Zinc molybdenum oxide sub-micron plates as electro-catalysts for hydrogen evolution reactions in acidic medium

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ABSTRACT

Zinc molybdenum oxide (ZnMoO_4) sub-micron plates were efficaciously synthesized by hydrothermal method for electro-catalytic energy conversion applications. Electron microscopic studies show plate like morphology of the synthesized materials. The electrochemical experiments were conducted to investigate the catalytic performance of ZnMoO_4 for hydrogen evolution reactions (HER) in acidic medium using 0.5 M H_2SO_4 electrolyte. The onset over potential, over-potential at 10 mA/cm^2, and Tafel of ZnMoO_4 sub-micron plates for HER were found to be of ~45 mV, ~140 mV, and ~230 mV/dec respectively.

1. Introduction

Transition metal molybdates are considered as low cost promising electrode materials for multifunctional electrochemical performance due to the variable oxidation states of the elements. Transition metal molybdates as electrode materials include FeMoO_4 [1], CoMoO_4 [2,3], NiMoO_4 [4–6], CuMoO_4 [7] and ZnMoO_4 [8–10]. MMoO_4 (M: Cu, Zn, Ni and Fe) materials exhibited poor cycle stability during the electrochemical studies [11] which restrict the use of electrode materials for widespread applications. Among these metal molybdates, ZnMoO_4 material can be considered as one of the most effective materials due to high electrochemical capacity of ~952 mAh/g [11]. Recently, carbon supported ZnMoO_4 has been reported as efficient electro-catalysts for HER in alkaline medium [12]. This work is focused on the electrochemical testing of hydrothermally synthesized pure ZnMoO_4 sub-micron plates for HER in acidic medium.

2. Experimental

ZnMoO_4 sub-micron sized plates were synthesized using the modified hydrothermal method [13]. An appropriate stoichiometric composition of the precursors i.e. Zn(NO_3)_2·6H_2O (98%, Sigma Aldrich) and Na_2MoO_4·2H_2O (99.5%, Sigma Aldrich) was taken in 1:1 M ratio. Five ml of ethylene glycol (99%, Alfa Aesar) and 100 mg of polyethylene glycol (99%, Alfa Aesar) were added and make up 60% volume of 100 ml Teflon vessel with de-ionized water. The vessel was put in temperature controlled furnace at 140 °C/176 °C for 12 h. ZnMoO_4 powder sample was washed by de-ionized water to remove the organic/inorganic moieties and then dried at 60 °C. The crystallinity and phase purity of the prepared ZnMoO_4 powder were checked using powder x-ray diffraction (XRD) (Bruker D-8 Advance diffractometer with Cu-Kα radiation and ‘‘k’’ of 1.5406 Å). Vibrational studies of ZnMoO_4 powder were carried out using Bruker TENSOR 27 Fourier-transform infrared (FTIR) spectrometer. Field emission scanning electron microscopy (JEOL JSM-7600F FESEM) and high resolution transmission electron microscopy (JEOL JEM 2100 HRTEM) were employed to inveterate the morphology of ZnMoO_4 powder. Assessment of elemental composition of ZnMoO_4 powder was done by energy dispersive studies (EDS) equipped with TEM. The particle size distribution analysis was also conducted on dynamic light scattering ZS-90 Malvern instruments. The electrochemical measurements of ZnMoO_4 electro-catalysts for HER were conducted at three-electrode electrochemical workstation (CHI660). Standard Ag/AgCl, Pt-wire, and glassy carbon electrodes were used in electrolysis of water to HER. The catalytic ink of ZnMoO_4 powder for the working electrode was prepared by dispersing of electro-catalyst (5 mg) in 1 ml of ethanol solvent with 0.1 ml of 0.5 wt% of Nafion solution under ultrasonic process. 15 μl of ink sample was placed onto the surface of glassy carbon electrode (0.070 cm^2) to reach the catalyst loading of ~ 1.0 mg/cm^2. Cyclic voltammetry (CV) and linear sweep
voltammetry (LSV) experiments were run at various scan rates from 10 to 100 mV/s in acidic medium (0.5 M H₂SO₄). The electrolyte was de-oxygenated by passing N₂ gas for 10 min before to start the measurements for HER. Long-term cyclic stability using CV and chronoamperometry (CA) tests were also executed to confirm the stability of the electrodes.

3. Results and discussion

Surface morphology of the synthesized ZnMoO₄ materials was examined through SEM and TEM. Fig. 1a and b show low and high magnification field emission SEM (FESEM) of ZnMoO₄ respectively. FESEM studies reveal the formation of sub-micron sized plates of ZnMoO₄. Moreover, TEM studies confirmed the formation of sub-micron sized plates with the particle diameter size range from 250 to 350 nm (Fig. 1c). HRTEM of ZnMoO₄ sub-micron sized plates was also recorded and presented as Fig. 1d. HRTEM study provides the supporting information of the lattice spacing using the resulted fringes. The lattice spacing was found to be ~0.291 nm corresponding to (111) of ZnMoO₄ sub-micron plates. The quantitative elemental analysis of ZnMoO₄ sub-micron plates was examined by EDS (Fig. 2a). EDS study shows that the particles contain Zn, Mo and O. The resulting elemental composition of Zn and Mo matched with initial loaded elemental compositions of the precursor materials in 1:1 ratio. Particle size analysis was also carried using dynamic light scattering (Fig. 2b) that also supports the size obtained from TEM study. XRD studies were carried out to confirm the crystalline nature and phase purity of ZnMoO₄ sub-micron plates. Fig. 2c shows XRD patterns of ZnMoO₄ sub-micron plates. XRD patterns of ZnMoO₄ sub-micron plates could be indexed on the basis of monoclinic structure of ZnMoO₄ (JCPDS #25–1024) and also in good agreement with previous report [14]. The diffraction peaks at 2θ value of 15.4°, 18.95°, 23.90°, 24.60°, 30.70°, 31.24°, 36.26°, 36.80°, 38.41°, 41.27°, 44.64°, 48.88°, 50.24°, 51.58°, 53.92°, and 55.10° are associated with (101), (100), (011), (110), (111), (020), (021), (002), (200), (121), (112), (022), (220), (130), (221) and (131) planes of monoclinic crystal structure of ZnMoO₄ sub-micron plates. This is noticeable that no impurity phase was detected in XRD. The formation of ZnMoO₄ sub-micron plates was further analyzed by FTIR spectroscopy. FTIR spectrum of ZnMoO₄ sub-micron plates is shown in Fig. 2d. The IR bands at ~3400 and ~1700 cm⁻¹ agree with -OH stretching and bending vibrations, respectively. A broad band was appeared in the range from 550 to 1000 cm⁻¹ due to the Zn—O and Mo—O in ZnMoO₄ sub-micron plates. All these characterization techniques

Fig. 1. (a, b) Low and high magnification FESEM, (b) TEM and (c) HRTEM of ZnMoO₄.
strongly support to the formation of pure phase ZnMoO$_4$ sub-micron plates.

The electro-chemical performances of ZnMoO$_4$ sub-micron plates have been carried out for HER via electrolysis of water using 0.5 M H$_2$SO$_4$ electrolyte. The following cathodic reaction has been occurred at the surface of the electrode for HER: 2H$_2$O + 2e$^-$ → H$_2$ + 2OH$^-$. Cathodic CV scans of ZnMoO$_4$ sub-micron plates were conducted in the potential range from 0.0 to −1.8 V versus Ag/AgCl reference electrode at 50 and 100 mV/s for HER. CV studies reveal that the HER starts from −1.28 V. These results have been confirmed by LSV experiments. LSV polarization studies of ZnMoO$_4$ sub-micron plates confirmed low onset electrode potential of −1.29 V for HER via electrolysis of water as shown by CV. This is also noticeable that low onset electrode potential in cathodic region reveals high electro-catalytic efficiency of the electrode materials. The current densities of ZnMoO$_4$ sub-micron plates were observed to be 60, 67, 72 and 78 mA/cm$^2$ at 10, 25, 50 and 100 mVs$^{-1}$ respectively. This is also noteworthy that high current density also supports to high catalytic performance of the electrode materials, which is directly proportional to the HER. From LSV, the onset over potential of ZnMoO$_4$ sub-micron plates for HER was found to be −45 mV. The over-potential of pure ZnMoO$_4$ sub-micron plates was found to be −140 mV at 10 mA/cm$^2$ ($\eta_{10}$) in acidic medium. The over-potentials of Pt/C, ZnMoO$_4$/C, Cu$_x$Mo$_2$O$_9$/C, and MnMoO$_4$/C were also reported of 54, 124, 135 to 156 mV, respectively, at $\eta_{10}$ in alkaline medium [12]. Inset of Fig. 3b shows Tafel slop of ZnMoO$_4$ sub-micron plates at 10 mV/s in 0.5 M H$_2$SO$_4$. Tafel slope was found to be −230 mV/dec for HER. The stability tests of the ZnMoO$_4$ electrode materials for HER were also conducted using CV and CA experiments in 0.5 M H$_2$SO$_4$. CA studies show that the generated current density was found to be constant at various fixed potentials for 240 s for HER (Fig. 3c). CV curves also show constant long term cyclic stability for 50 segments at 10 mV/s and confirmed the stability of the electrodes for HER. An excellent electro-catalytic HER performance of ZnMoO$_4$ materials could make it an ideal HER electro-catalysts for clean energy production.

4. Conclusion

In summary, modified hydrothermally synthesized ZnMoO$_4$ sub-micron sized plates have shown excellent performance in electro-catalytic HER activity. The electrochemical CV, LSV and CA experiments reveal that ZnMoO$_4$ sub-micron plates exhibit as efficient electro-catalyst for HER in acidic medium (i.e. 0.5 M H$_2$SO$_4$ electrolyte). Low onset over potential, low over-potential at 10 mA/cm$^2$, and low Tafel values confirmed superior HER activity of ZnMoO$_4$ electro-catalyst.
CRediT authorship contribution statement

Jahangeer Ahmed: Conceptualization, Investigation, Methodology, Writing - review & editing. M.A. Majeed Khan: Resources, Writing - review & editing. Saad M. Alshehri: Supervision, Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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