



# Assessment of divergent functional properties of seed-like strontium molybdate for the photocatalysis and electrocatalysis of the postharvest scald inhibitor diphenylamine



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## ABSTRACT

The bifunctional activity of strontium molybdate (SrMoO<sub>4</sub>) in the photodegradation and electrocatalytic determination of diphenylamine (DPAH) was identified and demonstrated. The photocatalytic and electrocatalytic activity of SrMoO<sub>4</sub> were influenced by its structural properties. Those structural properties are scrutinized by various physical spectroscopic and microscopic tools. In this work, we mainly concentrated on two phenomena of SrMoO<sub>4</sub>, the photon absorption and electrochemical behavior. UV–visible spectroscopy was used to assess the photon absorption characteristics of SrMoO<sub>4</sub>, which mostly generates OH<sup>•</sup> radicals for the degradation of DPAH. The rate of photodegradation was demonstrated in terms of irradiation time, pH, catalyst loading, and initial concentration. On the other hand, voltammetry was used to evaluate the electrochemical behavior of SrMoO<sub>4</sub>. The overall reaction pathways of DPAH showed that the major contribution of the reaction is generation of radical cations (DPAH<sup>•+</sup>). Therefore, we can determine the concentration of DPAH by measuring DPAH<sup>•+</sup>. Differential pulse voltammetry is a suitable analytical tool to measure DPAH<sup>•+</sup>, which determined the DPAH in the linear range 0.1–35 μM and with a lowest detection limit of 30 nM. One of the greatest challenges of this determination is the selectivity, because DPAH<sup>•+</sup> is highly reactive toward similar functionalities such as anions and cations. Therefore, we carefully investigated and discussed the selectivity in the presence of interfering compounds.

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## 1. Introduction

Over the past two decades, the alkaline-earth metal molybdates (AMoO<sub>4</sub>; A = Mg, Ca, Sr, and Ba) have been extensively studied in terms of structure and physicochemical properties. Mostly, the scheelite-type structure (bivalent cations) exhibits excellent strength, high decomposition temperature, and chemical and thermal stability [1]. In particular, calcium molybdate (CaMoO<sub>4</sub>) was focused on due to its admirable photoluminescence properties, and it has been used as an anode material for Li ion batteries, solid-state lasers, solar cells, scintillators in medical devices, and fiber optic communications [2–6]. However, strontium molybdate (SrMoO<sub>4</sub>) has received little attention. Past studies documented its structural evolutions by high-pressure X-ray diffraction and neutron diffraction patterns [7,8]. Also, its crystal growth has been

investigated under various precipitation conditions [9]. In addition, various synthesis methodologies have been developed to control its morphology, such as co-precipitation [10], microwave irradiation [11], hydrothermal methods [12], microwave hydrothermal preparation [13], and solid-state metathetic synthesis [14]. The detailed structural studies are well documented but the applications of SrMoO<sub>4</sub> have not yet been studied. Hence, the present study concentrates on the electrochemical and photochemical applications of SrMoO<sub>4</sub>. The photochemical properties of SrMoO<sub>4</sub> are investigated for the [MoO<sub>4</sub>]<sup>2-</sup> tetrahedral unit, which absorbs light energy in the UV region and possibly contributes to photoluminescence properties [6]. On the other hand, the electrochemical properties of SrMoO<sub>4</sub> are inferred from the charge distribution between Sr<sup>2+</sup> and [MoO<sub>4</sub>]<sup>2-</sup> units. Inspired by these facts, we have applied SrMoO<sub>4</sub> to the electrochemical determination and photocatalytic degradation of diphenylamine (DPAH).

DPAH is a derivative of aniline and is mostly used as a postharvest scald inhibitor for apples and pears because of its excellent

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antioxidant properties, which protect the skins of apples and pears by preventing the oxidation of  $\alpha$ -farnesene in cold storage [15]. Industrially, there are several processes using DPAH, despite its low solubility, because of which it remains on the skins of apples and pears, and thus persists in fruit juices. Further, wastewater from storage factories is highly contaminated with DPAH and its derivatives. DPAH damages red blood cells, which causes erythropoiesis and hemosiderosis [16]. Therefore, DPAH is listed as a priority pollutants by the European Union (EU); EU directive 91/414/EEC establishes a maximum allowed concentration of DPAH of 5–10 mg kg<sup>-1</sup> [17]. Hence, the determination of DPAH is of considerable importance.

Hitherto, limited analytical procedures have been developed to determine DPAH, such as gas chromatography, high performance liquid chromatography, mass spectrometry, and spectrophotometry [18–21]. These techniques are quite costly and need instruments operated by highly skilled technicians. Electrochemistry offers an alternative method to determine the DPAH. To the best of our knowledge, there is only one report available for the electrochemical determination of DPAH by molecularly imprinted polymers [22]. Herein, we have developed an effective and efficient sensing platform to determine DPAH using SrMoO<sub>4</sub> catalyst.

The photodegradation of DPAH has been investigated in various pH solutions and for different irradiation times. Here also, only one report is available for the mechanistic investigation of DPAH degradation by a mixture of acetonitrile and DPAH [23]. As described in the literature, most of the reaction proceeds through OH radicals by which the oxidation of DPAH yields radicals on an aromatic ring. These radicals are further delocalized to produce aniline-type radicals. This reaction is initiated through radical formation on the aromatic ring or the aromatic amine group. Afterward, these radicals are rearranged to form a covalent bond between two aromatic rings or to initiate degradation of DPAH to other byproducts. The authors monitored direct photolysis by a liquid chromatographic–mass spectrometric technique and analyzed the byproducts. Finally, they concluded that the major degradation product is carbazole (CBZ). Following their work, we investigated the photodegradation of DPAH by time-dependent UV–visible spectra and proposed a photocatalytic mechanism for SrMoO<sub>4</sub> by the scavenger profile. This heterogeneous photocatalyst generates the OH<sup>•</sup> radicals that are the primary active species targeting the DPAH.

## 2. Experimental

### 2.1. Materials

Strontium chloride (SrCl<sub>2</sub>), sodium molybdate (Na<sub>2</sub>MoO<sub>4</sub>), diphenylamine (DPAH, C<sub>12</sub>H<sub>11</sub>N), magnesium chloride (MgCl<sub>2</sub>), sodium chloride (NaCl), calcium chloride (CaCl<sub>2</sub>), urea (CH<sub>4</sub>N<sub>2</sub>O), diuron (C<sub>9</sub>H<sub>10</sub>C<sub>12</sub>N<sub>2</sub>O), carbofuran (C<sub>12</sub>H<sub>15</sub>NO<sub>3</sub>), chlorpyrifos (C<sub>9</sub>H<sub>11</sub>C<sub>13</sub>NO<sub>3</sub>PS), and all other chemicals were purchased from Sigma-Aldrich and Alfa Aesar companies and used as received without further purification. A phosphate buffer (PB) electrolyte solution was prepared by using a mixture of monosodium phosphate (NaH<sub>2</sub>PO<sub>4</sub>) and disodium phosphate (Na<sub>2</sub>HPO<sub>4</sub>). All required solutions were prepared using double-distilled (DD) water.

### 2.2. Apparatus and electrochemical measurements

The structural characterization of seed-like SrMoO<sub>4</sub> was carried out by powder X-ray diffraction (XRD) on a Rigaku MiniFlex II instrument. Fourier transform infrared spectroscopy (FT-IR) was performed using an FT/IR-6600 spectrophotometer. The Raman spectrum was obtained using a Raman spectrometer (Dong Woo 500i, Korea) equipped with a charge-coupled detector. The X-ray

photoelectron spectra (XPS) of SrMoO<sub>4</sub> were obtained using a ULVAC-PHI 5000 Versa Prob X-ray photoelectron spectrometer. The surface morphology was probed by transmission electron microscopy (TEM- TECNAI G2). Scanning electron microscopy (SEM) and energy dispersive X-ray spectral studies were carried out with a Hitachi S-3000 H scanning electron microscope (SEM Tech Solutions, USA) and HORIBA EMAX X-ACT, respectively. The electrocatalytic behavior and the detection of DPAH were performed by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) using CHI 405a and CHI 900 (CH Instruments, USA). A conventional three-electrode system was used for electrocatalytic studies, where the modified GCE is the working electrode (0.07 cm<sup>2</sup>), platinum wire is the auxiliary electrode, and Ag/AgCl is used as a reference electrode.

### 2.3. Preparation of seed-like SrMoO<sub>4</sub>

The seed-like SrMoO<sub>4</sub> was prepared by the simple precipitation method. In a typical synthesis, 40 mL of 0.2 M Na<sub>2</sub>MoO<sub>4</sub> was taken and stirred at 1000 rpm and 40 mL of 0.1 M SrCl<sub>2</sub> was added to the stirred solution of Na<sub>2</sub>MoO<sub>4</sub>. This mixture was then stirred for 1 h. The clear solution of Na<sub>2</sub>MoO<sub>4</sub> was completely turned into a white precipitate while SrCl<sub>2</sub> solution was added. The precipitate was washed with copious amounts of water and absolute ethanol and dried overnight at 80 °C. Finally, the dried SrMoO<sub>4</sub> was annealed at 500 °C for 2 h.

### 2.4. Fabrication of modified electrodes

Before modification, the GCE was polished with 0.05 μm alumina slurry and washed with several amounts of DD water to remove the alumina particles on the GCE surface. The as-prepared seed-like SrMoO<sub>4</sub> was redispersed in DD water and sonicated for 20 min. After that, about 8 μL of seed-like SrMoO<sub>4</sub> suspension was drop coated on the surface of GCE (GCE working area = 0.07 cm<sup>2</sup>). The drop-coated electrodes were allowed to dry at room temperature and then gently rinsed with water to remove the loosely bound particles. These modified electrodes were further used for the electrochemical characterizations.

### 2.5. Photocatalytic activity of SrMoO<sub>4</sub>

The photocatalytic activity of the as-synthesized SrMoO<sub>4</sub> for the degradation of DPAH solution under visible light irradiation was evaluated. For these photocatalysis measurements, our previously reported procedure was followed with a slight modification [24,25]. In a typical procedure, 50 mg of the catalysts was dispersed in 100 mL of DPAH solution (20 mg/L) and stirred for 2 h under dark conditions to reach adsorption–desorption equilibrium between the DPAH solution and the catalyst. After that, the suspension was irradiated with light: a 500 W tungsten incandescent lamp ( $\lambda > 400$  nm) was used as the light source. At 5 min time intervals, 4 mL of the suspensions was collected and the concentration change of DPAH was monitored by a UV–vis spectrophotometer. In a recycle test, the seed-like SrMoO<sub>4</sub> photocatalyst was separated from the reaction mixture by centrifugation after the photodegradation experiments and washed with water, and then dried and used again.

## 3. Results and discussion

### 3.1. Characterizations

The structure and crystal lattice parameters of the as-prepared SrMoO<sub>4</sub> were examined by XRD pattern analysis and are shown in Fig. 1A. The obtained discrete peaks at 18.0°, 27.6°, 29.7°, 33.2°, 35.2°, 38.2°, 40.2°, 42.2°, 44.2°, 46.2°, 48.2°, 50.2°, 52.2°, 54.2°, 56.2°, 58.2°, 60.2°, 62.2°, 64.2°, 66.2°, 68.2°, 70.2°, 72.2°, 74.2°, 76.2°, 78.2°, 80.2°, 82.2°, 84.2°, 86.2°, 88.2°, 90.2°, 92.2°, 94.2°, 96.2°, 98.2°, and 100.2° are indexed to the SrMoO<sub>4</sub> phase.

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