

# Photochromic behavior of Li-stabilized MoO<sub>3</sub> sol–gels

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## Abstract

Photochromic behavior of Li-doped MoO<sub>3</sub> sol–gels prepared by the peroxo sol–gel method was studied in details using various experimental techniques, including UV–vis, XRD, Raman, EPR, and XPS. The lithium doping has drastically enhanced the stability of the MoO<sub>3</sub> sol–gels. Upon UV-light irradiation from a high-pressure mercury lamp, the Li-doped MoO<sub>3</sub> sol turned from yellowish into deep blue, and the sol in ethanol exhibited much more intense color change than the sol in water. The UV-light exposure has the effect of re-arranging the structural units of MoO<sub>3</sub> and building up short-range order inside the solid. The formation of a blue colored bronze in the photo-irradiated sols because of the reduction of Mo<sup>6+</sup> to Mo<sup>5+</sup> is also evidenced by the experimental data. Based on these data, a mechanism for the photochromic behavior is proposed.

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## 1. Introduction

Recently, transition-metal oxides such as WO<sub>3</sub> and MoO<sub>3</sub> are attracting much attention as electrochromic and photochromic materials due to their high optical contrast and reversible color change. Thin films of MoO<sub>3</sub> are considered as advantageous to be used in displays, reflective mirrors and smart windows, etc. since they are more akin to the sensitivity of human eyes, have a better open-circuit memory, and possess a ‘grey color’. MoO<sub>3</sub> thin films have been prepared by various techniques, such as evaporation, chemical vapor deposition, electrodeposition, sputtering, and sol–gel [1,2]. Among them, the sol–gel process is attractive due to its easy control over compositions, low cost, and easy handling.

However, a significant drawback of MoO<sub>3</sub> to be used as electrochromic or photochromic materials lies in its structural instability and consequently poor reversibility of color-

ation [3]. Crystals of MoO<sub>3</sub> belong to the AMO<sub>3</sub> perovskites with vacant A sites [4]. Li<sup>+</sup> ions, if introduced as a dopant to MoO<sub>3</sub>, may enter into the empty A sites and function as a structure-stabilizing agent for MoO<sub>3</sub>. Meanwhile, the introduction of Li ions will not create new energy levels in the band diagram of MoO<sub>3</sub>, and thus will not affect adversely the optical absorption properties of the solid. In a previous paper [5], we reported that Li-doping can significantly improve the stability of MoO<sub>3</sub> sol–gels and consequently the electrochromic performance of MoO<sub>3</sub> thin films. As shown by Yao et al. [6], electrolytically pre-treated MoO<sub>3</sub> thin films, which contain residual Li ions, exhibit partially reversible visible-light induced photochromism. Thus, in this work we were motivated to investigate the photochromic properties of Li-doped MoO<sub>3</sub> sol–gels and the related mechanism of photo-coloration.

## 2. Experimental

The Li-doped MoO<sub>3</sub> sol–gels were prepared using the peroxo sol–gel method [7]. Metallic molybdenum powder

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was dissolved in an aqueous solution of  $\text{H}_2\text{O}_2$  (30 wt%). To this solution, lithium hydroxide monohydrate ( $\text{LiOH} \cdot \text{H}_2\text{O}$ ) was added slowly under stirring at room temperature according to a Li/Mo molar ratio of 1/10, and a stable yellow solution was obtained. This solution can transform into a yellow gel upon the decomposition of the excessive  $\text{H}_2\text{O}_2$  and the partial evaporation of the water solvent after stirring for a long time. To expedite the process, in this work the yellow solution was dried at  $40^\circ\text{C}$  in an oven for 24 h to form a xerogel powder. The Li content in the powder was determined by ICP to be 10.0 at.%, indicating that all the added lithium is retained in the product. Excessive  $\text{H}_2\text{O}_2$  in the powder was not detectable using  $\text{KMnO}_4$  titrimetric analysis. The xerogel powder holds 1.97  $\text{H}_2\text{O}$  per  $\text{MoO}_3$  according to the thermogravimetric analysis. For simplicity, the compositions of the Li-doped  $\text{MoO}_3$  sols and gels will be denoted below as  $\text{Li}_{0.1}\text{MoO}_x$ .

The above-described xerogel powder can be readily re-dispersed in water or ethanol, forming stable yellowish sols. The pH of the sol in water was measured as to be 3–4 using a strip of pH-testing paper, while that of the sol in ethanol was not measurable using the same method. To investigate the photochromic behavior of the sols, 1.0 g of the xerogel powder was dissolved in 5 mL of deionized water contained in a quartz tube, and irradiated using a 500 W high-pressure Hg lamp (no light filter is used; intensity:  $40\text{ mW}/\text{cm}^2$ ) for approximately 100 h. And 1.0 g of the powder was dissolved in ethanol, and irradiated for 8 h using the same Hg lamp. After the irradiation, both the sols in water and in ethanol were dried in an oven at  $60^\circ\text{C}$  for 10 h to form xerogel powders for further analysis. Note that all the experiments in this work were operated in air.

Several techniques were used to characterize the Li-doped  $\text{MoO}_3$  sol–gels, including UV–visible absorption spectroscopy, powder X-ray diffraction (XRD), Raman microprobe spectroscopy, electron paramagnetic resonance (EPR), and X-ray photoelectron spectroscopy (XPS).

UV–vis absorption spectra were recorded with a Shimadzu UV1601 spectrophotometer. XRD experiments were performed on a D/max-rB X-ray diffractometer with  $\text{Cu K}_\alpha$  radiation. Raman spectra were obtained using a LABRAM Raman microscope spectrometer. The excitation wavelength was 632.8 nm, supplied by a He–Ne laser. To prevent possible laser-induced phase transformation or damage of the samples, a low power level of 1.5 mW was used in the measurements [8].

EPR spectra were measured on a BRUKER ER2000-SRC spectrometer at the frequency of 9.55 GHz with a homodyne system using 2.5 KHz modulation of the magnetic field. The center magnetite was 3500 G, the scan length was 1000 G, and the microwave power was 20 mW. The sample powders were held in a quartz cylinder of 3 mm in diameter. The  $g$  factor was calibrated by reference to a powder of 1,1-di-phenyl-2-picrylhydrazyl (DPPH,  $g = 2.0037 \pm 0.0002$ ).

XPS spectra were measured with a MICRO LAB MK II surface analyzer using  $\text{Mg K}_\alpha$  as the exciting resource. The

background pressure of the system was less than  $10^{-8}$  Torr, and all binding energies were corrected using C1s peak at 284.6 eV as the reference. XPS peaks were fitted using Gaussian-like curves and the binding energy values of peaks were given with an accuracy of  $\pm 0.1$  eV.

### 3. Results and discussion

#### 3.1. UV–vis absorption spectra

The  $\text{Li}_{0.1}\text{MoO}_x$  xerogel powder and the sols obtained by re-dispersing the powder into water or ethanol look yellowish. This color indicates the existence of some residual Moperoxide complexes. As shown in Fig. 1(a), the sol in water exhibits an absorption edge starting from  $\sim 480$  nm, but has no absorption in the longer wavelength range. Upon irradiation with UV-light, the sols in water and in ethanol build up strong and broad absorption in the visible and NIR regions, with a peak appearing at 720 nm (Fig. 1(b) and (c)). However, the photo-coloration rate for the sol in ethanol is much higher than the sol in water since 8 h of irradiation of the sol in ethanol has created higher absorption at the peak wavelength of 720 nm than 100 h of irradiation of the sol in water. This might be explained as follows. Ethanol is a stronger electron donor than water, and the ethanol solvent can create a reducing environment for the formed bronze to prevent it from being re-oxidized by the oxygen in air.

#### 3.2. XRD patterns

The as-dried  $\text{Li}_{0.1}\text{MoO}_x$  xerogel powder is amorphous, as shown by the X-ray diffraction data in Fig. 1(a). Upon annealing at  $400^\circ\text{C}$  for 2 h, it becomes polycrystalline with well-developed diffraction peaks that can be indexed according to the orthorhombic phase (JCPDS card No. 12-517) (Fig. 1(b)). The xerogel powder obtained from

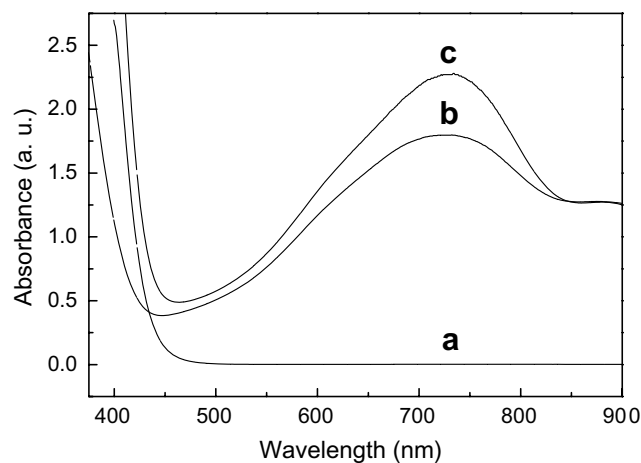


Fig. 1. UV–visible absorption spectra of the  $\text{Li}_{0.1}\text{MoO}_x$  sol in water before (a) and after (b) 100 h of UV-irradiation, and the  $\text{Li}_{0.1}\text{MoO}_x$  sol in ethanol after 8 h of UV-irradiation (c).

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