimoda, A. Matsushita, T. Shishido, *J. Photochem. Photobiol. A: Chem.*, **148**, 79 (2002).
2. X. Zhang, Z. Ai, F. Jia, L. Zhang, X. Fan, Z. Zou, *Mater. Chem. Phys.*, **103**, 162 (2007).
3. H. Kato, H. Kobayashi, A. Kudo, *J. Phys. Chem. B*, **106**, 12441 (2002).
4. R. Konta, H. Kato, H. Kobayashi, A. Kudo, *Phys. Chem. Chem. Phys.*, **5**, 3061 (2003).
5. C. Julien, *Ionics*, **6**, 30 (2000).
6. L. Zhou, Y. Liang, L. Hu, X. Han, Z. Yi, J. Sun, S. Yang, *J. Alloys Comp.*, **457**, 389 (2008).
7. M. Milanova, R. Iordanova, M. Tatsumisago, A. Hayashi, P. Tzvetkov, D. Nihianova, P. Markov, Y. Dimitriev, *J. Mater. Sci.*, **51**, 3574 (2016).
8. R. Run, A. Wadsley, *Acta Cryst.*, **21**, 974, (1966).
9. N. Amdouni, H. Zarrouk, F. Soulette, C. Julien, *J. Mater. Chem.*, **13**, 2374 (2003).
10. L. Hurtado, E. Torres-García, R. Romero, A. Ramírez-Serrano, J. Wood, R. Natividad, *Chem. Eng. J.*, **234**, 327 (2013).
11. E. Baran, C. Cabello, A. Nord, *J. Raman Spectrosc.*, **18**, 405, (1987).
12. H. Hidaka, J. Zhao, E. Pelizzetti, N. Serpone, *J. Phys. Chem.*, **96**, 2226 (1992).

СИНТЕЗ, ОХАРАКТЕРИЗИРАНЕ И ФОТОКАТАЛИТИЧНИ СВОЙСТВА НА LiVMoO_6

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(Резюме)

Монофазен кристален LiVMoO_6 със структура от Бранеритов тип е получен успешно чрез механохимично активиран твърдофазен синтез. Смес от Li_2CO_3 , V_2O_5 и MoO_3 в молно съотношение на оксидите 1:1:2 е подложена на интензивна механична обработка за 10 минути във въздушна среда в планетарна топкова мелница (Fritsch-Premium line-Pulversette No 7). Механично обработената смес от прекурсорите е нагрята за 1 час при 450 °C. Така полученият образец е охарактеризиран чрез Рентгенова дифракция, Раманова спектроскопия и сканираща електронна микроскопия. Установено е, че предварителното механично третиране на сместа от реагенти в планетарна топкова мелница, води до значително активиране на реакционната смес от изходни компоненти и след последващо нагряване за кратък период от време (1 час) се получава кристален LiVMoO_6 , съдържащ кристали със субмикронен размер. Фотокаталитичната активност на полученият LiVMoO_6 беше изследвана чрез разграждане на органичното багрило Малахитово Зелено под ултравиолетово облъчване. Фотокаталитичните резултати показват, че органичното багрило първо се адсорбира на повърхността на LiVMoO_6 и след това започва неговото разграждане. След 210 минути време на облъчване, процентът на разграждане на Малахитово Зелено в присъствие на LiVMoO_6 е около 70%.