ABSTRACT

CO_2 is one of the greenhouse gases that mainly contribute to the major environmental issues such as global warming, ocean acidification, and acid rain. Several strategies have been developed to alleviate the effects of the increased atmospheric concentration of CO_2 such as capture, utilization, and storage. Among all the developed methods, the transformation of CO_2 to valuable chemicals is one of the promising strategies to control its atmospheric concentration and impact on our environment. The conversion of CO_2 to valuable products is a one bird-two stone approach as it does not only reduce the atmospheric concentration of CO_2 but also gives us the chemicals used in the manufacturing of daily life products and fuels to replace renewable energy sources. The conversion of CO_2 to chemicals can be done through electrochemical, biochemical, photochemical, thermochemical, and chemical fixation of CO_2. To commercialize these processes, highly efficient catalysts are required.

In our work, we synthesized the bimetallic nanoparticles as catalysts for CO_2 conversion to formate and cyclic carbonates via electrochemical reduction and chemical fixation of CO_2, respectively. The bimetallic nanoparticles were synthesized as the second metal influences the electronic properties of the other metal and thus improves the catalytic efficiency of the conversion. The synthesized catalysts include WO_3, Cs_xWO_3, and ZrO_2-Al nanoparticles. All of these nanoparticles were synthesized by hydrothermal method as hydrothermal method is famous for the synthesis of the porous catalysts. The fabricated nanoparticles were then characterized by UV-visible, FTIR, SEM-EDX, and XRD. The FTIR and EDX results showed that the nanoparticles are free from any impurity. SEM images revealed that all the synthesized catalysts have porous morphology.

The WO_3 and Cs_xWO_3 nanoparticles were then employed as working electrode in H-type cell and their electrochemical performance were evaluated by CV, LSV, and CA. The electrochemical results proved that the efficiency of WO_3 nanoparticles for CO_2 conversion to formate via electrochemical pathway was increased by alloying with Cs. LSV was used to calculate the onset potential, CV was carried out at different scan rates, and CA was done to check the stability of the catalyst at specific potential. The onset potential for Cs_xWO_3 was found to be -0.7 V *vs* Ag/AgCl. The electrochemical results showed that the maximum Faradaic efficiency and partial current density of formate over WO_3 nanoparticles were 50 % and -13.5 $mA.cm^{-2}$, respectively. The FE and partial current density were increased to 76 % and -19 $mA.cm^{-2}$ respectively when Cs_xWO_3 were employed as working electrode. Moreover, Cs_xWO_3

nanoparticles were found to stable at -1.33 V *vs* Ag/AgCl for 3 h. The high FE, low overpotential and stable electrocatalysis proved that catalysts with roughened surface exhibit more surface area, thus more active sites for CO_2 reduction, and thus more FE of the product.

The Cs_xWO_3 and ZrO_2-Al nanoparticles were also used to insert CO_2 into epoxide to obtain cyclic carbonates. These catalysts were found to be efficient catalysts for chemical fixation of CO_2 without the requirement of solvent and cocatalyst as these catalysts contain Lewis acid-Lewis base pair. Three major products *i.e.,* cyclohexene carbonate, monomer of polycyclohexene carbonate, and aliphatic carbonate were observed. Various factors that influence the conversion and selectivity of cyclic carbonates including time, temperature, and amount of catalyst were studied. It was observed that the conversion efficiency increases with the increase in the time and temperature of the reaction.

The synthesized bimetallic nanoparticles were found to be efficient, cost-effective and environment friendly catalysts for the conversion of CO_2 to formate and cyclic carbonates by electrochemical reduction and chemical fixation of CO_2 respectively. These catalysts canbe further applied on large scale.