Heteroatom Doped Metal Chalcogenide as a Superior Electrocatalyst in Acidic and Basic Medium

Abstract:

The convincing demand for high performances with operationally stable and inexpensive electrocatalyst for the hydrogen evolution, oxidation and oxygen evolution reaction have encouraged significant contribution towards research and development of the energy field. Until now, Pt/C and Ir/C contribute to some of the potential challenges on commercially available electrocatalysts but the main issues are associated with the high cost and inadequate long-term operational stability. Therefore, the replacement of Pt/C and Ir/C with a novel more effective catalyst is now a critical challenge and more important. These precious expensive metal catalysts demand a huge portion of the cost and degradation under harsh conditions. As previously, Ir/C also exhibit cost and stability issues. Hence a new strategy of electrocatalysts is trying to discover to reduce the cost of electrocatalysis with sufficient activity and stability. In view of this, we approach to construct different types of electrocatalysts for water splitting. The first attempt is to design unique N, P Co-doped WS_2 for searching out new low cost efficient electrocatalyst in acidic medium by exfoliation, ethching and codoping method. The monolayer dual atom nitrogen and phosphorus dope WS_2 ($PNEWS_2$) exhibit findings demonstrated $PNEWS_2$ as an efficient catalyst exhibited low overpotential (59 mV), small Tafel slope (35 mV $decade^{-1}$), large TOF (0.7 s^{-1}), exchange current density (1.15 mA cm^{-2}) and long-term stability (15 h) due to its large number of accessible active sites, high mesoporous surface area. Density functional theory (DFT) calculations highlighted the interactions between N and P with WS_2, leading to an increase in the density of states. Furthermore, P helps to downshift of the d-band center, assisted excellent hydrogen evolution reaction. The second is searching for a new type of electrocatalysts in the alkaline medium due to avoid any corrosion of glass electrodes. An unconventional catalysts Sb_2S_3 in alkaline medium integrate the water splitting performances. However, the comparison of performances is very difficult due to the use of different substrates. Further, the trial is doing upon group V metals sulfide Sb_2S_3 which provides unique morphology and abundant active sites in alkaline medium. The growth mechanism of the pellet drum-like structure furnishes orientation along the z-axis. N, Ru co-doped pellet drum bundle like Sb_2S_3 morphology exhibited its superior electrocatalytic performance in HER and HOR in alkaline medium as evident from small Tafel slope (193 mV per decade), lower overpotential (~ 72 mV), higher exchange current density (~1.42 $mAcm^{-2}$), long-term stability in alkaline medium and higher positive breakdown potential (0.6 V) at a loading of about 1.6 mg cm^{-2} respectively. However, its stability loss is further highlighted by its reaction in alkaline medium. After searching group V metals, we fervently search the catalysts among transition metal compounds. The work is carried on ruthenium doped CuO /MoS_2 which is prepared facile hydrothermal as well as solvothermal method. This work delivered exposed active sites, conductive junction, defective states as well as higher electronic states. Electrochemical

investigation revealed that Ru doped CuO/ MoS_2 (MSCR) showed its overpotential and Tafel slope of 198 mV, 113 mV dec^{-1} respectively. The anodic investigations on MSCR exhibited superior overpotential (201mV at 10 mA/ cm^2) and Tafel slope (229 mV dec^{-1}). MSCR also exhibited overpotential of ~ 1.68 V to achieve 10 mA/cm^2 of current density in an electrolyzer. In summary, the present thesis provides simple and effective ways for the development of low-cost and promising heteroatom doped metal sulphide based electrocatalysts for water splitting in acidic and alkaline medium.

Keywords: *transition metal sulphide, antimony sulphide, electrocatalyst, Alkaline water splitting, hydrogen evolution reaction, oxygen evolution reaction, hydrogen oxidation*