Chemical Engineering Journal 310 (2017) 179–186

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Facile scalable synthesis of MoO_2 nanoparticles by new solvothermal cracking process and their application to hole transporting layer for $CH_3NH_3PbI_3$ planar perovskite solar cells

Hanseul Choi [a,1], Jin Hyuck Heo [a,1], Su Ha [b,1], Byeong Wan Kwon [c], Sung Pil Yoon [c], Jonghee Han [c], Woo-Sik Kim [a], Sang Hyuk Im [a,*], Jinsoo Kim [a,*]

[a] Department of Chemical Engineering, Kyung Hee University, 1732 Deogyeong-daero, Giheung-gu, Yongin, Gyeonggi-do 17104, Republic of Korea
[b] Voiland School of Chemical Engineering and Bioengineering, Washington State University, P.O. Box 642710, Pullman, WA 99164-2710, USA
[c] Fuel Cell Research Center, Korea Institute of Science and Technology, 5, Hwarang-ro 14-gil, Seongbuk-gu, Seoul 02792, Republic of Korea

HIGHLIGHTS

- MoO_2 nanoparticles were synthesized via scalable solvothermal cracking process.
- The mechanism of solvothermal cracking process was systematically studied.
- The MoO_2 nanoparticles could be deposited on $CH_3NH_3PbI_3$ layer by orthogonal process.
- The MoO_2 nanoparticles used as dopant-free hole transporting materials in the perovskite solar cells.

ARTICLE INFO

Article history:
Received 19 August 2016
Received in revised form 12 October 2016
Accepted 24 October 2016
Available online 25 October 2016

Keywords:
Ultrasonic spray pyrolysis
Solvothermal cracking process
Molybdenum dioxides
Perovskite solar cell

ABSTRACT

~10 nm sized MoO_2 nanoparticles with high BET surface area of 170.14 m^2/g were synthesized via scalable new process of combining the ultrasonic spray pyrolysis and solvothermal cracking process. Initially, we synthesized polycrystalline MoO_3 microparticles by the ultrasonic spray pyrolysis at 500 °C or 600 °C. Then the MoO_3 microparticles were disassembled into crystalline grains and the grains were subsequently shattered to small MoO_2 nanoparticles through the solvothermal polyol reduction process because the polycrystalline MoO_3 microparticles are disassembled by thermal expansion and the crystalline MoO_3 grains are shattered by volume shrinkage due to phase transition from MoO_3 to MoO_2. Finally, we applied the MoO_2 nanoparticles/toluene solution to new inorganic hole transporting material for planar $CH_3NH_3PbI_3$ perovskite solar cells. The planar type $CH_3NH_3PbI_3$ perovskite solar cells exhibited stable efficiency of 14.8% for forward scan condition and 15.5% for reverse scan condition under illumination of 1 Sun (100 mW/cm^2).

1. Introduction

Molybdenum has been well known as an alloying element in various steels to improve corrosion resistance, as well as a refractory metal used for high temperature applications [1]. Although it has oxidation states from +2 to +6, most of molybdenum oxides exist in two forms: molybdenum trioxide (MoO_3) and molybdenum dioxide (MoO_2). MoO_3 is industrially produced by roasting molybdenum disulfide (MoS_2) which is the chief ore of molybdenum [2], and has been used in various applications such as a semiconductor [3], a field-emitter [4], an electrochromic material [5] and a gas sensor [6,7]. Recently, MoO_2 has attracted a lot of attentions due to its unusual metallic electrical conductivity, which is associated with its mixed interatomic bonding and a relatively high density states at the Fermi level [8]. The existence of these free electrons may enhance the catalytic activity of Mo^{+4} in MoO_2, unlike Mo^{+6} in MoO_3, where all the valence electrons of the metal are bonded to neighboring oxygen atoms [9]. Due to its electrical and catalytic properties, MoO_2 has been of great interest as a fuel reforming catalyst [8–10], alternative anode material for solid oxide fuel cells [11,12], anode material for secondary lithium ion batteries [13,14], hole injection or transporting layer for organic light emitting diodes (OLEDs) [15], and hole transporting layer for solar cells (SCs) [16].

* Corresponding authors.
E-mail addresses: imromy@khu.ac.kr (S.H. Im), jkim21@khu.ac.kr (J. Kim).
[1] These authors (H. Choi, J.H. Heo, S. Ha) have contributed equally to this work.

http://dx.doi.org/10.1016/j.cej.2016.10.110
1385-8947/