



Molybdenum oxide nanosheets meet ascorbic acid: Tunable surface plasmon resonance and visual colorimetric detection at room temperature



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ABSTRACT

Here we report a simple, rapid, and environmentally friendly method for the preparation of non-stoichiometric MoO₃ (MoO_{3-x}) nanosheets using ascorbic acid (AA) as a reducing agent under an acidic environment at room temperature. The resultant MoO_{3-x} nanosheets show an intense blue color and strong localized surface plasmon resonance (LSPR) in the visible and near-infrared region, which can be tuned by changing the pH values of the preparation solution. The hydrogen ions intercalate into the lattice of MoO₃ and bond to oxygen atoms to generate water molecules, and the electron of the AA is transferred to Mo cations, which results in the reduction of Mo⁶⁺ and formation of oxygen vacancies, giving rise to the LSPR. Additionally, a visual colorimetric assay has been developed for the detection of AA in aqueous solutions and serum samples. The absorbance at 820 nm is linearly related to the logarithm of the AA concentration in the range of 1 mM–100 mM with a limit of detection of 0.09 mM at a signal-to-noise ratio of 3.

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1. Introduction

Localized surface plasmon resonance (LSPR) is a phenomenon in which collective electron charge oscillations by light excitation are confined to a nanoparticle [1]. These resonances create intense LSPR absorption bands and strong local electromagnetic field enhancements, which shows great potential applications in sensing, photothermal therapy, photovoltaics, catalysis, as well as single-molecule spectroscopy [2–5]. Noble metal nanoparticles such as gold nanoparticles (AuNPs) and silver nanoparticles (AgNPs) are the most common plasmonic nanomaterials, and their LSPRs can be tailored by morphologies, sizes, and surrounding mediums because of their high charge carrier density and good stability [6–8]. However, AuNPs and AgNPs have some drawbacks in terms of excessive losses at optical frequencies and low levels of abundance, which restricts their applications, especially in development of several devices [9].

Alternatively, LSPR has also been reported in heavily doped semiconductor nanomaterials spanning from transition-metal oxides (TMOs) to transition-metal chalcogenides [10,11]. As a TMO,

MoO₃ nanosheets are good candidates for the hosts of LSPR because they have unique outer-d valence electrons [11]. The transformation of the stoichiometric MoO₃ into non-stoichiometric MoO_{3-x} nanosheets produces a LSPR absorption thanks to the formation of aliovalent heteroatoms or lattice vacancies [12,13]. There are a few reports on preparation of MoO_{3-x} nanosheets including solvothermal method [14,15], Pd-catalyzed hydrogenation [12,16], supercritical carbon dioxide [17], and laser irradiation [18]. Nevertheless, the solvothermal and supercritical methods require high temperatures and pressures, and the Pd-catalyzed hydrogenation methods need to pre-prepared Pd/MoO₃ hybrids as a precursor and use sodium borohydride with a high toxicity and explosive property. Meanwhile, it is easy for the laser irradiation method to produce a thermal effect and its power consumption is obvious. Consequently, it is still a great challenge to synthesize MoO_{3-x} nanosheets using a simple, rapid, and environmentally friendly experimental condition.

In the present work, we developed a simple, rapid, efficient and environmentally friendly method to prepare MoO_{3-x} nanosheets using ascorbic acid (AA) as a reducing agent under an acidic environment at room temperature. The resultant MoO_{3-x} nanosheets display a strong LSPR in the visible and near-infrared region, which can be tuned by altering the pH value. Additionally, owing to the

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LSPR response of the MoO_{3-x} nanosheets to the concentration of AA, a highly selective visual colorimetric assay for AA is also fabricated.

2. Experimental

2.1. Chemicals

Bulk MoO_3 powders, AA, glutathione, and boric acid were purchased from Aladdin (Shanghai, China). Ethanol (95%), phosphoric acid, acetic acid, and sodium hydroxide were obtained from Sinopharm Chemical Reagent Co., Ltd. All the chemicals were used as received without further purification. Deionized water was used for the preparation of various solutions.

2.2. Experimental instrumentation

Atomic force microscopy (AFM) images were taken using a Bioscope Catalyst AFM (Bruker Corporation). Ultraviolet-Visible-Near Infrared (UV-vis-NIR) absorption spectra were collected on a spectrophotometer (Shimadzu UV-1800, Japan). X-ray powder diffraction (XRD) patterns were recorded on an X'Pert PRO X-ray diffractometer using $\text{Cu K}\alpha$ radiation. X-ray photoelectron spectroscopy (XPS) measurements were conducted on an ESCALAB 250 photoelectron spectrometer.

2.3. Preparation of MoO_3 nanosheets

MoO_3 nanosheets were prepared by a previously reported liquid exfoliation method [19–21]. Typically, 0.4 g of bulk MoO_3 powder was grounded for 1 h, followed by the dispersion in the mixture of 23.6 mL deionized water and 26.4 mL ethanol. Then, the mixture was ultra-sonicated for 2 h at the power of 100 W, which was further centrifuged at 8000 r/min for 20 min. The colorless supernatant was collected and stored at 4 °C before use.

2.4. Preparation of MoO_{3-x} nanosheets

Briefly, 1 mL of MoO_3 nanosheets dispersion was mixed with 1.7 mL of Britton-Robinson (BR) buffer with different pH values (2.0–11.2). After that, 0.3 mL of 0.01 M AA solution was injected into the mixture above at room temperature, during which the solution gradually turned to deep blue, suggesting the formation of MoO_{3-x} nanosheets. The resultant MoO_{3-x} nanosheet dispersion was also placed at 4 °C before use.

2.5. Detection of AA using MoO_3 nanosheets

For the detection of AA, 1.4 mL of BR buffer (pH 2.9) and 1 mL of MoO_3 nanosheet dispersion were transferred to several glass reaction vessels with a volume capacity of 5 mL. Subsequently, 0.6 mL of AA solutions with different concentrations (0–200 mM) were added stepwise to the mixture and incubated for 30 min at room temperature. After the reaction, the UV-vis absorption spectra were measured, and the absorption peaks were employed for the quantitative determination of AA.

3. Results and discussion

3.1. Preparation and characterization of MoO_{3-x} nanosheets

The MoO_3 nanosheet was synthesized by a reported liquid exfoliation method [19–21]. The MoO_{3-x} nanosheets were prepared by direct addition of AA solution into MoO_3 nanosheet dispersion under an acidic medium. Fig. 1A displays the UV-vis-NIR absorption spectra of the MoO_3 nanosheets and corresponding photographs before and after AA reduction at room temperature. Before addition of AA, the MoO_3 nanosheet dispersion with a micrometer lateral width (Fig. S1) is colorless without any absorption in the wavelength range of 400–1000 nm. On the contrary, upon AA reduction, the resultant MoO_{3-x} nanosheets show a deep blue color

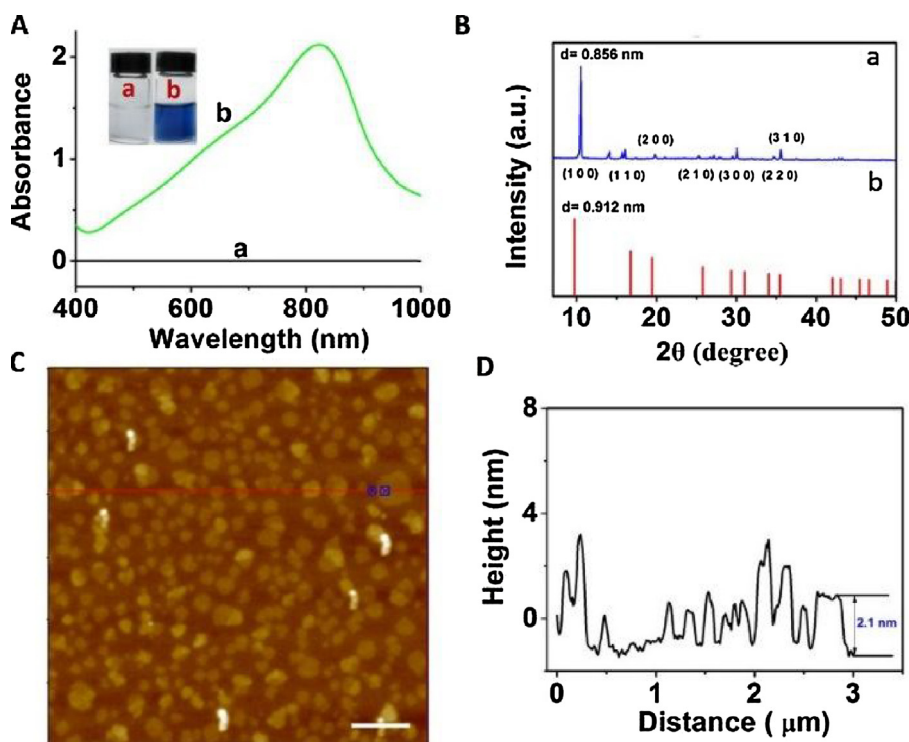


Fig. 1. (A) UV-vis-NIR absorption spectra of (a) MoO_3 nanosheet and (b) MoO_{3-x} nanosheet dispersions. Inset is the corresponding photographs. (B) XRD pattern of (a) the MoO_3 nanosheets, and (b) the standard card of hexagonal phase of MoO_3 from JCPDS card no. 21-0569. (C) AFM image of MoO_{3-x} nanosheets (scale bar, 500 nm). (D) Height profiles taken along the red solid lines in (C). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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