Enhancement of Photocatalytic Activity of Tris (bipyridine) Ruthenium by Encapsulation in Zeolitic Imidazolate Framework-11 and 12

Hyun Sung Kim*
Department of Chemistry, Pukyong National University, Busan 48513, Republic of Korea

*Corresponding author E-mail: kimhs75@pknu.ac.kr

ABSTRACT
In this study, Ru(bpy)$_3^{2+}$@ZIF-11 and Ru(bpy)$_3^{2+}$@ZIF-12 catalysts (bpy = 2,2'-bipyridine) were synthesized by encapsulating [Ru(bpy)$_3$]$_{2}^{2+}$ in zeolitic imidazolate frameworks (ZIFs) ZIF-11 and ZIF-12, respectively, and their photocatalytic activities were compared. Samples of different composites were prepared from their powders, and their crystal morphologies and photocatalytic activities were evaluated by X-ray diffraction analysis and UV-visible absorption spectrometry. [Ru(bpy)$_3$]$_{2}^{2+}$@ZIF-12 catalysts possessed excellent photocatalytic stability and exhibited a synergistic effect of [Ru(bpy)$_3$]$_{2}^{2+}$ and Co in the Ru(bpy)$_3$@ZIF-12 composite, and efficient electron transfer from the [Ru(bpy)$_3$]$_{2}^{2+}$ moiety to the ZIF-11 framework.

Keywords: Zeolitic imidazolate frameworks, Photocatalyst, Photosensitizer, Ru(bpy)$_3^{2+}$, Encapsulation

1. Introduction
The [Ru(bpy)$_3$]$_{2}^{2+}$ (bpy = 2,2'-bipyridine) as redox photosensitizer has been intensively investigated for molecular photocatalysis and assist in absorbing visible light wavelength range to induce the charge transfer. However, the dimerization and self-degradation of the pyridyl ruthenium complex limit its lifetime and photocatalytic activity [1,2]. Numerous attempts have been made to encapsulate ruthenium complexes inside porous inorganic scaffolds such as zeolites, owing to their excellent chemical stability [3–5]. Zeolitic imidazolate frameworks (ZIFs), which are topologically isomorphic with zeolites, have recently been reported as host materials, and many studies evaluating their applications are underway. However, the encapsulation of the photosensitizer [Ru(bpy)$_3$]$_{2}^{2+}$ in ZIF cages is yet to be reported.

However, this strategy which uses a molecular linker, encounters some drawbacks, such as limited immobilization of the catalyst on the pore surface, small diffusion coefficients of target molecules in the nanopores, and leaching out due to breaking the molecular linker.

Zeolitic imidazolate framework-11 (ZIF-11) is formed by the extended 3D zeolitic network (RHO) with zinc ions and tetrahedral-coordinated benzimidazole (BIm) linkers. ZIF-11 is an ideal host material for encapsulating large functional molecules because of its large pore diameter (14.9 Å) and narrow aperture (3.3 Å) [6,7]. In particular, ZIF-11 has a kinetic molecular diameter (13.5 Å) similar to that of [Ru(bpy)$_3$]$_{2}^{2+}$; therefore, its pore cage is suitable for the encapsulation of [Ru(bpy)$_3$]$_{2}^{2+}$, as displayed in Fig. 1.

Herein, we demonstrate a facile method to encapsulate [Ru(bpy)$_3$]$_{2}^{2+}$ in the cages of ZIF-11 and ZIF-12, which are isoostructural (denoted as [Ru(bpy)$_3$]$_{2}^{2+}$@ZIF-11 and [Ru(bpy)$_3$]$_{2}^{2+}$@ZIF-12). Furthermore, [Ru(bpy)$_3$]$_{2}^{2+}$@ZIF-11 and [Ru(bpy)$_3$]$_{2}^{2+}$@ZIF-12 not only preserve the photocatalytic activity of [Ru(bpy)$_3$]$_{2}^{2+}$, but also exhibit a more intense photocatalytic activity than [Ru(bpy)$_3$]$_{2}^{2+}$@ZIF-11 due to efficient electron transfer from the excited [Ru(bpy)$_3$]$_{2}^{2+}$ moiety to the ZIF-12 framework. To the best of our knowledge, this study is the first to demonstrate the encapsulation of [Ru(bpy)$_3$]$_{2}^{2+}$ in a ZIF host and enhance the photocatalytic effect during reduction.

2. Experimental details
2.1. Materials
Metal ion sources, viz. zinc acetate dihydrate (Zn(CH$_3$COO)$_2$·2H$_2$O, 98 %) and cobalt(II) acetate tetrahydrate (Co(CH$_3$COO)$_2$·4H$_2$O, 98 %), were purchased from Samchun Pure Chemical Co., Ltd., Korea. Benzimidazole (BIm, C$_6$H$_7$N$_2$, 98 %), tris(bipyridine)ruthenium(II) chloride (Ru(bpy)$_3$)Cl$_2$·6H$_2$O, 99.95 %), and ammonium hydroxide (NH$_4$OH, 28–30 % aqueous solution) were purchased from Alfa Aesar, USA, and used without additional purification.

2.2. Synthesis of ZIF-11 and ZIF-12
Following a procedure reported previously, BIm (0.12 g, 1 mmol), which is the ligand of ZIF-11 and ZIF-12, was introduced into a glass...
vial (capacity: 20 mL) containing methanol (2.5 mL), followed by the addition of toluene (4.6 g, 50 mmol) and ammonium hydroxide (0.1 g) under mild stirring at 25 °C. Zinc acetate dihydrate (0.11 g, 0.5 mmol) and cobalt(II) acetate tetrahydrate were used as metal ion sources for ZIF-11 and ZIF-12, respectively, and each was dissolved in a separate glass vial (capacity: 20 mL) containing methanol (2.5 mL). Each as-prepared metal–methanol solution was poured into the respective previously prepared ligand solution and stirred for 3 h at room temperature to initiate crystallization. The solutions gradually turned into milky suspensions. The as-synthesized product (ZIF-11 or ZIF-12) was obtained by centrifugation, washed with ethanol, and thereafter dried overnight at room temperature in air. The yields of ZIF-11 and ZIF-12 were approximately 75 and 70 %, respectively.

2.3. Synthesis of Ru(bpy)$_3$·Cl·ZIF-11 and Ru(bpy)$_3$·Cl·ZIF-12 in toluene–ethanol solution

The procedure for the encapsulation of [Ru(bpy)$_3$]Cl$_2$ in the different ZIF cages was identical to that described in subsection 2.2, excepting the addition of an appropriate amount of Ru(bpy)$_3$·Cl$_2$ to the ligand solution. Following crystallization, a dense yellow product was obtained by centrifugation and washed with ethanol until a colorless supernatant solution was formed.

2.4. Photocatalytic performance test

To investigate the photocatalytic performance of the series of ZIF composites, in-situ spectroscopic measurements were performed of the conversion of the methyl viologen ion MV$_2^{2+}$ to the viologen radical cation MV$^{2+}$. MV$^{2+}$ is a widely used molecular redox mediator in photochemistry, and its conversion into MV$^{2+}$ in acetonitrile was investigated by UV–vis spectrometry. Identical round pellets were made from all the ZIF composites to test their photocatalytic activities under identical conditions. A 10-mg round pellet (d = 7 mm) of each ZIF composite was placed on a glass plate (7.7 mm × 15 mm) and thereafter transferred into an airtight quartz cell, following which, 4 mL of 0.65 mM acetonitrile solution of MV$_2^{2+}$ and 65 mM of triethanolamine (TEOA) were gently introduced into the quartz cell for each test. The cell was sealed and filled with high-purity argon for 5 min in darkness. The airtight quartz cell was subsequently irradiated using a blue light-emitting diode (LED) lamp (445 nm, 1 W) at room temperature, and the absorbance spectrum for MV$^{2+}$ was recorded.

2.5. Instrumentation

X-ray diffraction (XRD) patterns of the samples were recorded on an X’Pert-MPD System (PHILIPS, Eindhoven, Netherlands) using monochromatic Cu K-α radiation in the 2θ range of 10–60° at 40 kV and 30 mA. Scanning electron microscopy (SEM) images were obtained using a JEM-2100F scanning electron microscope (JEOL, Kyoto, Japan). All UV–vis absorption spectra were recorded by a UV-2600 UV–vis spectrophotometer (Shimadzu, Kyoto, Japan).

3. Results and discussion

Ru(bpy)$_3$·Cl·ZIF-11 and Ru(bpy)$_3$·Cl·ZIF-12 were synthesized by directly mixing their metal source solution with the solution containing BMM and Ru(bpy)$_3$·Cl$_2$, respectively, at room temperature. During the in-situ encapsulation reaction, we observed that the mixed synthetic solution changed from a transparent red to turbid red, indicating the formation of Ru(bpy)$_3$·Cl·ZIF-11 and Ru(bpy)$_3$·Cl·ZIF-12. The crystals of Ru(bpy)$_3$·Cl·ZIF-11 and Ru(bpy)$_3$·Cl·ZIF-12 were observed to be ∼5 μm in size, and they were almost identical in morphology to pristine ZIF-11 and ZIF-12, respectively, as seen in the SEM images (Fig. 2). The XRD patterns of Ru(bpy)$_3$·Cl·ZIF-11 and Ru(bpy)$_3$·Cl·ZIF-12 obtained from in-situ growth are displayed against the pristine ZIF-11 and ZIF-12 patterns, respectively, in Fig. 3. The diffraction patterns of Ru(bpy)$_3$·Cl·ZIF-11 and Ru(bpy)$_3$·Cl·ZIF-12 were identical to those of their respective pristine samples following encapsulation, indicating that the encapsulation of [Ru(bpy)$_3$]Cl$_2$ did not significantly affect the structure of ZIF-11 and ZIF-12. The characteristic metal-to-ligand charge-transfer band of Ru(bpy)$_3$ at 500 nm as seen in the insets in Figs. 4(b) and 4(c) was observed nearly identically in the samples of Ru(bpy)$_3$·Cl·ZIF-11 and Ru(bpy)$_3$·Cl·ZIF-12.

All the photocatalysts were irradiated by the blue LED lamp (1 W, 445 nm) in the presence of TEOA, which acted as an external electron donor [8]. The characteristic absorption peaks of viologen radical cation, MV$^{2+}$ at 399 and 603 nm were observed following 5 min of irradiation [Fig. 4(d)]. In the cases of pristine ZIF-11 and ZIF-12 pellets, MV$^{2+}$ did not form despite irradiation with 450-nm light for 1 h using LED lamps. This indicated that the pristine ZIF-11 or ZIF-12, which are the host materials, did not exhibit photocatalytic activity. The formation of MV$^{2+}$ in these solutions is associated with a change in color...
from colorless to green. Upon irradiating the Ru(bpy)$_3$$^2+$@ZIF-11 pellet, the solution turned blue, and the color intensified with increasing irradiation time. The UV–vis spectrum of the deep blue solution appeared the characteristic peaks at 608 nm corresponding to MV$^•+$, whose intensity gradually increased with irradiation time. The profile of the yield with respect to reaction time is shown in Fig. 4(e).

The photocatalytic performance of ZIF-12, containing Co$^{2+}$ as cocatalysts, at the reduction of MV$^2+$ was evaluated in a visible-light-driven catalytic system under identical photocatalytic conditions. As seen in Fig. 4(c), Ru(bpy)$_3$$^2+$@ZIF-12 achieved superior photocatalytic reduction of MV$^2+$ than Ru(bpy)$_3$$^2+$@ZIF-11 did, showing an almost linear increase with irradiation time. This indicates that ZIF-12 is an effective host material for efficient electron transfer from the excited [Ru(bpy)$_3$$^2+$] moiety to the ZIF framework and also possessed excellent photocatalytic stability. These results suggest that ZIF-11 and ZIF-12 can act as encapsulating hosts for ruthenium-based photosensitizers. These findings may open up potential opportunities for developing photocatalytic systems by capturing various photocatalytic compounds inside porous ZIF materials.

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