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Synthesis of molybdenum oxide quantum dots with better dispersity and bio-imaging ability by reduction method

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ABSTRACT

A reduction method was proposed to synthesize better dispersed molybdenum oxide quantum dots (MoO_x QDs) with stable fluorescence properties by using molybdenum disulfide (MoS_2) and hydrogen peroxide (H_2O_2) as precursor and oxidant, and using ethanol as reducing agent and surfactant of oleylamine as modified agent. The morphology of the as-prepared MoO_x QDs with average size of 1.96 nm were observed, calculated and analyzed from TEM and AFM detections. Excitation-dependent photoluminescence emission of MoO_x QDs could be obtained and MoO_x QDs exhibited blue fluorescence under UV light irradiation. Factors that influenced the syntheses of MoO_x QDs were discussed, and the highest value of fluorescence intensity was exhibited with the adding of 5 mL oleylamine and the reaction time of 24 h. The cell imaging behaviors, the physiological stabilities and in vitro cytotoxicity testing of MoO_x QDs were further discussed with HeLa cells as model. And the results showed that it might be a promising biomedical material as high quality fluorescent probes for bio-imaging.

1. Introduction

Transition metal oxide (TMO) QDs have attracted great attention in basic scientific researches due to their unique electrical, optical, and mechanical properties [1–5]. And MoO_x QDs [6–8], with a wider band gap than that of MoS_2 [9], and with relative high stability, low toxicity and better biocompatibility, special quantum size effect and surface effect characteristic [10], have concentrated increasing efforts for researchers on the synthesis of MoO_x nanomaterials and on their potential applications in more and more fields [11–14].

Lu et al. prepared MoO_3 QDs through combining intercalation and thermal exfoliation procedures, and obtained MoO_3 QDs with average size of 3.8 nm [15]. Xiao et al. proposed a one-pot method to synthesize highly photoluminescent MoO_x QDs with lateral sizes of 2.02 nm from chemical oxidation of MoS_2 at room temperature for a photoluminescent probe in 2,4,6-trinitrotoluene (TNT) determination [16] and constructing a new off-on photoluminescence sensor for phosphate determination [17]. Xu et al. proposed an efficient method to synthesize MoS_2 QDs with lateral size of ∼3.3 nm by combining sonication and solve-thermal treatment of bulk MoS_2/WS_2 at a mid-temperature for in vitro cell imaging due to their low cytotoxicity and strong fluorescence [18]. Since the electrical, optical, magnetic, and chemical properties of thus QDs are greatly dependent on the sizes and size distributions of the obtained nanocrystals [19], so better dispersions of MoO_x QDs with uniform sizes are of significant importance [20].

With the appearances of some breakthroughs in the researches for the synthesis of QDs [21–25], they were also studied as a new type of high quality fluorescent probes for bio-imaging [26–28] due to their high fluorescence intensity [29], better stability and adjustable sizes in the recent years. Moreover, all colors of QDs can be inspired by a single light source. While if QDs, such as CdSe [30,31] and CdTe [32], that containing heavy metal elements, are used as the main component in the biological application fields, QDs will have biological toxicity because of the existence of heavy metal elements. For this reason, scientists start to synthesize the QDs to apply in the biological field by using low-toxicity or non-toxicity elements [33]. At present, many non-cadmium QDs, such as $CuInS_2$ QDs [34,35], MoS_2 QDs [36–38], were synthesized to apply in the field of cell imaging. Some researches on the application of MoO_x in the biological fields as fluorescent probes have been reported. For instance, the group of Kourosh Kalantar-zadeh investigated the tunable plasmonics of hydrogen doped MoO_x nanodisks and explored their application to ultrasensitive plasmonic biosensing for the first time. And MoO_x used for a variety of bioapplications were reported, such as thermal agent for tumor ablation, toxicity detection toward cancer cell [39–41].

In this work, MoO_x QDs with better dispersity and higher stability in the applied environments have been designed and synthesized via reduction method, which used molybdenum disulfide (MoS_2) powder and hydrogen peroxide (H_2O_2) as the precursor and oxidant, respectively, and ethanol as reducing agents and oleylamine as modified agent. This

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can be interpreted that MoS_2 were oxidized to the higher oxidation states accompanied by the existence of high concentration of oxygen vacancies. H_2O_2 as an excess oxygen supplier can prompt the exfoliation and oxidation of MoS_2. Then the fluorescence behaviors of the better dispersed MoO_x QDs prepared by thermal exfoliation in the presence of ethanol and oleylamine were detected and the bio-imaging abilities of the QDs of HeLa cells were investigated in details.

2. Materials and methods

2.1. Materials and reagents

MoS_2 powder was purchased from Sinopharm chemical reagent Co., Ltd.. Ethanol and H_2O_2 was purchased from Tianjing Guangfu Technology Development Co., Ltd.,China. Oleylamine (OM, 80–90%) was purchased from the Aladdin Reagent Company. All reagents were in analytical grades and used without further purification. The experiments used deionized (DI) water that purified through Ultra pure water system.

2.2. Synthesis of MoO_x QDs and characterization

Typically, 20 mg MoS_2 powder was dispersed into 20 mL mixed solution of deionized water(16 mL) and H_2O_2 (4 mL, 30 wt% aqueous solution). The dispersion was stirred at room temperature overnight in a 50 mL glass vial. The color of the mixed solution turned from black to shallow yellow owing to the spontaneous exfoliation caused by oxidation. The excess H_2O_2 was removed by heating under 60–70 °C for about 30–60 min until the disappearance of bubbles. Then, 0.5 mL aqueous solution of the above prepared precursor was added to 13 mL solution mixed with 3.5 mL deionized water, 3 mL ethanol and 6.5 mL oleylamine. The mixture was kept stirring at 70 °C for 12 h under sealed condition.

The morphology of the obtained MoO_x QDs were observed by JEOL Ltd. JEM-2010 transmission electron microscope (TEM, Japan) and Bruker MultiMode 8 atomic force microscope (AFM) with the ScanAsyst mode, respectively. The solution of QDs was diluted and dropped onto the ultrathin carbon film for TEM testing. When the solution of QDs was diluted, and the solution of QDs was dropped on the surface of silicon wafer whose roughness was less than 0.5 nm for AFM testing. The XRD patterns of the QDs were recorded on a Bruker AXS D8Focus diffractometer operating at 40 kV and 40 mA, with Cu target Kα-ray irradiation. Scans were collected over 2θ range from 10° to 90° with a step of 2°/min. Fourier transform infrared spectra (FTIR) were measured by KBr tablet technology on a Nicolet 5700 FTIR spectrometer (Nicolet). The UV–visible (UV–vis) absorption analysis was measured by the UV-1800 spectrophotometer (Shimadzu, Japan) and all fluorescence measurements were carried out using the Hitachi F-4500 fluorescence spectrofluorometer (Tokyo, Japan) at room temperatures.7

2.3. Cell incubation and fluorescence image capturing

HeLa cells (1.0×10^4) were incubated on glass cover slides loaded in 24-well culture plates containing 1000 μL of Dulbecco's modified Eagle's medium (DMEM) for 12 h. The medium was then replaced with fresh Opti-MEM (900 and 800 μL) that containing MoO_x QDs (100 and 200 μg/mL) and was cultivated for 4 h. After that, it was washed twice by phosphate buffered saline (PBS) (0.1 M, at pH of 7.4), and fresh DMEM medium (1000 μL) was added to culture for another 24 h. Fluorescence image of HeLa cells were then captured by fluorescence microscope (CLSFV1200Olympusor Olympus FluoviewFV1000, Japan).

2.4. Cellular toxicity detection

HeLa cells (5.0×10^4) were cultured for 12 h in a 96-well plate containing Dulbecco's modified Eagle's medium (DMEM) (200 μL) in each well, and for another 4 h after the medium was replaced with fresh Opti-MEM or medium containing MoO_x QDs. Then, the Opti-MEM was substituted with 200 μL fresh DMEM and was incubated for 24 h. MTT (40 μL, 5 mg/mL) was then added to every cell well. The media was removed after 4 h, and sodium dodecyl sulfate (DMSO, 100 μL) was added to dissolve formazan dye. After stirring (at 37 °C and under 120 rpm) for 15 min, the absorbance values of each well were measured using a ELx 808 enzyme-linked immune assay instrument (BioTek, USA) at a wavelength of 530 nm. The cytotoxicity of MoO_x QDs was estimated by the percentage of growth inhibition (growth inhibition,%) that calculated with the formula of $(1-A_{text}/A_{control}) \times 100$ (and A represents the value of absorbance after the cell incubation, and the suffix of text and control represent the absorbance values that with and without the QDs).

3. Results and discussion

3.1. Synthesis and characterization of MoO_x QDs

The synthesis procedures of MoO_x QDs from bulk molybdenum disulfide powder were shown in Fig. 1. MoS_2 powder and H_2O_2 were used as precursor and oxidant, respectively. MoS_2 were oxidized to higher oxidation states accompanied by the existence of high concentration of oxygen vacancies. H_2O_2 as an excess oxygen supplier can prompt the exfoliation and oxidation of MoS_2 [42]. Subsequently, MoO_x QDs were formed with the reduction by thermal exfoliation in the presence of ethanol. The MoO_x layers were then broken into small particles by thermal exfoliation in the presence of ethanol and intercalation in the presence of oleylamine. And the existence of the surfactant of oleylamine favored the formation of well dispersed QDs. The existence of the olefinic bonds within oleylamine was beneficial to the directional growth of QDs.

To investigate the morphology of the prepared QDs, AFM measurements were carried out and the results were shown in Fig. 2. The

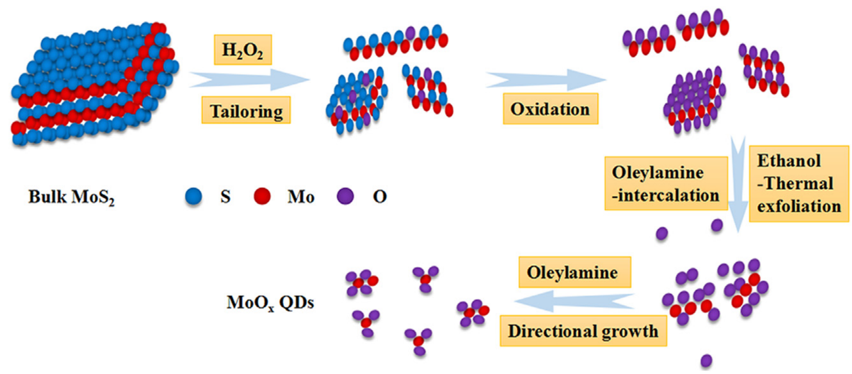

Fig. 1. Schematic illustration of the synthesis of MoO_x QDs from bulk MoS_2.