



Cyclic Microwave-Assisted Metathetic Synthesis and Characterization of Ag-SrWO₄/Zeolite Composites

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Silver incorporated SrWO₄/zeolite (Ag-SrWO₄/zeolite) composites were successfully synthesized by a cyclic microwave-assisted metathetic route followed by heat treatment. The crystallized Ag-SrWO₄/zeolite composites were formed at 600 °C for 3 h, showing a well immobilized morphology with particle sizes of 3-5 μm. The synthesized Ag-SrWO₄/zeolite composites were characterized by scanning electron microscopy, energy-dispersive X-ray spectroscopy and Fourier transform infrared spectroscopy. The optical properties were examined using photoluminescence emission and Raman spectroscopy.

Keywords: Cyclic microwave-assisted metathetic synthesis, Ag-SrWO₄/zeolite composite, Photoluminescence, Raman spectroscopy.

INTRODUCTION

Metal tungstates have attracted considerable attention for potential applications in photoluminescence, scintillators, as photocatalyst and humidity sensors^{1,2}. The physical, chemical and photochemical properties of metal tungstates are dependent on the manufacturing method. Several processes have been developed over the past decade to enhance the applications of metal tungstates prepared by a range of processes, such as coprecipitation³, solvothermal method⁴, spray pyrolysis⁵, reverse micelle system⁶, solution synthesis⁷, sol-gel⁸, mechanochemical method⁹, molten salt method¹⁰, hydrothermal method¹¹, microwave-assisted synthesis¹² and solid-state metathetic reaction¹³. Wet chemical methods have disadvantages, such as complicated synthetic steps, use of expensive equipment, high synthesis temperatures and long sintering times. On the other hand, solid-state reactions require complex apparatus and techniques, which are becoming gradually unpopular due to the excessive energy consumption.

Compared with the usual methods, microwave synthesis has the advantages of a very short reaction time, a small particle size, a narrow particle size distribution and a high purity method for preparing polycrystalline samples. Microwave heating is delivered to the surface of the material by radiant and/or convection heating, which is transferred to the bulk of the material *via* conduction. Microwave energy is delivered directly to the material through molecular interactions under an electromagnetic field. This makes possible the rapid and uniform heating of thick materials^{14,15}. Cyclic microwave-

assisted metathetic (MAM) synthesis is a simple and cost-effective method that provides high yield with easy scale-up and is emerging as a viable alternative approach for the synthesis of high-quality novel inorganic materials in short time periods^{16,17}.

Silver incorporated SrWO₄/zeolite (Ag-SrWO₄/zeolite) composites are expected to have excellent adsorption and synergy effects in an immobilization mechanism of metallic catalysts for a wide range of applications, such as sensors, photocatalysts, luminescence, anti-bacterial matrices and optical effects in the UV and visible region. However, the study of Ag-SrWO₄/zeolite composites by a cyclic MAM method has not been published previously. Therefore, the precise nature of the optical properties and cyclic MAM synthesis of Ag-SrWO₄/zeolite composites are required for a wide range of applications. In this study, Ag-SrWO₄/zeolite composites were synthesized using a cyclic MAM. The characteristics of the MAM reaction of Ag-SrWO₄/zeolite composites are discussed in detail based on the exothermic reactions accompanying the formation of a high lattice energy of by-product NaCl. The synthesized Ag-SrWO₄/zeolite composites were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and Fourier transform infrared spectroscopy (FTIR). The optical properties were examined using photoluminescence (PL) emission and Raman spectroscopy.

EXPERIMENTAL

SrCl₂·6H₂O and Na₂WO₄·2H₂O of analytic reagent grade were used to prepare the SrWO₄ compound. The preparation

of SrWO_4 was carried out by reacting well-ground mixtures of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ at a molar ratio of 1:1. The sample mixtures were dried at 100°C for 12 h and 5 wt % AgNO_3 and 20 wt % synthetic zeolite-A were then added for the composition of $\text{Ag-SrWO}_4/\text{zeolite}$. The mixtures were transferred into 120 mL Teflon vessels, respectively. Each Teflon vessel was placed into a microwave oven operating at a frequency of 2.45 GHz with a maximum out-power of 1250 W for 23 min. The working cycle of the MAM reaction was controlled very precisely between 30 s on and 30 s off for 8 min and followed by a further treatment of 30 s on and 60 s off for 15 min. The resulting samples were treated with ultrasonic radiation and washed many times with hot distilled water. The white precipitates were collected and dried at 100°C in a dry oven. The final products were heat-treated at 600°C for 3 h.

The microstructure and surface morphology of the synthesized $\text{Ag-SrWO}_4/\text{zeolite}$ composites were observed using SEM (JSM-5600, JEOL, Japan) and EDS. FTIR (Nicolet IR 200, Thermo Electron Corporation, USA) was used to examine the thermal-decomposition behaviour of the MAM reaction and heat-treated $\text{Ag-SrWO}_4/\text{zeolite}$ composites over the frequency range, $4000\text{--}400\text{ cm}^{-1}$. The photoluminescence spectrum was recorded using a spectrophotometer (Perkin Elmer LS55, UK) at room temperature. Raman spectroscopy measurements were performed using LabRam HR (Jobin-Yvon, France). The 514.5 nm line of an Ar-ion laser was used as excitation source and the power on the samples was kept at 0.5 mW.

RESULTS AND DISCUSSION

Fig. 1 shows a SEM image of the synthesized $\text{Ag-SrWO}_4/\text{zeolite}$ composites. The as-synthesized samples are well crystallized with a fine and homogeneous morphology and particle size of 3–5 μm . The spherical small particles of silver were well immobilized in the porous $\text{SrWO}_4/\text{zeolite}$ matrix. The $\text{Ag-SrWO}_4/\text{zeolite}$ composites were well synthesized in a green manner without the generation of solvent waste, because the microwave radiation provided the energy required to overcome the energy barrier. It helped to heat the bulk of the material uniformly resulting in fine particles with a controlled morphology and to fabricate the product in a green manner without the generation of solvent waste. The MAM reaction, such as $\text{SrCl}_2 + \text{Na}_2\text{WO}_4 \rightarrow \text{SrWO}_4 + 2\text{NaCl}$, involves the exchange of atomic/ionic species, where the driving force is the exothermic reaction accompanying the formation of NaCl ^{12–15}. Microwave-assisted metathetic reactions occur so rapidly that the exothermic reaction is essentially used to heat up the solid products. The MAM reaction provides a convenient route for the synthesis of the $\text{Ag-SrWO}_4/\text{zeolite}$ composites, which were obtained in the form of loosely connected micrometer-sized particles at considerably lower temperatures than those usually employed for their synthesis. For the $\text{Ag-SrWO}_4/\text{zeolite}$ composite materials to be used for practical applications, control of the particle size distribution and morphology of the particles is needed. The well-defined features of the $\text{Ag-SrWO}_4/\text{zeolite}$ composites synthesized by the MAM reactions have a control over the morphology of the final particles and can be used for technological applications.

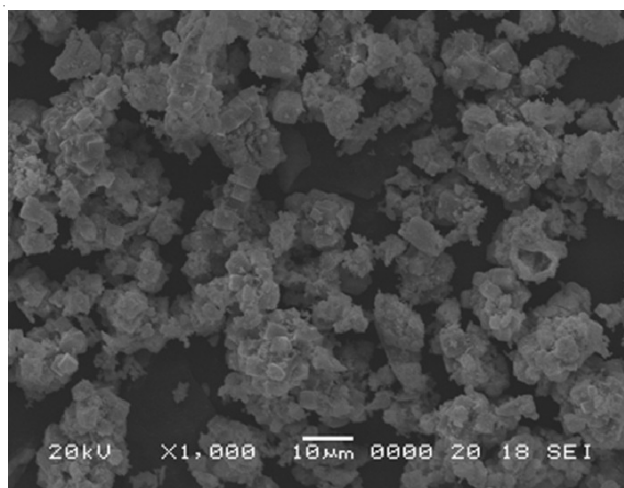


Fig. 1. A SEM image of the synthesized $\text{Ag-SrWO}_4/\text{zeolite}$ composites

Fig. 2 shows EDS patterns (a), qualitative compositions (b), a SEM image (c) and quantitative results (d) of the synthesized $\text{Ag-SrWO}_4/\text{zeolite}$ composites. The EDS patterns and qualitative compositions in Fig. 2(a,b) could be assigned to the $\text{Ag-SrWO}_4/\text{zeolite-A}$ composite. This means that the $\text{Ag-SrWO}_4/\text{zeolite}$ composite can be successfully synthesized using this MAM reaction followed by heat treatment at 600°C for 3 h. Post heat-treatment plays an important role in a well-defined crystallized morphology. To achieve a well-defined crystalline morphology, the $\text{Ag-SrWO}_4/\text{zeolite}$ composites need to be heat treated at 600°C for 3 h. The crystals of SrWO_4 were primarily co-mixed with porous zeolite-A. The quantitative results of the morphology in Fig. 2(d) were composed of Ag, SrWO_4 and zeolite-A.

Fig. 3 shows FTIR spectrum of the $\text{Ag-SrWO}_4/\text{zeolite}$ composites at the wavenumber range of $4000\text{--}480\text{ cm}^{-1}$. The stretching vibration was detected as a strong W-O stretch in the $[\text{WO}_4]^{2-}$ tetrahedra at 823 cm^{-1} . Similar characteristics absorption bands of MWO_4 ($\text{M} = \text{Ba}, \text{Ca}, \text{Sr}$) for the Scheelite oxides having S_4 site symmetry in this region have been reported in the literature⁶. The $[\text{WO}_4]^{2-}$ is constituted by four internal modes ($\nu_1(\text{A}_1)$, $\nu_2(\text{E})$, $\nu_3(\text{F}_2)$ and $\nu_4(\text{F}_2)$) specified as symmetric stretching, symmetric bending, asymmetric stretching and asymmetric bending modes¹². All these modes are Raman active, whereas only $\nu_3(\text{F}_2)$ and $\nu_4(\text{F}_2)$ are IR active.

Fig. 4 presents the photoluminescence emission spectrum of the $\text{Ag-SrWO}_4/\text{zeolite}$ composites. It is generally assumed that the measured emission spectra of metal tungstates are mainly attributed to the charge-transfer transitions within the $[\text{WO}_4]^{2-}$ complex^{18,19}. With excitation at 250 nm, the spectra show rugged peaks, which are composed of three types of groups. The first major peaks are located at the blue wavelength 425–450 nm, the second neighbored shoulders at 460–490 and the third sloped shoulders at 530–550 nm. The emission spectrum of 4–8 narrow neighbored and sloped shoulders, namely the spread-eagle-shape, at 460–550 nm are considered to form from defect structures²⁰. Generally, the presence of Gaussian components indicates that the electronic levels corresponding to relaxed excited state of an emission center belong to a degenerate excited state influenced by some perturbation, e.g., a local low symmetry crystal field²¹. Such

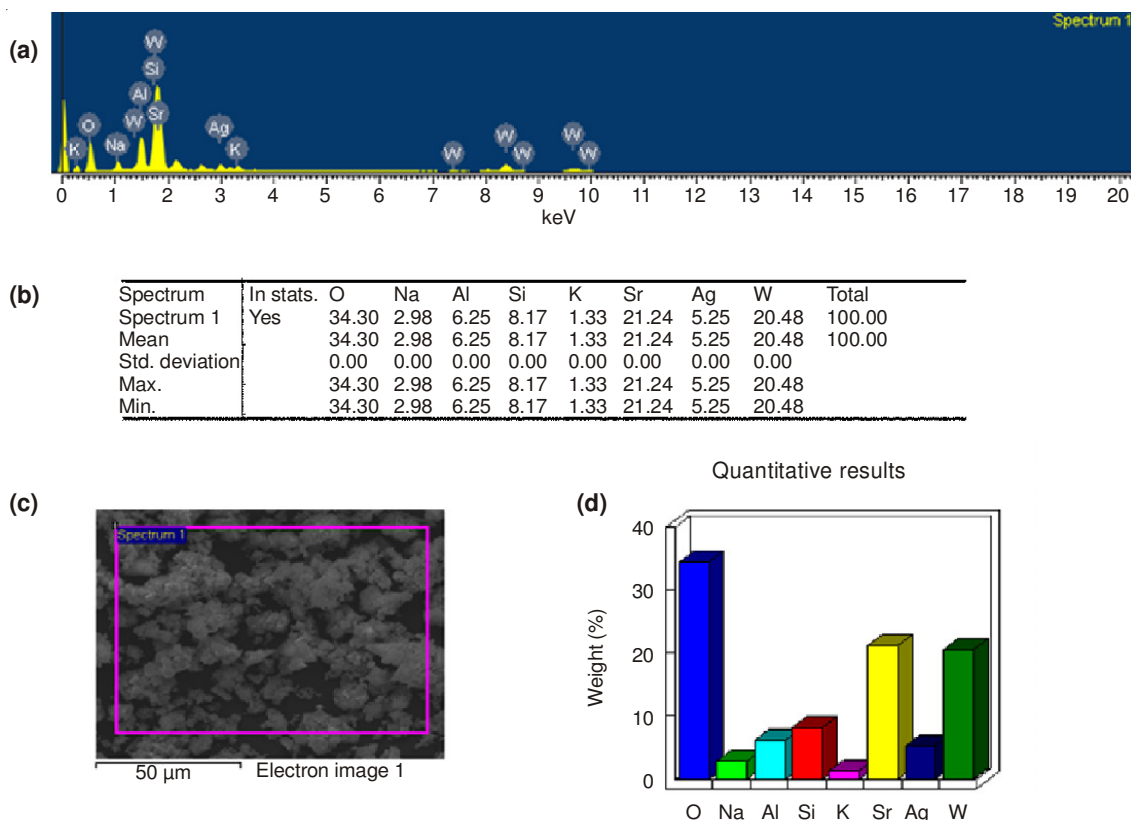


Fig. 2. EDS patterns (a), qualitative compositions (b), SEM image (c) and quantitative results (d) of the synthesized Ag-SrWO₄/zeolite composites

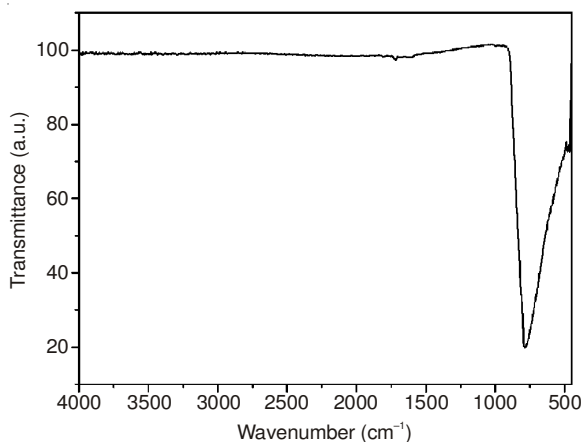


Fig. 3. FT-IR spectrum of the Ag-SrWO₄/zeolite composites

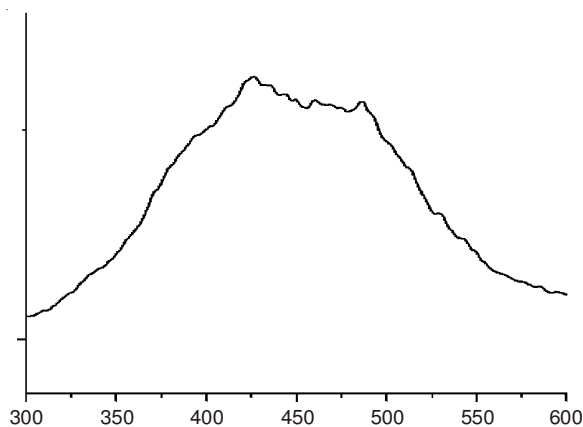


Fig. 4. PL emission spectrum of the Ag-SrWO₄/zeolite composites excited at 250 nm

emission peaks can be explained by the influence of the Jahn-Teller effect²² on the degenerated excited state of [WO₄]²⁻ tetrahedron.

Fig. 5 shows a Raman spectrum of the Ag-SrWO₄/zeolite composite excited by the 514.5 nm line of an Ar-ion laser kept at a power of 0.5 mW on the samples. The vibration modes in the Raman spectrum of the Ag-SrWO₄/zeolite composite are classified into two groups, internal and external²¹. The internal vibrations are related to the [WO₄]²⁻ molecular group with a stationary mass center. The external vibrations or lattice phonons are associated with the motion of the Sr²⁺ cation and rigid molecular units. In the free space, [WO₄]²⁻ tetrahedra show T_d-symmetry. The Raman modes for the Ag-SrWO₄/zeolite composites in Fig. 5 were detected as ν₁(A_g), ν₃(B_g), ν₃(E_g), ν₄(E_g), ν₄(B_g) and ν₂(B_g) vibrations at 920, 836, 798, 371, 334 and 235 cm⁻¹, respectively, which provide evidence of a Scheelite structure. The well-resolved sharp peaks for the Ag-SrWO₄/zeolite composites indicate that the synthesized particles are highly crystallized. A free rotation mode was detected at 187 cm⁻¹ and external modes were localized at 133 cm⁻¹. This result is in agreement with that reported in the literature²³. The internal vibration mode frequencies exhibited a dependence on the lattice parameters and the degree of the partially covalent bond between the cation and molecular ionic group [WO₄]²⁻. The type of cations (Ca²⁺, Sr²⁺, Ba²⁺) can influence the Raman modes by changing the size of the crystal unit cell and by a covalent cation effect²³.

Ag-SrWO₄/zeolite composites were successfully synthesized by the MAM route. The as-synthesized samples are well crystallized with a fine and homogeneous morphology and particle size of 3-5 μm. The spherical small particles of silver

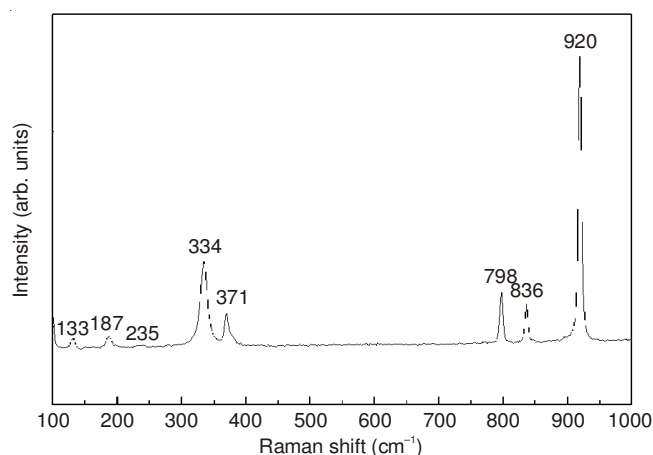


Fig. 5. Raman spectrum of the Ag-SrWO₄/zeolite composites excited by the 514.5 nm line of an Ar ion laser at 0.5 mW on the samples

were well immobilized in the porous SrWO₄/zeolite matrix. The stretching vibration in FTIR was detected as a strong W-O stretch in the [WO₄]²⁻ tetrahedra at 823 cm⁻¹. With excitation at 250 nm, the major peaks of photoluminescence are located at the blue wavelength of 425-450 nm. The emission spectrum of 4-8 narrow neighbored and sloped shoulders were considered to form from defect structures, which was explained by the influence of the Jahn-Teller effect. The well-resolved Raman spectrum for the Ag-SrWO₄/zeolite composite at 920, 836, 798, 371, 334 and 235 cm⁻¹ provide evidence of a Scheelite structure. A free rotation mode was detected at 187 cm⁻¹ and the external modes were localized at 133 cm⁻¹.

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