Investigation of low cost metal bipyridyldiamine complexes as co-catalysts for hydrogen evolution from aqueous media

Tarun Chand Vagvala[a,*], **Takashi Ooyabe**[b], **Munetoshi Sakai**[a], **Yusuke Funasako**[b],
Vit Kalousek[a], **Keita Ikeue**[a, b].

[a] *Advanced Material Research Institute, Tokyo University of Science-Yamaguchi, Sanyo-Onoda, 7560884, Japan*
[b] *Department of Applied Chemistry, Tokyo University of Science-Yamaguchi, Sanyo-Onoda, 7560884, Japan*
**Corresponding author:T. C. Vagvala Fax number +81-836-88-3400, E-mail address: tarunchandv@rs.tusy.ac.jp*

Abstract: Metal 4,4'-diamino-2,2'-bipyridyl (dabpy) complex with Co(III), Ni(II), Cu(II) metal centers were synthesized and their catalytic activity for hydrogen generation from aqueous media was compared. The optimum concentration of co-catalyst was determined. At a given concentration, Cu(II) complex showed relatively superior catalytic properties. Redox potentials of the metal complexes were determined by cyclic voltammetry. Cu(II) complex showed lower redox potential compared to Co(III) and Ni(II) complexes. Therefore, the relatively high catalytic properties of Cu(II) complex could be due to better electron transfer ability from photosensitiser.

Keywords: metal complex, catalyst, hydrogen generation, aqueous media.

1. Introduction

Hydrogen is one of the key clean fuels which is being developed for transportation and storage[1]. Much attention has been paid to photocatalytic H_2 production from the viewpoint of solar energy utilization. Many inorganic semiconductor-based photocatalysts and organic molecular catalysts have been reported for H_2 evolution from aqueous media. Although the efficiency of molecular catalyst systems containing noble metals for H_2-evolution are well known[2], the high cost and the scarcity of these noble metals seriously limits their application potential[3]. In the present study, we have synthesized new non-noble Co(III), Ni(II) and Cu(II) 4,4'-diamino-2,2'-bipyridyl complexes and investigated their co-catalyst properties for H_2 evolution photocatalytic system consisting of Erythrosine B and triethanolamine (TEOA) as a sacrificial agent.

2. Experimental

Co(III), Ni(II) and Cu(II) 4,4'-diamino-2,2'-bipyridyl complexes were synthesized by the following method. 4,4’-diamino-2,2’-bipyridyl dissolved in ethanol-water mixture was added drop wise to metal chloride aqueous solution while stirring at room temperature. After stirring for 3 h diethyl ether was added. The reaction mixture was kept at 5 °C overnight for precipitation. The obtained precipitate was separated by suction filtration and washed twice with hexane. The structural analysis of synthesized metal complexes was performed by FT-IR, Mass analysis and single crystal XRD. The photocatalytic H_2 evolution from water in the presence of a sacrificial agent was conducted in an external irradiation pylex cell. The reaction was carried out under irradiation from a 500 W Xe lamp with cut-off filter ($\lambda > 420$ nm). Redox potentials for Co(III), Ni(II), Cu(II) complexes were determined by a cyclic voltammetry in DMF solution and 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte.

3. Results and discussion

The molecular structures of $[M(dapdy)_n]^{3+/2+}$ cations (M = Co, Ni, Cu) in the metal complexes were determined by single crystal XRD. In the Co(III) and Ni(II) complexes, three dabpy ligands with metal ions formed six-coordinate octahedral $[M(dapdy)_n]^{3+/2+}$ complexes. In the Cu(II) complex, two dabpy ligands with

Cu^{2+} ions form four-coordinate $[Cu(dadpy)_2]^{2+}$ complex with distorted square-planar geometry. These structures were also supported by Mass and FT-IR analysis.

To determine the optimum amount of co-catalyst, photocatalytic activity was performed using different concentration of Cu(II) complex. Figure 1 shows the dependence of H_2 evolution rate on the concentration of Cu(II) complex. The H_2 evolution rate showed maximum value at 26.4 µM. To analyze and compare the effect of type of metal with the same ligand on hydrogen evolution, photocatalytic activities with 26.4 µM Co(III), Ni(II) and Cu(II) complexes were performed and presented in Figure 2. The photocatalytic system including Cu(II) complex showed the highest photocatalytic activity for H_2 evolution compared to that including other metal complexes.

Cyclic voltammetry was performed to determine the redox properties of metal complexes. Cu(II) complex showed the lowest reduction potential. It is, therefore, suggested that Cu complex could be have effective electron transfer ability from photosensitiser compared to Co(III) and Ni(II) complexes, resulting in higher hydrogen production.

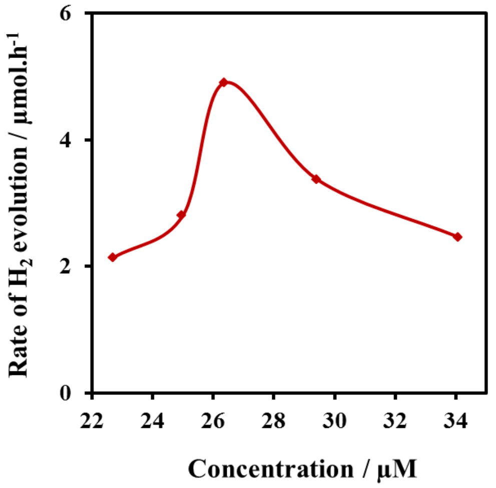

Figure 1 The dependence of H_2 evolution rate on the concentration of Cu (II) complex.

4. Conclusion

New non-noble Co(III), Ni(II) and Cu(II) 4,4'-diamino-2,2'-bipyridyl complexes were successfully synthesised and utilized as co-catalysts for hydrogen production from aqueous media. To determine optimum concentration and the effect of metal center for effective catalytic activity, photocatalytic activity was performed. Cu(II) complex showed the most effective catalytic activity among our synthesized metal comlex. From the Cyclic voltammetry analysis, Cu(II) complex have relatively lower redox potential compared to Ni(II) and Co(III) complexes. This results suggested that the high catalytic activity of Cu(II) complex is due to relatively enhanced ability to receive electrons from the photosensitiser.

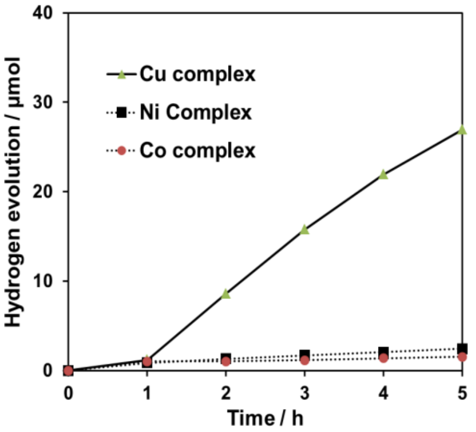

Figure 2 H_2 evolution from the solution including 113.6 µM Erythrosine B, 26.4 µM metal-4,4'-diamino-2,2'-bipyridine complex, 15 mL of sacrificial electron donor TEOA at pH=10.

References

1. J. Kothandaraman, S. Kar, R. Sen, A. Goeppert, G. A. Olah, G. K. S. Prakash, J. Am. Chem. Soc., 139 (2017) 2549.
2. N. D. Knçfel, H. Rothfuss, J. Willenbacher, C. Barner-Kowollik, P. W. Roesky, Angew. Chem. Int. Ed., 56 (2017) 1.
3. Roger, M. A. Shipman, M. D. Symes, Nat. Rev. Chem., 1 (2017) 1.

Acknowledgements: This work was financially supported by Regional Innovation Strategy Support Program 2014 of Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT). We thank T. Tominaga and Prof. T. Mochida (Kobe University) for help with X-ray crystallography. We also thank Dr. Kurashige and Prof. Negishi (Tokyo University of Science) for help with Mass analysis.