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メタデータ	言語: English 出版者: Elsevier 公開日: 2023-09-13 キーワード (Ja): 酸化ガリウム キーワード (En): Ag nanoparticles, Chemical and physical states of Ag co-catalyst, Ga_2O_3, Photocatalytic CO_2 reduction, In-Situ UV–vis observation 作成者: 北嶋, 乃樹, 山本, 宗昭, 田邉, 哲朗, 吉田, 朋子 メールアドレス: 所属: Osaka City University, Osaka City University, Osaka City University, Osaka City University
URL	https://ocu-omu.repo.nii.ac.jp/records/2019704

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Citation	Catalysis Today. 375; 501-505
Issue Date	2021-09-01
Version of Record	2021-06-22
Type	Journal Article
Textversion	Author
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DOI	10.1016/j.cattod.2020.04.063Get

Kitajima, D., Yamamoto, M., Tanabe, T., & Yoshida, T. (2021). Real time measurements of UV-vis diffuse reflectance of silver nanoparticles on gallium oxide photocatalyst. *Catalysis Today* (Vol. 375, pp. 501–505). Elsevier BV. https://doi.org/10.1016/j.cattod.2020.04.063

REAL TIME MEASUREMENTS OF UV-VIS DIFFUSE REFLECTANCE OF SILVER NANOPARTICLES ON GALLIUM OXIDE PHOTOCATALYST

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Abstract

Ag loaded Ga_2O_3 photocatalysts are well known to be highly active for the CO_2 reduction with water to CO. However, Ag changes its chemical state during the reaction, resulting in the decrease of its photocatalytic activity. To examine the chemical state change during the photocatalytic CO_2 reduction, we have attempted a real time observation of the change in the chemical and physical states of Ag co-catalyst loaded on Ga_2O_3 by monitoring UV-Vis reflectance spectra under the atmosphere simulating the photocatalytic CO_2 reduction. In UV-Vis spectra, two characteristic absorptions appeared at around 450 nm and 600nm corresponding to resonance absorptions of localized surface plasmon (LSPR) of Ag nanoparticles (Ag-NPs) and Ag in metallic state. The LSPR absorption appeared as light irradiation started and grew with the time. It was revealed that Ag on Ga_2O_3 was initially in the oxidized state and reduced by the light irradiation to be Ag-NPs. Further light irradiation enlarged the size of Ag-NPs to be the metallic state especially under atmosphere with water. Under CO_2 atmosphere, Ag-NPs remained small after further light irradiation. These results suggest that Ag initially loaded on Ga_2O_3 in the oxidized state was reduced to be dissolved as Ag^+ in water and precipitated as Ag-NPs. Then, some of Ag-NPs aggregated to be larger Ag particles or in the metallic state. Such reduction process depends on gas species of the system, i.e. water promoted the formation of Ag-NPs while CO_2 suppressed the formation Ag-NPs.

Keywords

Ag nanoparticles, Chemical and physical states of Ag co-catalyst, Ga_2O_3, Photocatalytic CO_2 reduction, in-situ UV-Vis observation

1. Introduction

Recently, massive consumption of fossil fuels has caused significance increase of carbon dioxide (CO_2) in the atmosphere, resulting in environmental problems such as global warming [1, 2]. To deal with the problems, photocatalytic reduction of CO_2 with using clean solar energy is attracting attention because it converts CO_2 into carbon resources [3-7]. In particular, photocatalytic CO_2 reduction using metal oxides as a catalyst has been widely studied because of the simplicity of the reduction system and easy recovery of its reduction products.

In previous studies, it has been reported that silver (Ag) loading as a co-catalyst on metal oxide photocatalysts enhances the activity of photocatalytic CO_2 reduction [8-16]. In them, Ag is considered to work as an effective electron sink to promote the separation of photogenerated electron-hole pairs as well as the reaction site of the CO_2 reduction to produce carbon monoxide (CO). It has been also reported that the particle size and chemical state of the Ag co-catalyst should affect the photocatalytic activity, and loading of Ag nanoparticles (Ag-NPs) uniformly on metal oxides enhances the photocatalytic CO_2 reduction with water [17-21]. Nevertheless, the role of the Ag co-catalyst on the reduction process has not been clarified yet. The difficulty of understanding seems to lie in the fact that physical and chemical states of the Ag co-catalyst often change during the reduction processes depending on their surrounding atmosphere, light irradiation time, and so on [22, 23]. This motivates us to examine changes of physical and chemical states of the Ag co-catalyst on Ga_2O_3 during the photocatalytic CO_2 reduction process with different surrounding atmosphere. It is well known that Ag-NPs exhibit a characteristic optical absorption in the visible wavelength region caused by the resonance excitation of localized surface plasmon (referred to as LSPR, hereafter) [24]. Therefore, in the present work, we have tried in-situ observation of UV-Vis diffuse reflectance of Ag-NPs loaded on Ga_2O_3 (Ag/Ga_2O_3), in the controlled atmosphere representing photocatalytic CO_2 reduction condition using a specifically designed new system.

2. Experimental

2.1. Preparation of Ag/Ga_2O_3 photocatalysts

The Ag/Ga_2O_3 photocatalyst was prepared by an impregnation method [13, 19]. Powders of Ga_2O_3 (Kojundo Chemical Laboratory Co. Ltd. purity 99.99 %) and of $AgNO_3$ (Kishida Chemical Co. Ltd. purity 99.8 %) with respective masses of 1.984 g and 0.016 g were dispersed into 200 mL distilled water, filtered and then dried at approximately 373 K. Afterwards materials filtered out were calcined in air at 723 K for 2 h to get Ag/Ga_2O_3 samples. The amount of Ag loaded on Ga_2O_3 was 0.5 wt%.

2.2. TEM measurements

The morphology of the samples was observed with TEM (JEM-2100M) operated at high voltage of 200 kV. For the TEM observation, the sample was mounted on a carbon covered copper mesh.

2.3. In-situ UV-Vis measurements

In-situ observation of UV-Vis diffuse reflectance for the Ag/Ga_2O_3 samples were carried out using a specifically designed system to simulate photocatalytic CO_2 reduction in different gas atmospheres such as CO_2, Ar, CO_2/H_2O (CO_2 gas and water vapor) and Ar/H_2O (Ar gas and water vapor) as shown in Figure 1. A diffuse reflectance unit is consisting of a reaction cell with a radius of 5 mm quipped with light guiding systems for incident and reflected light. The Ag/Ga_2O_3 sample with its mass of 0.05 g was put into the reaction cell. For the observation of diffuse reflectance spectra, a 300 W Xe lamp was used as the incident light in flowing gas atmosphere with the flowing rate of 100 mL/min. The gas used was either Ar, CO_2, CO_2/H_2O or Ar/H_2O. Water (H_2O) was added on Ar and CO_2 with their bubbling through a water bottle at an ambient temperature. The incident light intensity was 7.0 $\mu W/cm^2$ at around 400 nm. UV-Vis diffuse reflectance spectra were recorded at room temperature using a multichannel analyzer (HAMAMATSU PMA-12) with the acquisition time of 500 ms. $BaSO_4$ was used as a reference of the UV–Vis diffuse reflectance spectra.

3. Results

Figure 2 shows time courses of the UV-Vis diffuse reflectance spectra of Ag/Ga_2O_3 photocatalysts under the flowing gas atmosphere and the UV light irradiation. The sharp absorption edge appeared at ca. 290 nm is corresponding to the bandgap transition of Ga_2O_3 and an intense peak in the visible light region are corresponding to the LSPR absorption of Ag-NPs. The LSPR absorption appeared immediately after starting the light irradiation and increased with the irradiation time. This indicates that Ag species loaded on Ga_2O_3 was initially in oxidized state and reduced by the light irradiation to form nanoparticles (Ag-NPs). The reduction of the Ag species to be Ag-NPs was also confirmed by XAFS measurements [23]. The increase of the LSPR absorption with the light irradiation time corresponds to the increase of number density of Ag-NPs on Ga_2O_3.

The changes of the peak position and width of LSPR were different depending on gas species. Under the flow of Ar or CO_2, the LSPR peak position remained unchanged. Under the flow of CO_2/H_2O, it gradually shifted to the longer wavelength region. Under the flow of the Ar/H_2O, the peak position initially shifted to longer wavelength region and afterward the shift turned to the shorter wavelength region. The reason for this shift will be shown in the discussion part.

It should be noted that the absorption spectra include at least one additional broad absorption around 600 nm which is attributed to the appearance of Ag species having metallic character or larger Ag particles [25-27]. Figure 3 compares the time courses of the peak intensity at around 450 nm and 600 nm in the UV-Vis diffuse reflectance spectra given in Figure 2. It is well known that the peak position and intensity of the LSPR absorption of Ag-NPs change depending on their size, shape and dielectric property of the surrounding medium [28-32]. After the long time light irradiation, the intensities at 450 nm and 600 nm saturated under the flow of Ar or CO_2 with higher saturated intensity for the former, while both intensities continued to increase under the flow of Ar/H_2O or CO_2/H_2O. It is also noted that the intensities were higher for Ar atmosphere compared to those for CO_2 atmosphere. These results suggest that water contributed to increase the number density of Ag-NPs and promotes the aggregation of Ag-NPs to be larger Ag particles or metallic state, while CO_2 retarded the formation of Ag-NPs.

After the in-situ UV-Vis reflectance measurements, Ag-NPs on Ga_2O_3 were observed with TEM. Figs. 4 (a) and (b) shows TEM images for samples exposed to Ar/H_2O gas flow and CO_2 gas flow respectively. The images show that small particles with uniform contrast in their inside were precipitated on Ga_2O_3, which corresponds to the formation of Ag-NPs. In addition, larger particles (over 5 nm) occasionally appeared in the different fields. From the images taken from wider areas, the particle size distributions were determined as given in Figs. 4 (c) and (d), respectively. On the sample exposed to the Ar/H_2O gas flow (see Fig. 4 (a) and (c)), Ag-NPs with sizes of 2-6 nm were distributed on Ga_2O_3, while on the sample exposed to the CO_2 gas flow Ag-NPs (see Fig. 4 (b) and (d)) were kept a little smaller (1-2 nm). These TEM observations confirm that that water promoted the reduction of Ag in initially oxidized state to the precipitate of Ag-NPs, while CO_2 kept the sizes of Ag-NPs smaller except some larger ones appearing as the aggregation of NPs.

To confirm the effects of H_2O on the formation of Ag-NPs on Ga_2O_3, we have carried out an additional experiment in which the flowing gas was switched during the in-situ UV-Vis reflectance measurement, i.e. started with CO_2 and changed to CO_2/H_2O by adding water. The result is shown in Figure 5. Under the CO_2 gas flow, the absorption intensities at 450 nm and 600 nm initially increased and soon saturated. After adding water at 60 min, both intensities restarted to increase with the irradiation time. This is a clear evidence that water enhanced the reduction of Ag from the oxidized state to Ag-NPs as well as their aggregation to be larger particles or metallic state.

4. Discussion

Based on the results mentioned above, changes of the chemical state of Ag species loaded on Ga_2O_3 is discussed in the following. With the light irradiation, Ag initially loaded as the oxidized state was reduced to Ag into two different states; nanoparticles showing the LSPR absorption around 450 nm and metallic state showing broad absorption around 600 nm as indicated in Figure 2. The reduction process would proceed through the reduction of Ag in the oxidized state, (1) dissolution of Ag into water as Ag^+ [33, 34], (2) precipitation and aggregation of Ag as small Ag clusters followed by their growth to Ag-NPs which show LSPR absorption, and (3) growth or aggregation of Ag-NPs to larger Ag particles or metallic state as appeared as the absorption around 600 nm and large particles in the TEM images. Thus, it could be summarized that the role of water is the promotion of the reduction process by dissolving Ag as its ions into water (the oxidation of Ag) followed by the precipitation and aggregation of Ag to be Ag-NPs. The process and the role of water are confirmed by the in-situ UV-Vis diffuse reflectance measurements.

As seen in Figs. 2 and 3, under the flow of Ar/H_2O gas, the intensity of the LSPR absorption increased monotonously with the irradiation time while the peak position shifted to longer wavelength region and subsequently shifted to shorter wavelength region. It has been reported that the peak position depends on the particles size, i.e., it shifts to the longer wavelength region as the particle size increases [28-32]. Therefore, this result suggests that water would oxidize a part of large metallic Ag particles to be re-dissolved as Ag ions and then they precipitate again as Ag-NPs. On the other hand, adsorption of CO_2 on Ag in metallic state likely inhibits Ag re-dissolution into water. The least LSPR absorption intensity under CO_2 atmosphere suggests that the absorption of CO_2 on Ag in the oxidized state also suppresses the its reduction. However, the addition of water restarted and continued the reduction as shown in Figure 5.

5. Conclusions

It is known that Ag nanoparticles (Ag-NPs) on Ga_2O_3 provide high photocatalytic activity for the CO_2 reduction with water. However, their photocatalytic activity often decreases during the reduction probably owing to the aggregation of Ag-NPs to be larger particles in the metallic state. To examine the aggregation process, we have provided a new system for in-situ UV-Vis diffuse reflectance observation and applied the system to examine how Ag loaded on Ga_2O_3 changes its state with light irradiation under different gas flow condition of either Ar, CO_2, Ar/H_2O (Ar gas and water vapor) and CO_2/H_2O (CO_2 gas and water vapor).

Performing the observations under various conditions, we have concluded that (1) light irradiation with water reduces Ag initially deposited as the oxide state on Ga_2O_3 to be Ag-NPs, (2) the water enhances the reduction and tends to assist the aggregation of Ag-NPs, and (3) CO_2 adsorbed either or both of Ag in the oxide state and Ag in the metallic state retards the reduction and the aggregation. Gradual growth of the sizes of Ag-NPs and transformation to the metallic state would cause degradation of the photocatalytic activity of Ag/Ga_2O_3 during the photocatalytic reduction of CO_2 with water.

From these observations, we could claim that in order to exhibit high activity on photocatalytic CO_2 reduction for Ag loaded on Ga_2O_3, it is critical to deposit Ag-NPs uniformly on Ga_2O_3 with high density and to avoid their aggregation to be larger Ag or metallic state.

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Figure captions

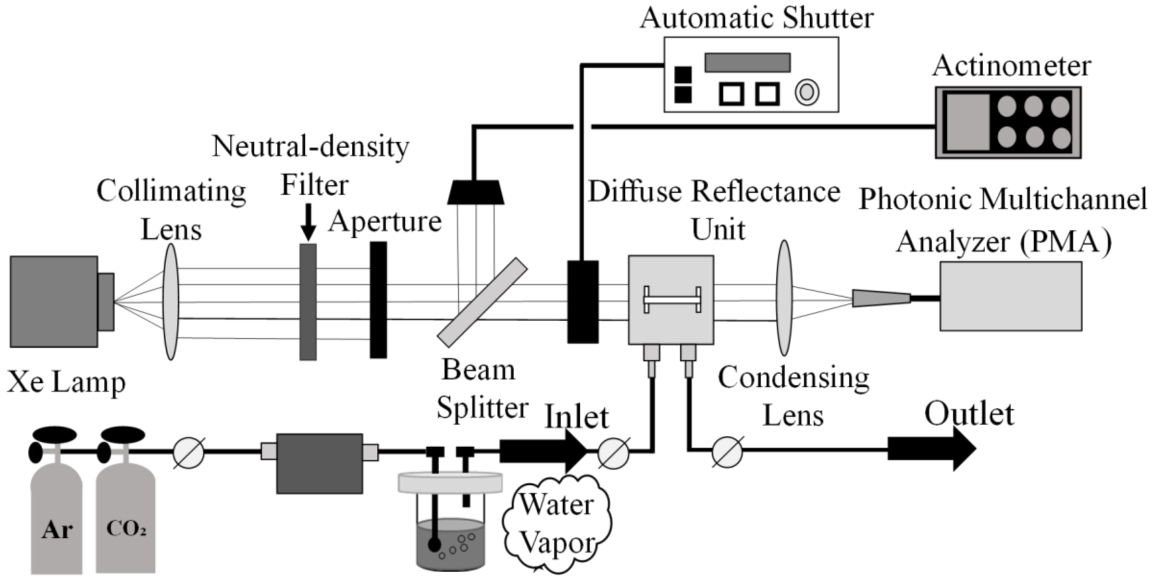
Figure 1. Schematic diagram of in-situ UV-Vis diffuse reflectance measurement system.

Figure 2. Time courses of the UV-Vis spectra of Ag loaded Ga_2O_3 under light irradiation and different gas flowing conditions (a) Ar, (b) CO_2, (c) Ar/H_2O, and (d) CO_2/H_2O.

Figure 3. Time courses of the absorption intensities of UV-Vis reflectance spectra at (a) 450 nm, and (b) 600 nm.

Figure 4. TEM images observed in two different fields of Ag-NPs on Ga_2O_3 after the in-situ UV-Vis measurements under gas flows of (a) Ar/H_2O and (b) CO_2, and respective size distributions of Ag-NPs are given in (c) and (d) with accounting of the total of 107 and 80 Ag-NPs, respectively.

Figure 5. Time courses of absorption intensities of UV-Vis reflectance spectra at (a) 450 nm, and (b) 600 nm under the light irradiation. At 60 min, the flowing gas was changed from CO_2 to CO_2/H_2O.



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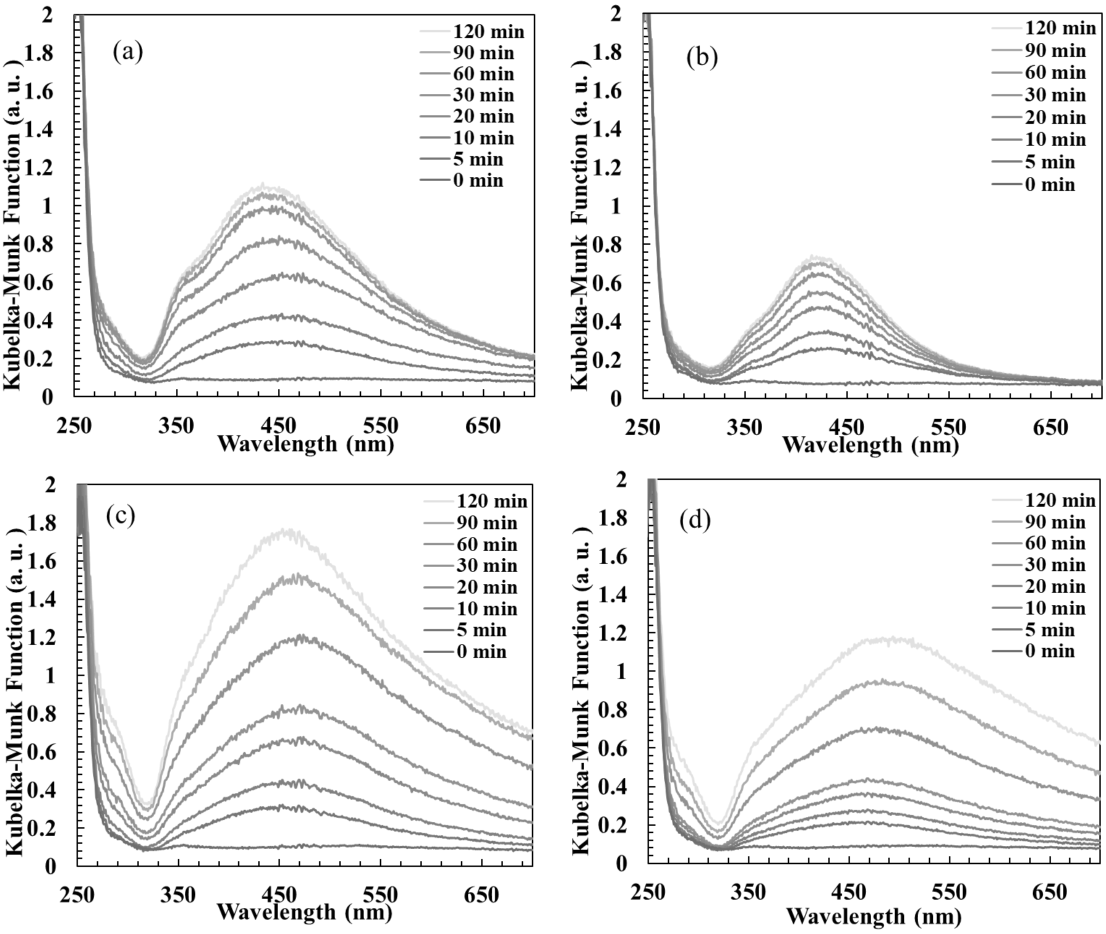

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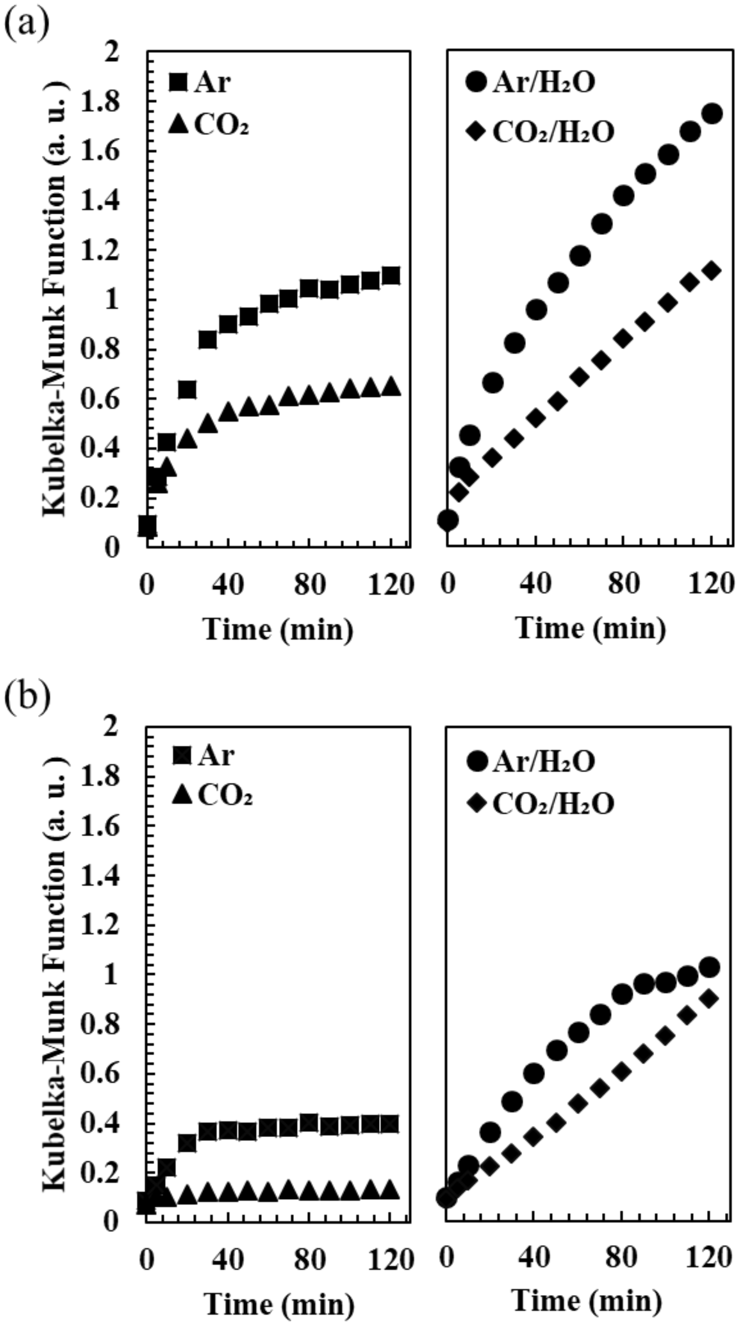

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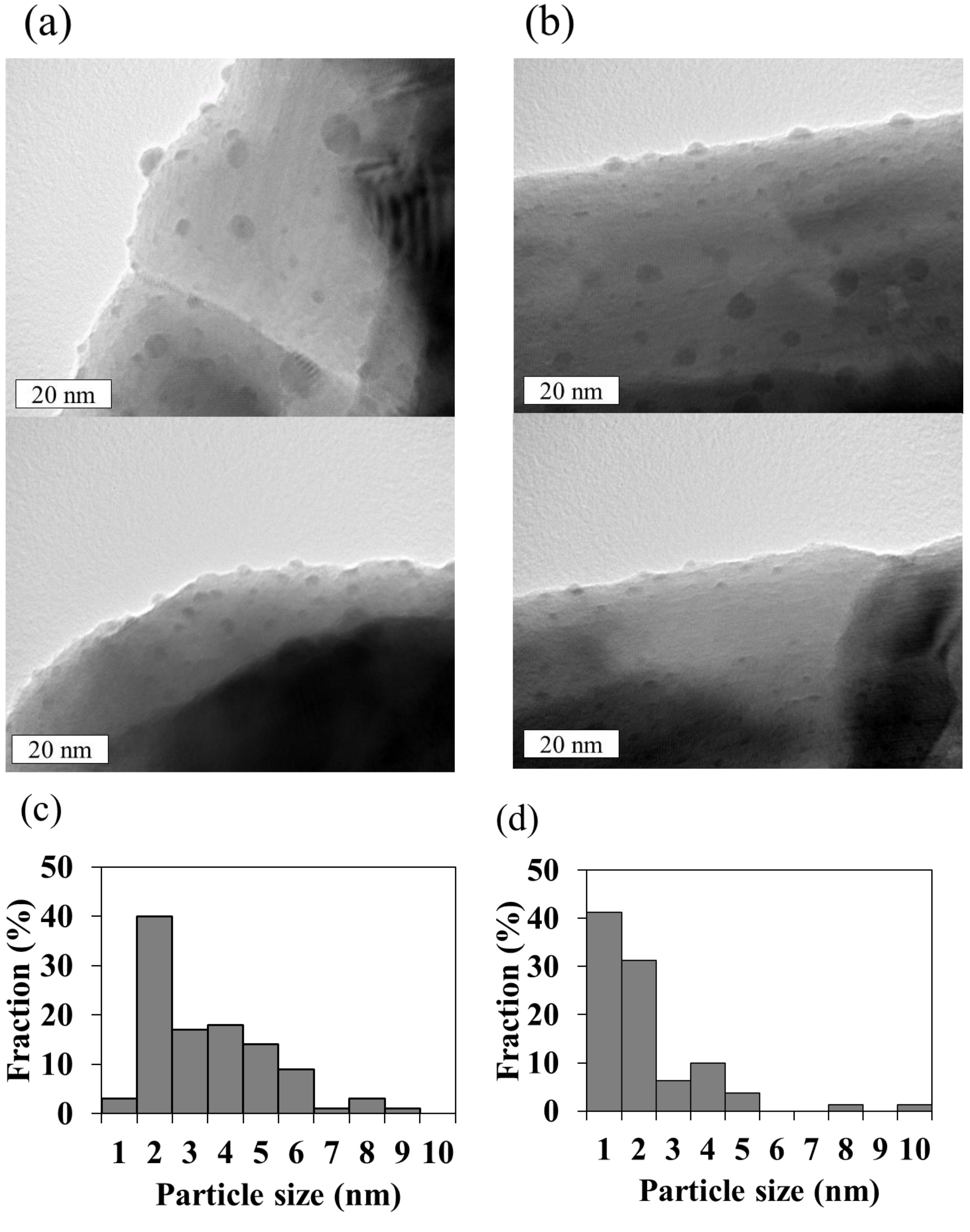

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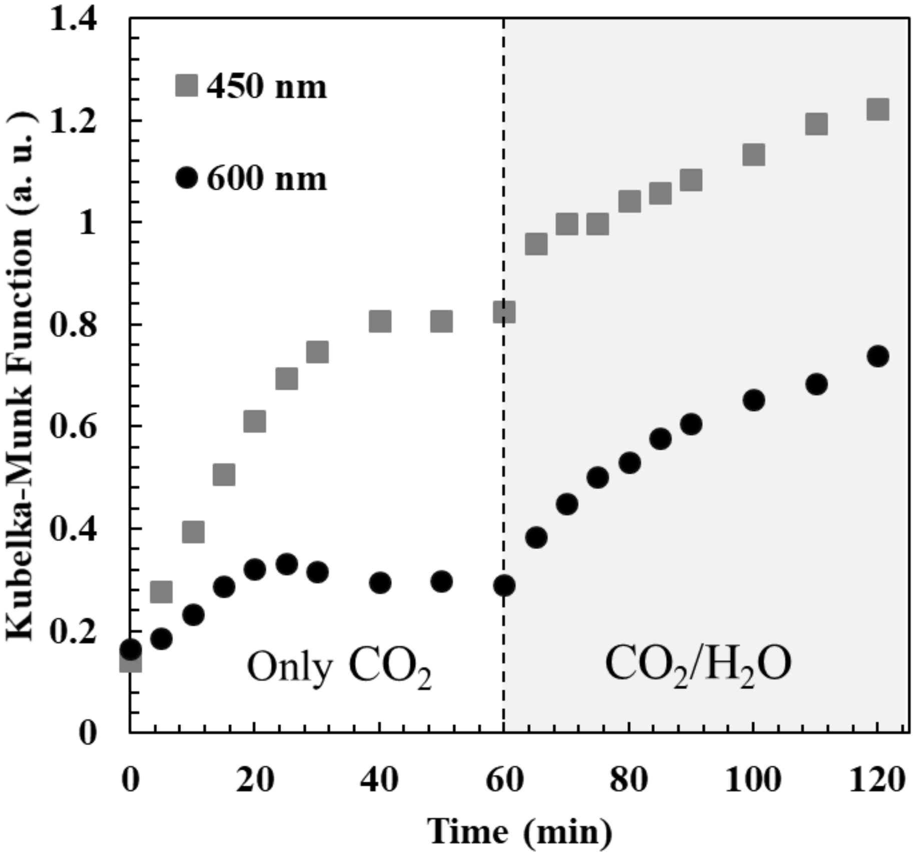

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