CO2 Reduction at Low Overvoltage in Neutral Aqueous Solution by Ni-cyclam Attached Polyallylamine Polymer

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Artificial photosynthesis comprise of a light-driven water oxidation reaction and an electrochemical CO2 reduction in dark. To achieve the efficient CO2 reduction by the excited electron from the light-driven anodic reaction, the lowering the overvoltage of CO2 reduction is an essential component. [Ni(cyclam)]2+ (cyclam=1,4,8,11-tetraazacyclotetradecane) and its derivatives are known to be efficient in CO2 to CO conversion and the macrocyclic ligand, cyclam is known to stabilize Ni(I) state. However, those compounds still have ca. 0.6 V of overvoltages and the use of mercury electrode is essential to suppress hydrogen evolution on the electrode at such a negative potential. We found that the incorporation of the Ni(cyclam) unit into polyallylamine (PALA) backbone by Schiff’s base condensation via axial coordination of 4-pyridine carboxaldehyde is effective in lowering overvoltage and it enables the catalyst to be used with carbon electrode material in neutral aqueous solution. The resulting redox polymer, Ni(cyclam)-PALA converts CO2 to CO near its thermodynamic potential, -0.78 V vs. Ag/AgCl in pH 8, 50 mM tris buffer on glassy carbon electrode with current efficiency of over 90%. The axial coordination of 4-pyridine unit is mainly responsible for lowering the overpotential and the attached polyallylamine partly helps.

References