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Short Communication

Synthesis of perovskite $KMgF_3$ with microemulsion for photocatalytic removal of various pollutants under visible light

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ABSTRACT

The perovskite-type fluoride $KMgF_3$ photocatalysts were prepared by microemulsion and sol–gel methods. The as-prepared catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and UV–vis diffuse reflectance spectra (UV–vis DRS). Photocatalytic activity of the samples was evaluated in the degradation of rhodanmine B, methyl orange, phenol, and chlorophenol under visible light irradiation. Results demonstrated that photocatalytic activities of $KMgF_3$ synthesized by microemulsion method were superior to those of sol–gel method. It is considered that the excellent photocatalytic activities of $KMgF_3$ have a close relation to the crystal defects of fluorine vacancies.

1. Introduction

An unrestrained exploitation of natural resources and reckless industrialization have caused serious environmental problems. In particular, the pollution of water resources by organic pollutants, such as phenolic compounds, various dyes, etc. threatened the health of human beings. In order to remove pollutants from water, researchers used absorbents to physically remove them and achieved good results [1,2], while further treatment of absorbents and adsorbents might bring secondary pollution. In recent decades, the degradation of organic pollutants via photocatalysis has drawn great attention for its high efficiency and green process. Titania in anatase phase is often used as an active component in photocatalyst because of its high activity, stable chemical property, and non-toxicity [3,4]. However, the wide band gap of titania (3.2 eV) together with low quantum efficiency limits the usage efficiency of solar energy and application in industry [5].

Perovskite photocatalyst family including ABO_3, double perovskites $A_2B'B''O_6$ and a typical Lanthanum-based pervoskite-type $La_2Ti_2O_7$ (a layered perovskite) were found to be alternative visible-light photocatalytic active photocatalysts for water splitting [6–9] and pollutant degradation [10,11,22] due to their unique perovskite structure and property. However, all the perovskite-type photocatalysts reported belong to oxygen-containing compound, those non-oxygen perovskites used for photocatalysis are seldom reported. As important inorganic functional materials, the ternary compound belonging to the group of fluoroperovskites, having the general formula ABF_3, where A and B stands for alkali metals and alkaline earth metals, respectively [12]. Among them, $KMgF_3$ has recently received extensive attention for its great application in scintillator [13], dosimeter [14,15], and ultraviolet-transparent window materials [16,17]. Besides, perfect $KMgF_3$ crystals exhibited high transparencies in the sunlight wavelength region, but doped $KMgF_3$ crystals [18] or those with lattice defects [19] absorb visible light. Therefore, they may have the potential to be used as visible light responsive photocatalyst.

In this work, $KMgF_3$ were prepared by microemulsion and sol–gel methods. Photocatalytic activities of the $KMgF_3$ prepared by the two methods were investigated by degradation of rhodamine B, methyl orange, phenol and chlorophenol under visible light irradiation.

2. Experimental

2.1. Preparation

2.1.1. Microemulsion method

Cetyltrimethylammonium bromide (CTAB)/iso-octanol (2-EH)/water (mass ratio m_{CTAB}:$m_{2\text{-}EH}$:m_{H2O} = 12.79%:76.72%:10.49%) were used as starting materials. Firstly, CTAB and 2-EH solutions were mixed with vigorous stirring till a transparent microemulsion was formed, then a mixed solution of $Mg(NO_3)_2$ and KNO_3 and NH_4F were added, followed by a continuous stirring for 1 h. Then the mixture was centrifuged and hydroxide precursor precipitate was washed with absolute methanol three times and dried at room temperature for 24 h. Then the precipitate was subjected to calcination at 400 °C for 30 min in reducing atmosphere (H_2 5%:N_2 95%) [20]. The obtained powders were labeled as $KMgF_3$-1.

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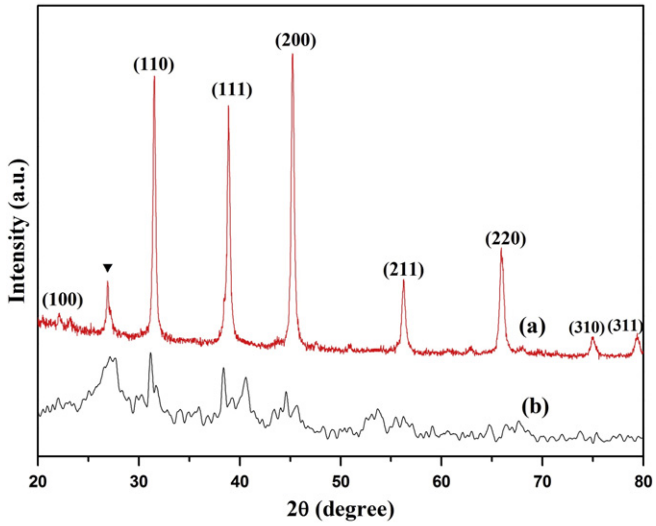

Fig. 1. XRD patterns of (a) $KMgF_3$-1; (b) $KMgF_3$-2 (▼: MgF_2).

2.1.2. Sol–gel method

Molar ratio of the materials was $[Mg(NO_3)_2 \cdot 6H_2O]$:$[KNO_3]$:$[NH_4F] = 1$:1:3. Firstly, $Mg(NO_3)_2 \cdot 6H_2O$, KNO_3 and NH_4F were dissolved in deionized water with vigorous stirring till a transparent solution was formed, then citric acid was added (molar ratio of citric acid to $KMgF_3$ was set at 2). Secondly, the mixed solution was evaporated at 70 °C until a transparent viscous gel was formed, and the gel was dried in a vacuum oven at 110 °C for 24 h. Finally, it was calcined at 400 °C for 30 min in reducing atmosphere ($H_2$5%:$N_2$95%). The synthesized samples were denoted as $KMgF_3$-2.

2.2. Characterization

The X-ray power diffraction patterns were recorded with a Rigaku D/MAX 2500 X-ray diffractometer using Cu $K_{\alpha 1}$ radiation ($\lambda = 0.1541$ nm) and scanning over the range of 20–80°. The TEM images of the samples were obtained with a FEI Tecnai G2 S-Twin transmission electron microscope with a field emission gun operating at 200 kV. X-ray photoelectron spectra (XPS) were recorded on a VG Escalab 200R spectrometer using MgK_α X-ray source ($h\nu = 1254.6$ eV), calibrated relative to C1s peak at 284.8 eV. The UV–visible diffuse reflectance spectra were recorded on a Perkin-Elmer Lambda 35 spectrophotometer in 200–800 nm.

2.3. Photocatalytic process

The photocatalytic activity of $KMgF_3$ catalysts were investigated in four test reactions: the photocatalytic degradation of phenol, chlorophenol, methyl orange and rhodanmine B in aqueous solutions. The above four common organic pollutants were extensively used by previous researchers [10,21–24] due to their toxicity and being sources of water contamination. The experiment was carried out on a SGY-I multifunctional photochemical reactor [22]. A 300 W halogen lamp was used as visible light source. In each run of photocatalysis reaction, 250 mL of pollutants with an initial concentration of 20 mg/L and 250 mg of catalyst were added into the reactor, keeping stirring in the dark for 30 min for adsorption–desorption equilibrium before photocatalytic reaction. Then the solution was exposed to visible light irradiation, the sampling was performed every 30 min. The supernatant liquor of the reaction was analyzed by an ultraviolet spectrophotometer (UV-7504PC) after centrifugation, which was performed at the maximum absorption wavelength of each pollutant, 270 nm for phenol, 280 nm for chlorophenol, 460 nm for methyl

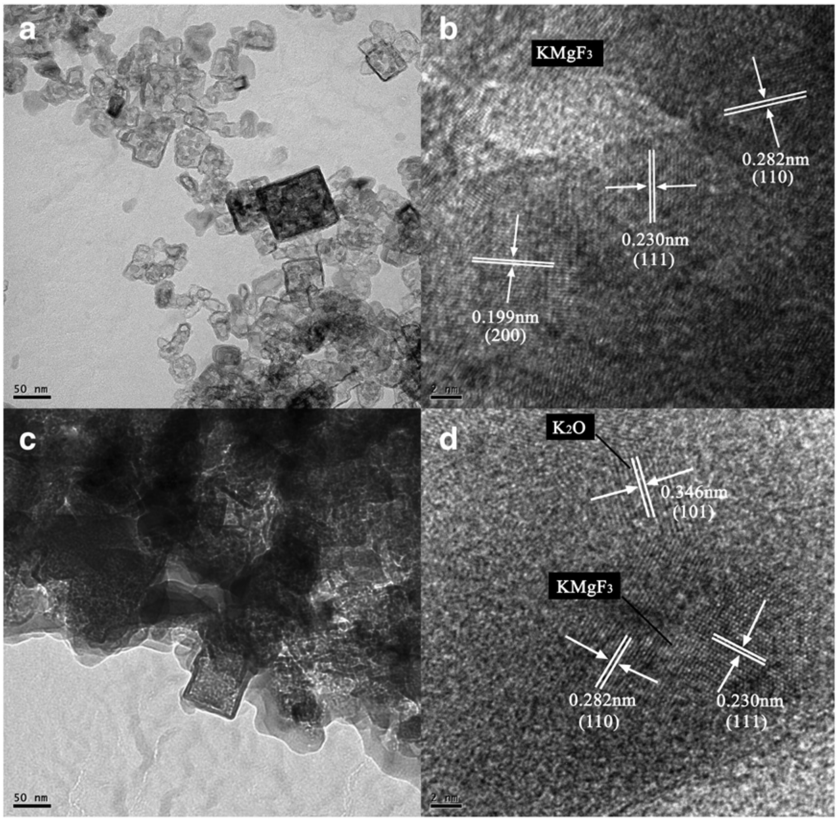

Fig. 2. TEM and HRTEM images of $KMgF_3$-1: (a), (b); $KMgF_3$-2: (c), (d).