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Photocatalytic Conversion of Carbon Dioxide Using Zn–Cu–Ga Layered Double Hydroxides Assembled with Cu Phthalocyanine: Cu in Contact with Gaseous Reactant is Needed for Methanol Generation

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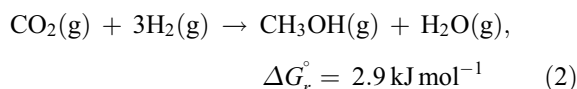
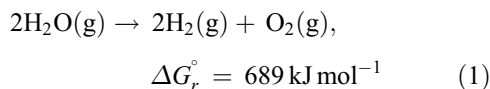
Abstract — Photocatalytic conversion of CO₂ into fuels is an attractive option in terms of both reducing the increased concentration of atmospheric CO₂ as well as generating renewable hydrocarbon fuels. It is necessary to investigate good catalysts for CO₂ conversion and to clarify the mechanism irradiated by natural light. Layered Double Hydroxides (LDH) have been attracting attention for CO₂ photoreduction with the expectation of sorption capacity for CO₂ in the layered space and tunable semiconductor properties as a result of the choice of metal cations. This study first clarifies the effects of Cu doping to LDH comprising Zn and Al or Ga. Cu could be incorporated in the cationic layers of LDH as divalent metal cations and/or interlayer anions as Cu(OH)₄²⁻. The formation rates of methanol and CO were optimized for [Zn_{1.5}Cu_{1.5}Ga(OH)₈]⁺₂Cu(OH)₄²⁻·mH₂O at a total rate of 560 nmol h⁻¹ g_{cat}⁻¹ irradiated by UV-visible light. Cu phthalocyanine tetrasulfonate hydrate (CuPcTs⁴⁻) and silver were effective as promoters of LDH for CO₂ photoreduction. Especially, the total formation rate using CuPcTs-[Zn₃Ga(OH)₈]⁺₂CO₃²⁻·mH₂O irradiated by visible light was 73% of that irradiated by UV-visible light. The promotion was based on HOMO-LUMO excitation of CuPcTs⁴⁻ by visible light. The LUMO was distributed on N atoms of pyrrole rings bound to central Cu²⁺ ions. The photogenerated electrons diffused to the Cu site would photoreduce CO₂ progressively in a similar way to inlayer and interlayer Cu sites in the LDH in this study.

Résumé — Conversion photocatalytique du dioxyde de carbone par des hydroxydes doubles lamellaires de Zn–Cu–Ga promus par la phtalocyanine de Cu : nécessité du contact entre le Cu et le réactif gazeux pour la synthèse du méthanol — La conversion photocatalytique de CO₂ est une option attractive pour limiter la concentration du CO₂ atmosphérique quand elle a pour objectif la production de produits hydrocarbonés utilisés comme carburants renouvelables. Néanmoins, des études sont encore nécessaires pour étudier les catalyseurs de conversion de CO₂ et clarifier les mécanismes réactionnels. Des Hydroxydes Doubles Lamellaires (HDL) sont des catalyseurs intéressants pour la photoréduction de CO₂ et l'on s'attend à obtenir une capacité d'adsorption du

CO₂ dans l'espace interlamellaire et des propriétés semi-conductrices adaptables par le choix des cations métalliques. La présente étude démontre tout d'abord les effets du dopage du Cu dans les HDL comprenant du Zn et de l'Al ou du Ga. Le cuivre pourrait être incorporé dans les couches cationiques des HDL sous forme de cations métalliques divalents et/ou d'anions inter-feuillets sous forme de Cu(OH)₄²⁻. Les taux de formation du méthanol et du CO ont été optimum pour le [Zn_{1.5}Cu_{1.5}Ga(OH)₈]⁺₂Cu(OH)₄²⁻·mH₂O correspondant à une vitesse totale de 560 nmol h⁻¹ g_{cat}⁻¹, sous irradiation UV visible. Le tétrasulfonate-hydrate de phthalocyanine de Cu (CuPcTs⁴⁻) et l'argent se sont avérés être des promoteurs efficaces de HDL pour la photoréduction du CO₂. En particulier, le taux de formation total en utilisant du CuPcTs-[Zn₃Ga(OH)₈]⁺₂CO₃²⁻·mH₂O irradié par la lumière visible représentait 73% de celui irradié par de la lumière UV visible. La promotion a été attribuée à une excitation HOMO–LUMO du CuPcTs⁴⁻ par la lumière visible. Le LUMO répartie sur l'atome d'azote des cycles des pyrroles lié à l'ion central Cu²⁺. Les électrons photogénérés diffusés sur le site de Cu photoréduiraient le CO₂ sur les sites cationiques (dans les couches) ou anioniques (interfeuillets) des HDL.

INTRODUCTION

Photocatalytic conversion of CO₂ into fuels has emerged as an attractive option, in terms of both reducing the increased concentration of atmospheric CO₂ as well as generating renewable hydrocarbon fuels that can be directly supplied to our present energy infrastructure (Costentin *et al.*, 2013; Corma and García, 2013; Genevese *et al.*, 2013; Habisreutinger *et al.*, 2013; Indrakanti *et al.*, 2009; Izumi, 2013; Kubacka *et al.*, 2012; Lewis and Nocera, 2006; Lv *et al.*, 2012; Roy *et al.*, 2010). The photocatalytic conversion of CO₂ involves two reaction steps:



It is important to investigate good catalysts for CO₂ conversion into fuels using hydrogen as a reductant (Eq. 2), which is potentially obtained from photocatalytic water splitting (Eq. 1) (Izumi, 2013; Ahmed *et al.*, 2011).

In this study, catalysts for converting CO₂ into methanol using hydrogen and UV–visible light were investigated. Layered Double Hydroxides (LDH) [M^{II}_{1-x}M^{III}_x(OH)₂]^{x+}X²⁻·mH₂O (M^{II} = Zn, Cu; M^{III} = Al, Ga; X = CO₃, Cu(OH)₄; m~1/2) were chosen with the expectation of:

- sorption capacity for CO₂ in the layered space,
- tunable semiconductor properties as a result of the choice of metal cations

(Ahmed *et al.*, 2013; Cavani *et al.*, 1991; Fan *et al.*, 2014; Li *et al.*, 2014; Sideris *et al.*, 2008; Zümreoglu-Karan and Ay, 2012).

Furthermore, to utilize visible light as the major part of the solar spectrum, dyes/nanoparticles were mixed with the LDH. Especially, the effects of Cu phthalocyanine tetra-sulfonate hydrate (CuPcTs⁴⁻) combined with LDH were studied.

1 EXPERIMENTAL SECTION

A LDH compound of [Zn₃Ga(OH)₈]⁺₂CO₃²⁻·mH₂O was synthesized using a reported procedure from metal nitrates, Na₂CO₃, and NaOH controlled at pH 8 (Ahmed *et al.*, 2011). This compound is abbreviated as Zn₃Ga|CO₃. Similarly, LDH comprising various compositions of [M^{II}₃M^{III}(OH)₈]⁺₂X²⁻·mH₂O (X = CO₃, Cu(OH)₄) were synthesized from nitrates of Zn, Cu, Al and Ga, and sodium carbonate/ammonium tetrachlorocuprate dihydrate at pH 8 (Ahmed *et al.*, 2012). The formula is abbreviated as M^{II}₃M^{III}|X.

Na⁺₄CuPcTs⁴⁻ was purchased from Aldrich (purity >85%) and used without further purification. For the ion exchange method, we followed the procedure presented in reference (Parida *et al.*, 2007). Firstly, 0.50 g of Zn₃Ga|CO₃ powder was immersed in an aqueous solution of Na⁺₄CuPcTs⁴⁻ (0.60 mM, 25 mL) in a flask and magnetically stirred at 900 rotations per minute (rpm) for 24 h. The blue precipitates that were obtained were filtered using a polytetrafluoroethylene-based membrane filter (Omnipore JGWP04700, Millipore) with a pore size of 0.2 μm and washed well with deionized water (<0.06 μS cm⁻¹; total 250 mL). The precipitates that were obtained were dried under vacuum at 290 K for 24 h. The blue sample was denoted as CuPcTs-Zn₃Ga|CO₃. The loading of Cu was 0.19 wt%.

~~Zn–Cu–Ga Layered Double Hydroxides Assembled with Cu Phthalocyanine: Cu in Contact with Gaseous Reactant is Needed for Methanol Generation~~
 Anion exchange of Zn₃Ga|NO₃ with Na₄CuPcTs⁴⁻ was performed following the procedure in the literature (Abellan *et al.*, 2012). All of the procedure until the drying under vacuum was conducted under an argon atmosphere. 0.30 g of Zn₃Ga|NO₃ powder was placed in a flask and an aqueous solution of Na₄CuPcTs⁴⁻ (5.0 mM, 200 mL) was slowly added and magnetically stirred at 900 rpm. Then, 30 mL of ethylene glycol and 30 mL of ethanol were added to the flask. The mixture was agitated by ultrasound (430 W, 38 kHz) for 10 min and then was magnetically stirred at 900 rpm for 3 days.

The precipitates that were obtained were filtered using an Omnipore JGWP04700 filter and washed well with ethanol (total 250 mL) and deionized water (total 250 mL). The precipitates that were obtained were dried at 290 K for 24 h under vacuum. The sample was denoted as Zn₃Ga|CuPcTs.

Ag nitrate was impregnated from aqueous solution with Zn₃Ga|CO₃. The loading of Ag was 0.36 wt% (Kawamura *et al.*, 2015). The sample was denoted as Ag-Zn₃Ga|CO₃. Separately, the assembly of Au nanoparticles with Zn₃Ga|CO₃ was obtained using the structural reconstruction of LDH in the aqueous solutions containing Au³⁺ (Carja *et al.*, 2013). Hence, 1.20 g Zn₃Ga|CO₃ powder was calcined in an oven at 773 K for 8 h. Freshly calcined Zn₃Ga|CO₃ powder was directly added to 200 mL aqueous solution of Au(III) acetate (>99.9%, Alfa Aesar; 0.10 g) stirring at a rate of 900 rpm. The pH of the solution was adjusted to 8.0 by the addition of NaOH aqueous solution (0.10 M). The reaction mixture was stirred at the rate of 900 rpm and 290 K for 20 min and at the rate of 150 rpm and 313 K for 5 h. Then, the precipitate was centrifuged at the rate of 10 000 rpm and dried in an oven at 353 K for 1 h. The color of the catalyst obtained was light purple. The sample was denoted as Au-Zn₃Ga|CO₃.

Optical spectroscopic measurements were performed using a UV–visible spectrophotometer (model V-650, JASCO) using D₂ and halogen lamps for wavelengths between 200 and 340 nm and 340 and 800 nm, respectively. An integrating sphere (model ISV-469, JASCO) was used for the Diffuse Reflectance (DR) measurements. The samples were set in contact with the quartz window glass in gas-tight DR cells. Measurements were performed at 290 K within the wavelength range 200–800 nm using 70 mg of sample. DR spectra were converted to absorption spectra on the basis of the Kubelka–Munk equation (Ahmed *et al.*, 2011, 2012). The band-gap (E_g) value was evaluated on the basis of either simple extrapolation of the absorption edge or the fit to the Davis–Mott equation:

$$\alpha \times hv \propto (hv - E_g)^n \quad (3)$$

in which α , h , and v are the absorption coefficient, Planck's constant and the frequency of light, respectively, and n is

1/2, 5/2, 2 and 3 for allowed direct, forbidden direct, allowed indirect and forbidden indirect electronic transitions, respectively (Wooten, 1972).

The Brunauer–Emmett–Teller surface area (S_{BET}) was calculated on the basis of eight-point measurements between 10 and 46 kPa in the N₂ adsorption isotherm at 77 K. The X-Ray Diffraction (XRD) pattern was observed using a D8 ADVANCE diffractometer (Bruker) at the Center for Analytical Instrumentation, Chiba University, at a Bragg angle of $2\theta_B = 3\text{--}60^\circ$ with a scan step of 0.01° and a scan rate of 5 s per step. The measurements were performed at 40 kV and 40 mA using Cu K α emission and a nickel filter.

Cu K-edge X-ray Absorption Fine Structure (XAFS) spectra were measured at 290 K in transmission mode in the Photon Factory Advanced Ring at the High Energy Accelerator Research Organization (Tsukuba) on beamline NW10A. The storage ring energy was 6.5 GeV and the ring current was 46.6–36.1 mA. A Si (311) double-crystal monochromator and platinum-coated focusing cylindrical mirror were inserted into the X-ray beam path. The X-ray intensity was maintained at 65% of the maximum flux using a piezo translator set to the crystal. The slit opening size was 1 mm (vertical) \times 2 mm (horizontal) in front of the ionization chamber. Part of the XAFS measurements were performed for a sample in a reactor equipped with polyethylene naphthalate windows (Q51-16, Teijin) irradiated by a xenon arc lamp (Morikawa *et al.*, 2014a; Izumi *et al.*, 2007). The Cu K-edge absorption energy was calibrated to 8 980.3 eV for the spectrum of Cu metal foil (Bearden, 1967).

The XAFS data were analyzed using an XDAP (X-ray absorption fine structure Data Analysis Program) package (Vaarkamp *et al.*, 2006). The pre-edge background was approximated by a modified Victoreen function $C_2/E^2 + C_1/E + C_0$. The background of the post-edge oscillation was approximated by a smoothing spline function and calculated by an equation for the number of data points, where k is the wavenumber of photoelectrons:

$$\sum_{i=1}^{\text{Data Points}} \frac{(\mu x_i - BG_i)^2}{\exp(-0.075k_i^2)} \leq \text{smoothing factor} \quad (4)$$

Multiple-shell curve-fit analyses were performed for the Fourier-filtered k^3 -weighted Extended X-ray Absorption Fine Structure (EXAFS) data in k - and R -space using empirical amplitude extracted from the EXAFS data for Na₄CuPcTs⁴⁻ (Izumi *et al.*, 2005, 2009). The interatomic distance (R) and its associated coordination number (N) for the Cu–N pair were set to 0.1950 nm with a N value of 4 (Carrera *et al.*, 2004). The many-body reduction factor S_0^2 was assumed to be equal for both the sample and the reference.

As-synthesized and preheated samples of the LDH CuPcTs–Zn₃Ga|CO₃, Ag–Zn₃Ga|CO₃ and Au–Zn₃Ga|CO₃

were tested for the photocatalytic conversion of CO_2 (Kawamura *et al.*, 2015). The tests were conducted in a closed circulating system (171 mL) equipped with a photoreaction quartz cell that had a flat bottom (23.8 cm^2). 100 mg of the LDH catalyst was uniformly spread in the photoreaction cell and was evacuated by rotary and diffusion pumps (10^{-6} Pa) at 290 K for 2 h until the desorbed gas was detected by an online Gas Chromatograph (GC). 2.3 kPa of CO_2 (0.177 mmol) and 21.7 kPa of H_2 (1.67 mmol) were introduced to both intact and pretreated LDH photocatalysts and were allowed to circulate for 30 min in contact with the catalyst to attain sorption equilibrium before irradiation.

The photocatalyst was then irradiated with UV–visible light from the 500-W xenon arc lamp (Ushio, model UI-502Q) upward through the flat bottom of the quartz reactor for 5 h. The distance between the bottom of the reactor and the lamp house exit window was set to 20 mm. The light intensity was 42 mW cm^{-2} at the center of the sample cell and 28 mW cm^{-2} at the periphery of the bottom plate of the sample cell. The temperature was within the range 305–313 K at the catalyst position during the illumination for 5 h. As a comparison, the photocatalyst was irradiated with visible light using one of the following UV-cut filters between the light exit of UI-502Q and the photocatalyst. Photocatalytic CO_2 reduction tests were performed systematically using L42, Y52, O58, R62, R66 and W-R715 sharp cut filters (Hoya) between the irradiation light exit and photoreactor. The thickness was 2.5 mm except for W-R715 (2.0 mm). These filters pass the light of wavelengths greater than 420, 520, 580, 620, 660 and 715 nm, respectively. The transmittance of nonfiltered light was more than 88% for L42, Y52, O58, R62 and R66, and almost 100% for W-R715 (manufacturer's web information¹). Products and reactants were analyzed using packed columns of a 13X-S molecular sieve and PolyEthylene Glycol (PEG-6000) supported on Flusin P (GL Sciences) set in the online GC equipped with a thermal conductivity detector (Shimadzu, model GC-8A).

The molecular orbitals for CuPcTs^{4-} were calculated using Gaussian 09 (Gaussian, Inc., Wallingford, Connecticut, USA) employing a polarized basis set of 6-31G(d) and in density functional theory mode to calculate the electron correlation using the functional B3LYP (Rauf *et al.*, 2012).

2 RESULTS

2.1 Characterization

The interlayer interval and S_{BET} of the LDH synthesized were between 0.751–0.792 nm and $35\text{--}70 \text{ m}^2 \text{ g}^{-1}$,

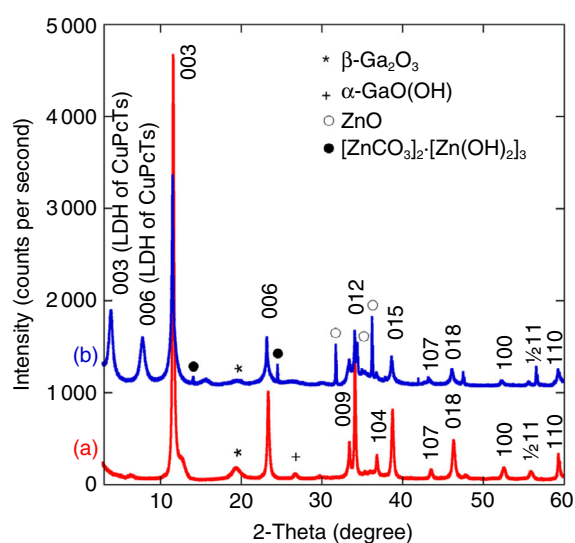


Figure 1

XRD patterns for a) $\text{CuPcTs-Zn}_3\text{GaCO}_3$ and b) $\text{Zn}_3\text{GaCuPcTs}$.

respectively, except for $\text{Zn}_3\text{GaCuPcTs}$. The metal cations existed in nearly identical octahedral MO_6 coordination environments in cationic sheets based on the similarity of the Zn K, Cu K and Ga K-edge X-ray Absorption Near-Edge Structure (XANES) (Ahmed *et al.*, 2011, 2012).

The layered structure of the LDH synthesized in this study was confirmed by XRD. The XRD pattern for $\text{CuPcTs-Zn}_3\text{GaCO}_3$ is depicted in Figure 1a. The diffraction peaks at $2\theta_{\text{B}} = 11.7^\circ, 23.4^\circ, 33.5^\circ, 34.2^\circ, 36.9^\circ, 38.8^\circ, 43.6^\circ, 46.4^\circ, 52.6^\circ, 56.9^\circ$ and 59.4° were assigned to (003), (006), (009), (012), (104), (015), (107), (018), (100), $(\frac{1}{2}11)$ $[(=01\bar{1}1)]$ and (110) diffraction, respectively, for the regular layered structure of the LDH. The interlayer interval value was evaluated at 0.755 nm on the basis of the (003) diffraction angle and changed negligibly as compared with Zn_3GaCO_3 (0.751 nm; Ahmed *et al.*, 2011).

The pattern is compared with that for $\text{Zn}_3\text{GaCuPcTs}$ (Fig. 1b-line). Two peaks at $2\theta_{\text{B}} = 4.04^\circ$ and 7.91° appeared assignable to (003) and (006) diffraction of the LDH with the interlayer anions of CuPcTs^{4-} (Abellán *et al.*, 2012). The interlayer interval value was evaluated at 2.18 nm on the basis of the (003) diffraction angle due to the intercalation of larger CuPcTs^{4-} anions. The diffraction peaks at $2\theta_{\text{B}} = 11.6^\circ, 23.3^\circ, 33.5^\circ, 34.2^\circ, 36.3^\circ, 38.7^\circ, 43.2^\circ, 46.2^\circ, 52.3^\circ, 56.6^\circ$ and 59.3° also appeared, and suggested the by-product phase of Zn_3GaCO_3 . The interlayer interval value was evaluated at 0.760 nm on the basis of the (003) diffraction angle for the by-product phase.

In the pattern for both samples, a very small amount of impurity peaks was observed at $19.5\text{--}19.6^\circ$ and 26.8° owing

¹ Hoya, web information of sharp cut filters: http://www.hoyaoptics.com/color_filter/sharp_cut.htm, <http://buyersguide.pennwell.com/Shared/User/pr9f6c58fba904eefa88c895cd0f5f336.pdf>.

TABLE 1
The band-gap values and the type of electronic transition based on UV–visible spectra for Zn–Cu–Ga LDH

Photocatalyst	Band gap (eV)	e^- transition
$\text{Zn}_3\text{Ga} \text{CO}_3$	5.6	Direct
$\text{Zn}_{1.5}\text{Cu}_{1.5}\text{Ga} \text{CO}_3$	3.5	Forbidden direct
$\text{Zn}_3\text{Al} \text{CO}_3$	5.7	Direct
$\text{Zn}_{1.5}\text{Cu}_{1.5}\text{Al} \text{CO}_3$	4.1	Direct
$\text{Zn}_3\text{Ga} \text{Cu}(\text{OH})_4$	4.2 (impurity phase: 3.2)	Direct
$\text{Zn}_{1.5}\text{Cu}_{1.5}\text{Ga} \text{Cu}(\text{OH})_4$	3.0	Direct

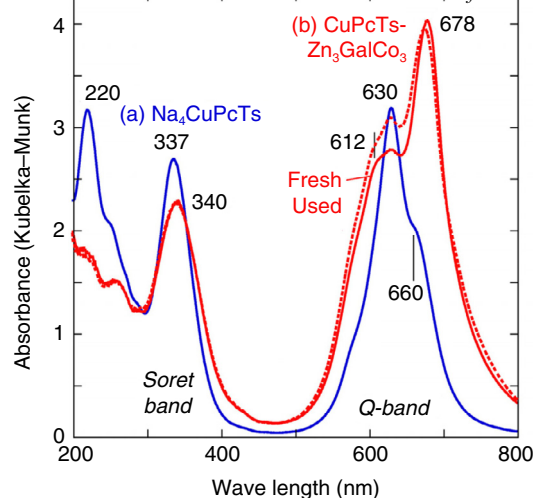


Figure 2

Diffuse-reflectance UV–visible absorption spectra for aqueous solution of a) $\text{Na}_4\text{CuPcTs}^{4-}$ ($6.0 \mu\text{mol L}^{-1}$) and b) $\text{CuPcTs-Zn}_3\text{Ga}|\text{CO}_3$. Solid line: fresh sample and dotted line: sample used after the photocatalytic test for 5 h.

to $\beta\text{-Ga}_2\text{O}_3$ and $\alpha\text{-GaO}(\text{OH})$, respectively (Fig. 1). In the pattern for $\text{Zn}_3\text{Ga}|\text{CuPcTs}$, a small amount of impurity peaks at 31.9° , 34.5° and 36.3° owing to ZnO and those at 14.2° and 24.6° owing to $[\text{ZnCO}_3]_2 \cdot [\text{Zn}(\text{OH})_2]_3$ also appeared (b-line).

The E_g values were evaluated by the extrapolation of the absorption edge in the UV–visible spectra. The values given were within the range 5.6–3.0 eV for $\text{Zn}_3\text{Ga}|\text{CO}_3$, $\text{Zn}_{1.5}\text{Cu}_{1.5}\text{Ga}|\text{CO}_3$, $\text{Zn}_3\text{Al}|\text{CO}_3$, $\text{Zn}_{1.5}\text{Cu}_{1.5}\text{Al}|\text{CO}_3$, $\text{Zn}_3\text{Ga}|\text{Cu}(\text{OH})_4$ and $\text{Zn}_{1.5}\text{Cu}_{1.5}\text{Ga}|\text{Cu}(\text{OH})_4$ (Tab. 1).

Besides the absorption edge for the LDH, an intense absorption peak appeared at 678 nm for $\text{CuPcTs-Zn}_3\text{Ga}|\text{CO}_3$ (Fig. 2b-line, solid line). The UV–visible spectrum for $\text{CuPcTs-Zn}_3\text{Ga}|\text{CO}_3$ basically resembled that for aqueous solution of $\text{Na}_4\text{CuPcTs}^{4-}$ (Fig. 2a-line); however, the peak intensity ratio in the range 600–700 nm was different: 678 nm (s), 630 nm (sh) and 612 nm (sh) for $\text{CuPcTs-Zn}_3\text{Ga}|\text{CO}_3$ versus 630 nm (s) and 660 nm (sh) for aqueous solution of $\text{Na}_4\text{CuPcTs}^{4-}$. As the peaks at 678–660 nm or 630 nm would be assigned to HOMO (a_{1u})–LUMO (e_g) electronic transition (Q-band, Fig. 3), the HOMO and/or LUMO of CuPcTs^{4-} were significantly perturbed by the interaction with the $\text{Zn}_3\text{Ga}|\text{CO}_3$ surface.

As compared with the Q-band, the peaks at 337–340 nm were assigned to transition from a_{2u} to LUMO (e_g) (Soret band). The peak at 220 nm was only observed for aqueous solution of $\text{Na}_4\text{CuPcTs}^{4-}$ (Fig. 2a-line). This peak would be a transition from a slightly deeper level than a_{2u} to LUMO (e_g) or from a_{2u} to a slightly shallower level than LUMO (e_g) (Marom et al., 2008).

The UV–visible spectrum for $\text{CuPcTs-Zn}_3\text{Ga}|\text{CO}_3$ used for photocatalytic tests under $\text{CO}_2 + \text{H}_2$ for 5 h was also measured (Fig. 2b-line, dotted line). The spectrum was essentially identical to that for the fresh sample (solid line), indicating the stability of CuPcTs^{4-} dispersed over $\text{Zn}_3\text{Ga}|\text{CO}_3$ under the photocatalytic reaction conditions.

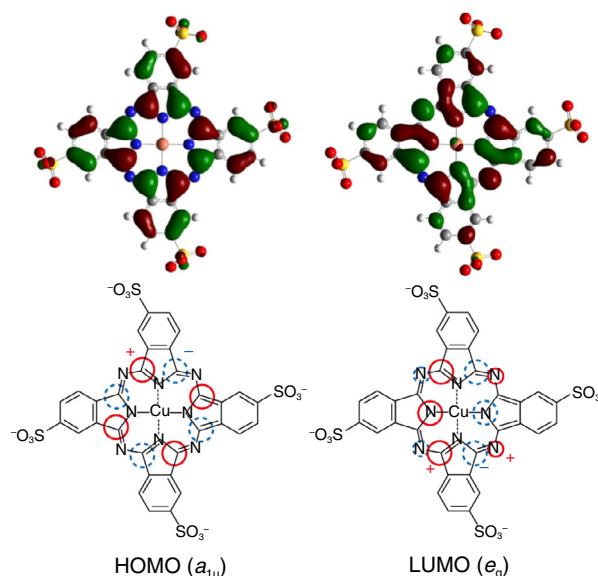


Figure 3

HOMO and LUMO for $\text{Na}_4\text{CuPcTs}^{4-}$ calculated using Gaussian 09.

$\text{Ag-Zn}_3\text{Ga}|\text{CO}_3$ and $\text{Au-Zn}_3\text{Ga}|\text{CO}_3$ exhibited a major absorption peak at 411 and 555 nm, respectively (not shown). These peaks are ascribed to Surface Plasmonic Resonance (SPR) of Ag and Au metallic nanoparticles.

The XANES spectra for $\text{Na}_4\text{CuPcTs}^{4-}$ and $\text{CuPcTs-Zn}_3\text{Ga}|\text{CO}_3$ are shown in Figure 4. The whole spectrum pattern changed negligibly by the dispersion of CuPcTs^{4-} over the $\text{Zn}_3\text{Ga}|\text{CO}_3$ surface as compared with

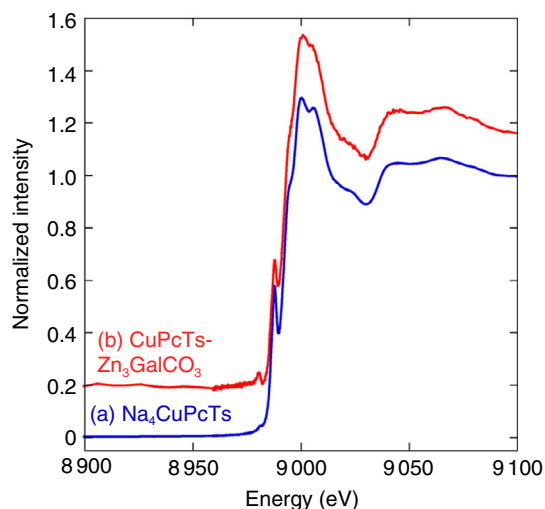


Figure 4

Normalized Cu K-edge XANES spectra for a) $\text{Na}_4\text{CuPcTs}^{4-}$ diluted by boron nitride and b) $\text{CuPcTs-Zn}_3\text{Ga}|\text{CO}_3$.

$\text{Na}_4\text{CuPcTs}^{4-}$ crystallines, suggesting that the framework structure of CuPcTs^{4-} was retained upon the dispersion over the $\text{Zn}_3\text{Ga}|\text{CO}_3$ surface. In contrast, a sharp shoulder peak at 8 988 eV became relatively weaker upon the dispersion over the LDH surface. This may be related to the perturbation of LUMO by the interaction with the LDH surface based on UV–visible spectrum change (Fig. 2).

The 1s-3d electronic transition peak appeared at 8 982 eV for both $\text{Na}_4\text{CuPcTs}^{4-}$ and $\text{CuPcTs-Zn}_3\text{Ga}|\text{CO}_3$ (Fig. 5-I). The transition is allowed for the Cu^{II} state of the $3d^9$ configuration, whereas the peak disappeared for the Cu^{I} state of the $3d^{10}$ configuration (Morikawa *et al.*, 2014a). Utilizing this difference, the reduction of Cu^{II} sites in $\text{Na}_4\text{CuPcTs}^{4-}$ and $\text{CuPcTs-Zn}_3\text{Ga}|\text{CO}_3$ was monitored irradiated by UV–visible light.

The Cu amount in $\text{Na}_4\text{CuPcTs}^{4-}$ charged was 118 μmol . The decreasing rate of the 1s-3d peak irradiated by UV–visible light for 64 min was $18.0\% \text{ h}^{-1}$ or $21.2 \mu\text{mol h}^{-1}$. In contrast, the Cu amount in $\text{CuPcTs-Zn}_3\text{Ga}|\text{CO}_3$ charged was 13.5 μmol . The decreasing rate of the 1s-3d peak irradiated by UV–visible light for 180 min was $20.2\% \text{ h}^{-1}$ or $2.72 \mu\text{mol h}^{-1}$ (Fig. 5-II). The photoreduction to the $\text{Cu}(\text{I})$ state was slightly faster for $\text{CuPcTs-Zn}_3\text{Ga}|\text{CO}_3$ than for $\text{Na}_4\text{CuPcTs}^{4-}$; however, exact comparison of the diffusion rates of photogenerated electrons to the $\text{Cu}(\text{II})$ site (Morikawa *et al.*, 2014a) was difficult in this case

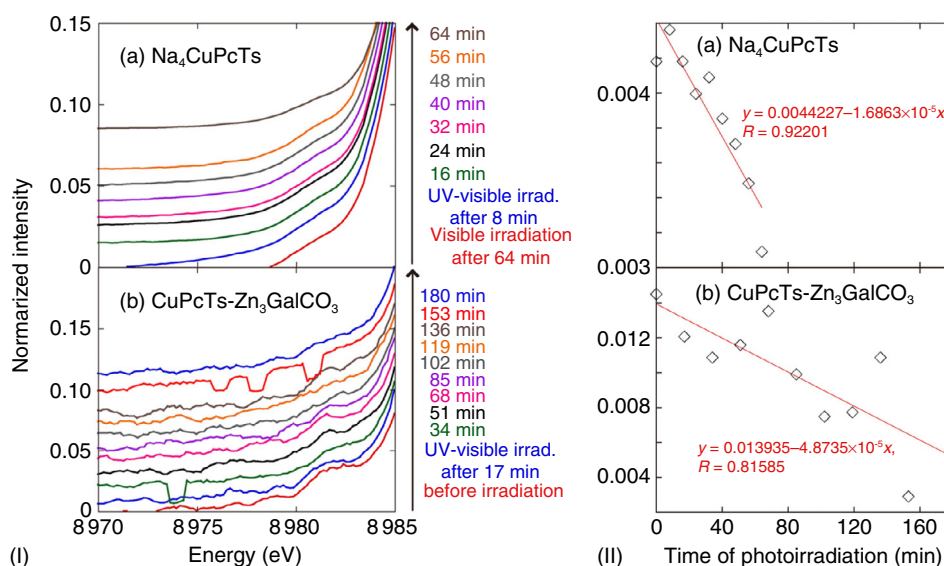


Figure 5

I) Expanded view of the 1s-3d pre-edge peak region of normalized Cu K-edge XANES spectra of a) $\text{Na}_4\text{CuPcTs}^{4-}$ under vacuum and b) $\text{CuPcTs-Zn}_3\text{Ga}|\text{CO}_3$ under CO_2 (2.3 kPa) + H_2 (21.7 kPa) and UV–visible light irradiation. II) Time course of the 1s-3d peak intensity for the two samples. The amount of $\text{Na}_4\text{CuPcTs}^{4-}$ and $\text{CuPcTs-Zn}_3\text{Ga}|\text{CO}_3$ charged in the photoreaction cell was 116 and 401 mg, respectively.

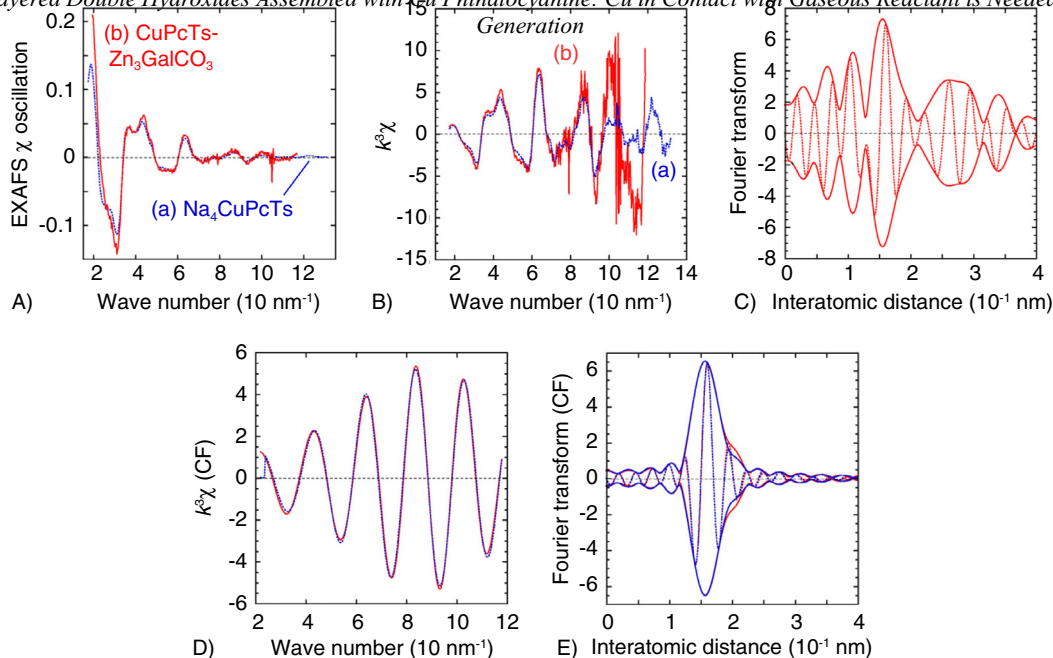


Figure 6

A) Cu K-edge EXAFS χ oscillation and B) k^3 -weighted EXAFS χ oscillation for $\text{Na}_4\text{CuPcTs}^{4-}$ diluted by boron nitride (a) and $\text{CuPcTs-Zn}_3\text{GaCO}_3$ (b), C) its associated Fourier transform, and D, E) best-fit results in k -space D) and R -space E) for $\text{CuPcTs-Zn}_3\text{GaCO}_3$. Solid line: magnitude and dotted line: imaginary part C, E). Red (thick) line: experimental and blue (thin) line: fit D, E).

due to the difference in the shape and light absorbance of the samples: dense crystallines of $\text{Na}_4\text{CuPcTs}^{4-}$ versus fine powder of $\text{CuPcTs-Zn}_3\text{GaCO}_3$. At least, as the UV–visible light absorbance was apparently higher for $\text{Na}_4\text{CuPcTs}^{4-}$, the possibility of faster electron accumulation for $\text{CuPcTs-Zn}_3\text{GaCO}_3$ than $\text{Na}_4\text{CuPcTs}^{4-}$ is high due to the injection of excited electrons in Zn_3GaCO_3 irradiated by UV light into CuPcTs^{4-} at the surface.

The EXAFS χ oscillation changed negligibly when $\text{Na}_4\text{CuPcTs}^{4-}$ was dispersed over the Zn_3GaCO_3 surface (Fig. 6A). This fact supported the retention of the CuPcTs^{4-} framework over that of the Zn_3GaCO_3 suggested by XANES. The curve-fit results for the Cu–N interatomic pair provided a distance of 0.198 nm (fit error ± 0.011 nm) with a N value of 3.3 (fit error ± 1.3) (Fig. 6D, E).

2.2 Photocatalytic Tests under $\text{CO}_2 + \text{H}_2$

In the photocatalytic reaction tests under $\text{CO}_2 + \text{H}_2$ irradiated by UV–visible light, Zn_3GaCO_3 produced CO and methanol (Tab. 2A, entry a). Using $\text{Zn}_{1.5}\text{Cu}_{1.5}\text{GaCO}_3$, the methanol formation rate increased by a factor of 3.3 (Tab. 2A entry g). Zn_3AlCO_3 was more active than Zn_3GaCO_3 , but the

major product was CO (entry h). When $\text{Zn}_{1.5}\text{Cu}_{1.5}\text{AlCO}_3$ was compared with Zn_3AlCO_3 , the methanol formation rate was promoted by a factor of 3.3 (Tab. 2b entry i) similarly to the Cu substitution into Zn_3GaCO_3 . The methanol formation rate using $\text{Zn}_3\text{GaCu(OH)}_4$ was enhanced by a factor of 5.9 compared with Zn_3GaCO_3 (Tab. 2A entries a, j). The methanol selectivity was nearly the same as that obtained with $\text{Zn}_{1.5}\text{Cu}_{1.5}\text{GaCO}_3$ (71–68 mol%). Using $\text{Zn}_{1.5}\text{Cu}_{1.5}\text{GaCu(OH)}_4$, the methanol formation rate and selectivity were further improved to $0.49 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$ and 88 mol% (Tab. 2A entry k).

The results in Table 2 were independently reported in this study and references (Ahmed *et al.*, 2011, 2012; Kawamura *et al.*, 2015). However, the rates and selectivity are comparable because common reaction apparatus connected to common online GC were used in these studies. The reproducibility of rates was checked for Zn_3GaCO_3 in this study and references (Ahmed *et al.*, 2011, 2012; Kawamura *et al.*, 2015), and the variation of formation rates of methanol and CO was always within 5%.

Furthermore, we reported control reaction tests in darkness, in the absence of a photocatalyst, and in the absence of CO_2 . No products were found in these control tests except

TABLE 2
Photocatalytic rates of CO₂ reduction with H₂ using LDH^(a)

Entry	Photocatalyst	Formation rate (nmol ⁻¹ g _{cat})			Selectivity to CH ₃ OH (mol%)	Reference
		CH ₃ OH	CO	Σ		
A) Irradiated by UV–visible light						
a	Zn ₃ Ga CO ₃	51	80	130	39	Ahmed <i>et al.</i> (2011)
b	CuPcTs–Zn ₃ Ga CO ₃	96	106	202	48	This work
b'	CuPcTs & Zn ₃ Ga CO ₃ ^(b)	28	41	69	41	This work
c	Zn ₃ Ga CuPcTs	<4	69	69	<5	This work
d	Na ₄ CuPcTs ^{4–}	<4	38	38	<9.5	This work
e	Ag–Zn ₃ Ga CO ₃	118	102	220	54	Kawamura <i>et al.</i> (2015)
f	Au–Zn ₃ Ga CO ₃ ^(c)	30	201	231	13	Kawamura <i>et al.</i> (2015)
g	Zn _{1.5} Cu _{1.5} Ga CO ₃	170	79	250	68	Ahmed <i>et al.</i> (2011)
h	Zn ₃ Al CO ₃	39	620	660	5.9	Ahmed <i>et al.</i> (2011)
i	Zn _{1.5} Cu _{1.5} Al CO ₃	130	370	500	26	Ahmed <i>et al.</i> (2011)
j	Zn ₃ Ga Cu(OH) ₄	300	130	430	71	Ahmed <i>et al.</i> (2012)
k	Zn _{1.5} Cu _{1.5} Ga Cu(OH) ₄	490	70	560	88	Ahmed <i>et al.</i> (2012)
B) Irradiated by visible light (λ > 420 nm)						
a	Zn ₃ Ga CO ₃	<4	<8	<12	<33	Ahmed <i>et al.</i> (2011)
b	CuPcTs–Zn ₃ Ga CO ₃	75	74	148	51	This work
c	Zn ₃ Ga CuPcTs	<4	33	33	<11	This work
d	Ag–Zn ₃ Ga CO ₃	36	88	124	29	Kawamura <i>et al.</i> (2015)
e	Au–Zn ₃ Ga CO ₃ ^(c)	<4	<8	<12	<33	Kawamura <i>et al.</i> (2015)

^a In CO₂ (2.3 kPa) + H₂ (21.7 kPa). The catalyst amount was 100 mg.

^b Physical mixture with the weight ratio of 3:97.

^c Preheated at 373 K for 30 min.

for water from the interlayer space of the LDH. When the reactant was switched from CO₂ to CO₂ + H₂, methanol and CO began to evolve using Zn_{1.5}Cu_{1.5}Ga|CO₃ (Ahmed *et al.*, 2011). When the Zn_{1.5}Cu_{1.5}Ga|CO₃ and Zn_{1.5}Cu_{1.5}Ga|Cu(OH)₄ photocatalysts were recycled four times (in total 20 h of reaction), the methanol and CO formation continued and the selectivity was kept at 68–57 mol% and 76–84 mol%, respectively (Ahmed *et al.*, 2011, 2013).

The addition of CuPcTs^{4–} to Zn₃Ga|CO₃ improved the total (methanol and CO) formation rates by a factor of 1.6 and the methanol selectivity increased to 48 mol% (Tab. 2A entry b; Fig. 7a-line). The formation of CO and methanol continued for more than 5 h, demonstrating the stability of dispersed CuPcTs^{4–} over the LDH irradiated by UV–visible light under CO₂ + H₂. In contrast, the performance

of Zn₃Ga|CuPcTs was lower than that of Zn₃Ga|CO₃ (Tab. 2A entry c and Fig. 7b-line). It should be noted that unsupported Na⁺₄CuPcTs^{4–} generated CO at a rate of 48% of that using Zn₃Ga|CO₃ (Tab. 2A entry d).

In a control kinetic test using the physical mixture of 3.0 wt% of Na⁺₄CuPcTs^{4–} and 97 wt% of Zn₃Ga|CO₃ LDH prepared by mixing using a mortar and pestle for 30 min, the formation rates of CO and methanol were 41 and 28 μmol h⁻¹ g_{cat}⁻¹, respectively (Tab. 2A entry b), suggesting the importance of close contact of CuPcTs^{4–} with the LDH surface for the CO₂ photoconversion using CuPcTs–Zn₃Ga|CO₃ (Fig. 7a-line).

The addition of Ag to Zn₃Ga|CO₃ similarly affected the addition of CuPcTs^{4–}. Total formation rates increased by a factor of 1.7 compared with Zn₃Ga|CO₃ and methanol

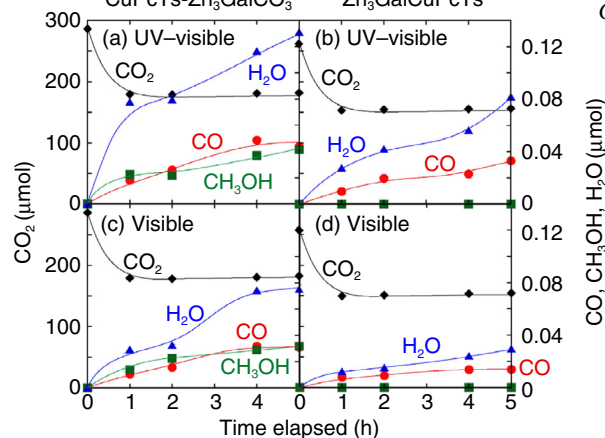


Figure 7

Time course of photocatalytic tests under CO_2 (2.3 kPa) and H_2 (21.7 kPa) using UV-visible light and a) CuPcTs- Zn_3GaCO_3 and b) $\text{Zn}_3\text{GaCuPcTs}$; and using visible light ($\lambda > 420$ nm) and c) CuPcTs- Zn_3GaCO_3 and d) $\text{Zn}_3\text{GaCuPcTs}$. CO_2 (♦; diamond), H_2O (▲; triangle), CH_3OH (■; square), and CO (●; circle).

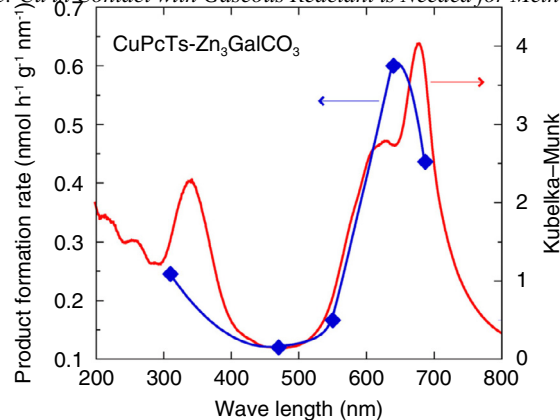


Figure 8

In-profile spectrum for CuPcTs- Zn_3GaCO_3 .

selectivity of 54 mol% (Tab. 2A entry e). The addition of Au to Zn_3GaCO_3 promoted the total formation rates by a factor of 1.8, but the methanol selectivity became only 13 mol% (Tab. 2A entry f).

Next, photocatalytic reduction tests of CO_2 by H_2 were conducted irradiated by visible light ($\lambda > 420$ nm). Although the Zn_3GaCO_3 LDH showed poor photoactivity irradiated by visible light (Tab. 2B entry a), the total formation rate using CuPcTs- Zn_3GaCO_3 irradiated by visible light was 73% of that irradiated by UV-visible light (Tab. 2B entry b). The methanol selectivity was maintained at 48–51 mol% (Fig. 7 c-line). Again, under the condition of visible light irradiation, the formation of CO and methanol continued for more than 5 h, demonstrating the stability of dispersed CuPcTs $^{4-}$ over the LDH under $\text{CO}_2 + \text{H}_2$.

The total formation rate using Ag- Zn_3GaCO_3 irradiated by visible light was 56% of that irradiated by UV-visible light (Tab. 2A entry c, Tab. 2B entry d). The selectivity to methanol decreased from 54 mol% (irradiated by UV-visible light) to 29 mol% (irradiated by visible light). Thus, Ag was less effective than CuPcTs $^{4-}$ as a promoter under the condition of visible light irradiation. In comparison with the addition of CuPcTs $^{4-}$ and Ag, Au- Zn_3GaCO_3 did not exhibit photocatalytic activity above the detection limit of GC irradiated under visible light (Tab. 2B, entry e).

The promotion effect of CuPcTs $^{4-}$ to Zn_3GaCO_3 was further investigated by plotting the in-profile (action) spectrum

of total formation rates (methanol and CO) based on the photocatalytic tests irradiated by the light of wavelengths progressively greater than 420, 520, 580, 620, 660 and 715 nm using sharp cut filters (Fig. 8). The in-profile spectrum and UV-visible absorption spectrum coincided well in the wavelength ranges 310 and 688 nm, demonstrating that the visible light absorption by CuPcTs $^{4-}$ dispersed over Zn_3GaCO_3 (Fig. 2b-line) led to electron excitation and then the reduction of CO_2 .

3 DISCUSSION

Zn_3GaCO_3 exhibited photocatalytic reduction of CO_2 by H_2 and UV-visible light at a total formation rate (methanol and CO) of $130 \text{ nmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$ (Tab. 2A, entry a). When the amount of photocatalyst varied between 25 and 100 mg, the formation rate (the unit: mol h^{-1}) was essentially proportional to the amount (Ahmed *et al.*, 2011; Yoshida *et al.*, 2012).

Copper ions were doped as a part of M^{II} cations in the cationic layer $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2]^{x+}$ of LDH and/or $\text{Cu}(\text{OH})_4^{2-}$ anions between the cationic layers. Both inlayer and interlayer Cu sites were effective for photocatalytic reduction of CO_2 (Ahmed *et al.*, 2011, 2012). As a result, the total formation rate using $\text{Zn}_{1.5}\text{Cu}_{1.5}\text{Ga}(\text{Cu}(\text{OH})_4)$ was $560 \text{ nmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$ (Tab. 2A, entry k). Copper sites were primarily active for photocatalytic reduction of CO_2 by H_2 .

The drawback of LDH comprising Cu was the limitation of the wavelength for excitation light. The estimated E_g values for the LDH used in this study were 5.6–3.0 eV (Tab. 1), indicating that only UV light was effective for CO_2 photoreduction using LDH comprising Cu. To overcome this drawback, CuPcTs $^{4-}$, Ag or Au was doped to Zn_3GaCO_3 .

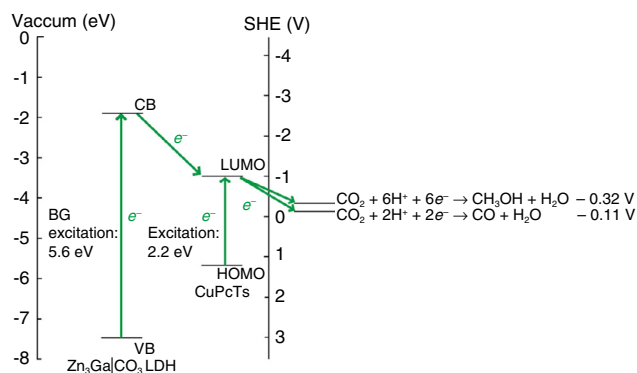


Figure 9

The energy diagram and proposed electron flows in CuPcTs-Zn₃Ga|CO₃ during photocatalytic reduction of CO₂.

CuPcTs⁴⁻, Ag or Au in CuPcTs-Zn₃Ga|CO₃, Ag-Zn₃Ga|CO₃ and Au-Zn₃Ga|CO₃ photocatalysts were effective at boosting methanol and CO formation rates by a factor of 1.6–1.8 compared with Zn₃Ga|CO₃, both irradiated by UV–visible light (Tab. 2A). The interlayer distance of the LDH changed negligibly for these photocatalysts (Fig. 1), demonstrating CuPcTs⁴⁻, Ag and Au were over the exterior surface of the LDH rather than the interlayer space (Kawamura *et al.*, 2015). Under UV–visible light, band-gap excitation of the LDH occurred by UV light (Tab. 1), while HOMO–LUMO excitation (2.2 eV, Fig. 9; Giraudeau *et al.*, 1980; Shang *et al.*, 2011) of CuPcTs⁴⁻ and SPR of Ag and Au nanoparticles occurred by visible light.

The photocatalytic effects of UV and visible light were clarified by the photocatalytic tests irradiated by visible light only (Tab. 2B), and also the in-profile spectrum of CO₂ photoreduction (Fig. 8). The formation rates of methanol and CO irradiated by visible light were 73–56% of those irradiated by UV–visible light using CuPcTs-Zn₃Ga|CO₃ and Ag-Zn₃Ga|CO₃, whereas Au-Zn₃Ga|CO₃ did not exhibit photocatalytic activity above the detection limit of GC under the irradiation of visible light. Thus, CuPcTs⁴⁻ was the best promoter for the LDH irradiated by visible light. The stability of CuPcTs⁴⁻ during photocatalytic tests was demonstrated (Fig. 2, 7a–c-line). Because the E_g value for Zn₃Ga|CO₃ was 5.6 eV (Tab. 1), the LDH did not participate in the catalysis under visible light but just dispersed CuPcTs⁴⁻ molecules on the external surface.

The energy diagram and proposed electron flow during CO₂ photoreduction using CuPcTs-Zn₃Ga|CO₃ are depicted in Figure 9. As the HOMO–LUMO gap positions between Valence Bands (VB) and Conduction Bands (CB) of Zn₃Ga|CO₃, band-gap excited electrons at CB and resultant

holes at VB transfer to LUMO and HOMO of CuPcTs⁴⁻, respectively, irradiated by UV light. In fact, photogenerated electrons diffused to the central Cu(II) site of CuPcTs⁴⁻ at the rates of 2.7–21 $\mu\text{mol h}^{-1}$ for Na⁺₄CuPcTs⁴⁻ and CuPcTs-Zn₃Ga|CO (Fig. 5). Na⁺₄CuPcTs⁴⁻ was able to photocatalyze CO₂ to CO by H₂ (Tab. 2A, entry d). When CuPcTs-Zn₃Ga|CO₃ was irradiated by visible light only, the band-gap excitation (5.6 eV) of Zn₃Ga|CO₃ did not take place and only HOMO–LUMO excitation (2.2 eV) of CuPcTs⁴⁻ was possible. The decrease in the formation rates of methanol and CO under visible light to 73% of those under UV–visible light (Tab. 2) can be explained by the decrease in the electron and hole supply from Zn₃Ga|CO₃ to CuPcTs⁴⁻.

The LUMO of CuPcTs⁴⁻ does not exactly populate Cu sites but N atoms neighboring Cu sites (Fig. 3). Thus, the electrons excited to the CB of the LDH would transfer to LUMO (and/or an unoccupied level near LUMO) of CuPcTs⁴⁻. The energy level diagram of the LDH and CuPcTs⁴⁻ supported this hypothesis (Fig. 9).

The HOMO dominantly distribute on C atoms of pyrrole rings, while the LUMO dominantly distribute on both C and N atoms of pyrrole rings for CuPcTs⁴⁻ (Rauf *et al.*, 2012). The N atoms of pyrrole are bonded to central Cu²⁺ ions and thus able to transfer the photo-excited electrons to Cu²⁺ (Fig. 3). CO₂ would be progressively reduced by the reduced Cu⁺ in a similar way to that by inlayer and interlayer Cu sites (Morikawa *et al.*, 2014a; Ahmed *et al.*, 2011, 2012). On the other hand, H₂ would donate an electron to the position around HOMO (Fig. 3) to form H⁺. The proton combines the electron and CO₂ at the Cu site and finally transforms into CO and methanol.

The SPR effect of Ag nanoparticles was already discussed in reference (Kawamura *et al.*, 2015). In contrast, SPR of Au was not effective for the photoreduction of CO₂ due to the greater work function of Au (5.31–5.47 eV) as compared with that of Ag (4.52–4.74 eV). Irradiated by UV–visible light, the Au surface played the role of an electron trap from Zn₃Ga|CO₃.

LDH compounds especially comprising Cu and Ga selectively photoproduced methanol from CO₂ + H₂ (68–88 mol%, Tab. 1). A reaction mechanism *via* hydrogen carbonate bound to Cu was proposed based on FTIR and XAFS (Ahmed *et al.*, 2011; Morikawa *et al.*, 2014a). These LDH photocatalysts would be combined with a photooxidation catalyst, *e.g.* WO₃, to produce methanol from CO₂ + H₂O (Morikawa *et al.*, 2014b).

CONCLUSIONS

LDH comprising Zn and Al or Ga photoreduced CO₂ to CO and methanol by H₂ and the irradiation of UV–visible light.

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When Cu ions were doped as cations in the cationic layer and/or as interlayer anions, the CO₂ photoreduction rates increased to as high as 560 nmol h⁻¹ g_{cat}⁻¹ (Zn_{1.5}Cu_{1.5}Ga|Cu(OH)₄ photocatalyst). Due to the wide band-gap nature of these LDH, UV light was effective for CO₂ photoreduction. The doping of CuPcTs⁴⁻ and Ag to the Zn₃Ga|CO₃ LDH boosted CO₂ photoreduction by a factor of 1.6-1.8 by H₂ and the irradiation of UV-visible light. CuPcTs⁴⁻ was especially effective doped to the LDH for CO₂ photoreduction irradiated by visible light only. The LUMO of CuPcTs⁴⁻ was distributed on N atoms of pyrrole rings bound to central Cu²⁺ ions. The photo-excited electrons diffused to central Cu²⁺ would progressively reduce CO₂ finally to CO and methanol in a similar way to the inlayer and interlayer Cu sites in the LDH in this study.

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