

Reduction of CO₂ to Methanol in Photoelectrochemical Cell: CM-n-TiO₂/Cu

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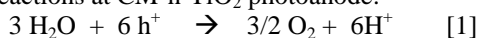
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INTRODUCTION

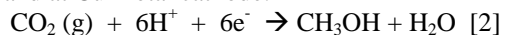
Each year about 1.0×10^9 tons of carbon dioxide (CO₂) gas is added to the atmosphere, and during the next half century at least there will be about 1.5 times increase in concentration from its present level of 390 ppm in the year 2012. Such large scale emissions of carbon dioxide into the atmosphere are believed to be partially responsible for present changes in global climate system. One potential solution in dealing with the large amounts of CO₂ that could be captured from fossil fuel combustion process, would be to convert by photoelectrochemical reduction to methanol, CH₃OH (a fuel for fuel cells or combustion engines) to minimize environmental pollution, global warming and climate change. By rough estimate, in a year about 5×10^{13} mol of methanol would be needed to drive the cars of the world on internal combustion and about half of that would be needed for cars powered by fuel cells.

Considering CO₂ emission at 2050 as 5×10^{14} moles, it is conceivable that, sometime in the future, a significant amount of CO₂ output could be converted to methanol as a convenient hydrogen carrier for automotive fuel and in fuel cells as well¹ using sunlight as a source of energy for the conversion process. However, transformation of CO₂ to hydrocarbons or CH₃OH, a reusable source of energy will benefit humans and the environment. Many researcher have shown that CO₂ can be reduced in water vapor or in aqueous medium by both electrocatalytic electrodes, photoelectrodes and photocatalyst such as TiO₂^{2,3} and ZnS.⁴ In an important communication Barton et al⁵ reported a selective solar-driven reduction of CO₂ to methanol using a pyridine catalyzed p-GaP based photoelectrochemical cell (PEC).

In this study we have reduced CO₂ and water in a PEC in which carbon modified titanium oxide (CM-n-TiO₂) was used as photoanode and folded copper metal gauze as cathode having reactions at CM-n-TiO₂ photoanode:



and at Cu-metal cathode:



having the overall reaction as:



EXPERIMENTAL

Carbon modified (CM)-n-TiO₂ samples were prepared using thermal flame oxidation method as described by Shaban and Khan.⁶ CO₂ was dissolved in a deionized water under pressure in a pressure cell at room temperature. An equal volumes of this carbonated water (20 mL) and 10.0 M NaOH (20 mL) was added to make the electrolyte concentration of 5.0 M NaOH (40 mL). Equal amounts of electrolyte was used in

each two compartments of the PEC connected by electrolyte soaked glass wool acted as a salt bridge to minimize the back reaction that will oxidize the product methanol to CO₂ and water. The surface of the photoanode was illuminated with light intensity of 100 mW cm⁻² from a 150-W Xenon arc lamp (Model LH 150/1) at applied potential of 0.3 volt vs open circuit potential (-0.9 V/SCE). Formation of methanol was tested after 5, 10, 20, 30, 40 min by GC analysis.

RESULTS AND DISCUSSION

The results of GC analysis shows that at 10 min the highest amounts of methanol was formed and after 10 min the methanol amounts started to decrease due to back reaction. Higher amounts of methanol production was observed when 1.0 mM amount of methanol was added in the electrolyte solution. This was attributed to autocatalysis by methanol to form higher amounts of it from carbon dioxide.

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