

Electrosynthesis of diphenyl carbonate catalyzed by Pd^{2+/0} (in situ NHC) redox catalyst promoted at Au anode

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Abstract The effects of Au anodes on electrochemical carbonylation of phenol with CO (1 atm) to diphenyl carbonate (DPC) catalyzed by Pd (in situ NHC) electrocatalyst were studied under galvanostatic electrolysis conditions. Au supported on carbon materials (Au/carbon) were effective anodes for oxidation of the homogeneous Pd electrocatalyst. Various carbon materials, Vulcan XC-72 carbon black (XC72), activate carbon, Ketjenblack, and graphene nanoplatelets (graphene-1, -2, -3) were tested as a support for Au. The Au/graphene-3 was the most effective anode for DPC formation. Effects of Au loadings and reducing agents (H₂ and NaBH₄) on the reactivity of the Au/graphene-3 anode for the DPC formation were studied and the materials were characterized using XRD spectroscopy and TEM analysis. These experimental facts indicated that small Au particles on the surface of graphene were superior for the DPC synthesis by the Pd (in situ NHC) electrocatalyst.

Keywords Diphenyl carbonate · Pd electrocatalyst · Au anode · Graphene support

Introduction

Diphenyl carbonate (DPC) is a key material for the production of polycarbonate [1, 2], which is one of the most useful engineering plastics due to its good heat resistance, mechanical properties, and transparency. In industrial processes, DPC is manufactured from phosgene or dimethyl carbonate and phenol (PhOH). However,

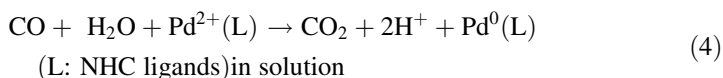
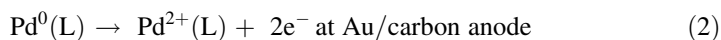
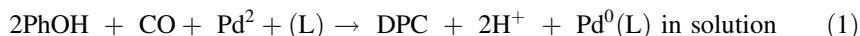
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these processes have disadvantages such as the use of toxic phosgene and consumption of a large amount of energy. Therefore, the development of direct oxidative carbonylation of PhOH with carbon monoxide and oxygen is an attractive subject from the viewpoint of green chemistry. So far, direct oxidative carbonylation of PhOH to DPC using homogeneous catalysts [3–7] and heterogeneous catalysts [8–14] have been reported. However, direct oxidative carbonylation requires an under pressure condition around 100 atm at higher temperature around 373 K and results in hydrolysis of DPC by water produced from oxygen. Recently, we have proposed the direct electrochemical carbonylation of PhOH to DPC by using Pd electrocatalysts [15–19]. This new synthesis of DPC was conducted in mild reaction conditions without the production of water; therefore, the hydrolysis of DPC did not proceed. Active homogeneous electrocatalyst of Pd coordinated *N*-heterocyclic carbene (NHC) has recently been found and, moreover, in situ generated NHC from imidazolium chlorides has been found to be an effective ligand. Active NHC ligands for PdCl₂(CH₃CN)₂ were 1,3-di-mesitylimidazol-2-ylidene (IMes), 1,3-di-isopropylimidazol-2-ylidene (IPr), and active precursors of in situ NHC were 1,3-di-alkyl-imidazolium chloride (IMesHCl, IPrHCl and *It*-BuHCl) and 1,3-di(*tert*-butyl)imidazoline chloride (SI*t*-BuHCl) [9, 10]. Efficiencies of ligands for Pd electrocatalyst were in situ IMes < IMes < in situ IPr < in situ *It*-Bu < in situ SI*t*-Bu. Therefore, a PdCl₂(in situ SI*t*-Bu) electrocatalyst was used in this work.

The electrochemical carbonylation of PhOH to DPC proceeds through the following reactions.



Oxidative carbonylation of PhOH with CO to DPC proceeds by Pd²⁺ (Eq. 1). Electrochemical oxidation of Pd⁰ to Pd²⁺ proceeds at the Au anode (Eq. 2). Reduction of H⁺ to H₂ proceeds at the cathode (Eq. 3). The formation of DPC (Eq. 1) was promoted by H⁺ acceptor (sodium phenoxide). In addition, oxidation of CO to CO₂ with H₂O proceeds by Pd²⁺ (Eq. 4). In our previous works, Au wire was used as the anode and a surface area of the Au wire was not large. If a new Au anode having higher surface area is used, an oxidation rate of Pd⁰ to Pd²⁺ (Eq. 2) will increase and the DPC formation rate will be accelerated. In this work, Au-supported carbon materials were prepared and were used for the anode [20, 21]. Effects of the Au/carbon anodes on the DPC formation catalyzed by Pd (in situ SI*t*-Bu) electrocatalyst were studied.

Experimental

Anode preparation

An Au anode for oxidation of Pd complex electrocatalyst was prepared from Au/carbon materials by the hot press method [15, 16]. Au/carbon materials were prepared by a conventional impregnation method. Activated carbon (AC, $1420 \text{ m}^2 \text{ g}^{-1}$, Wako Pure Chemical Industries), Vulcan XC-72 carbon black (XC72, $290 \text{ m}^2 \text{ g}^{-1}$, Cabot Co.), Ketjenblack EC600JD (KB_{JD}, $1100 \text{ m}^2 \text{ g}^{-1}$, Kao Co.) and three types of graphene nanoplatelets (graphene-1, $340 \text{ m}^2 \text{ g}^{-1}$; graphene-2, $470 \text{ m}^2 \text{ g}^{-1}$; graphene-3, $710 \text{ m}^2 \text{ g}^{-1}$, Strem Chemicals) were used as a carbon support of Au.

A typical preparation procedure of Au/graphene was described below. An aqueous solution of HAuCl_4 was mixed with graphene powder. Then, the solution was dried up to powder in air at 373 K. The HAuCl_4 /graphene powder was reduced with H_2 (1 atm.) in a quartz reactor for 2 h at 573 K. Au loadings on graphene were 1.0, 5.0, 10.0, 15.0, and 25.0 wt%.

In addition to the impregnation method, Au/graphene material was prepared by the deposition of Au on graphene using a reducing agent of NaBH_4 , according to a previous report [21]. After graphene powder was added into a HAuCl_4 aqueous solution (0.1 mM), the mixture was stirred for 30 min at 298 K. NaOH aqueous

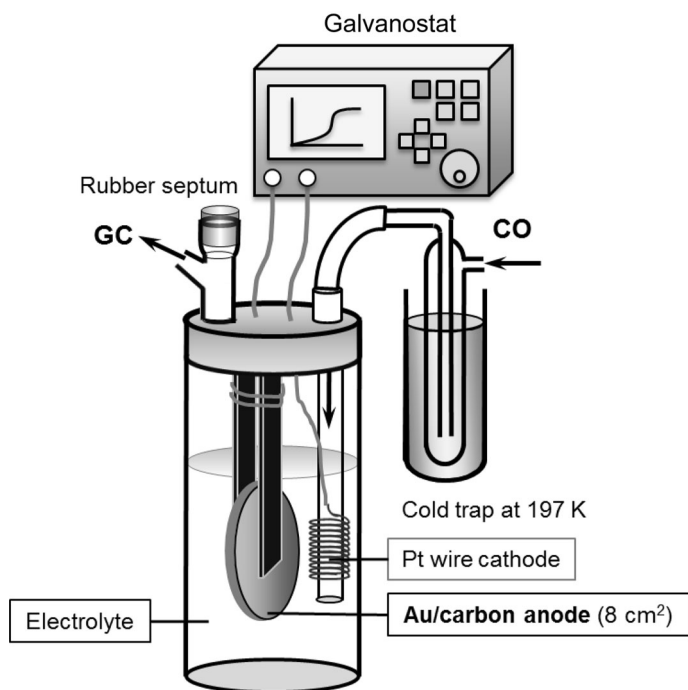


Fig. 1 Diagram of one-compartment electrolysis cell for DPC synthesis

solution (2.0 M) was added into the mixture to adjust pH at 10. An aqueous solution of NaBH_4 (0.1 M) was quickly added into the mixture under vigorous stirring. After filtration, the obtained Au/graphene was washed with water ($25 \text{ ml} \times 3$) and dried in decompression. The Au loading on graphene was 10.0 wt%.

The anode was prepared by the hot-press method [15, 16]. An Au/graphene powder (47 mg, Au 60 μmol), vapor-grown carbon fiber (125 mg, VGCF), and of polytetrafluoroethylene powder (40 mg, PTFE, F-104 Daikin Co.) were well mixed and kneaded to a clay lump. The clay lump was pressed and shaped on the hot-plate to a sheet anode (Au/graphene + VGCF anode). The geometric area of the anode was 8 cm^2 .

Electrolysis procedure

Electrochemical carbonylation was conducted using a one-compartment electrolysis cell. The cell was fabricated from an Au/carbon + VGCF anode, a platinum wire cathode, a gas inlet and outlet, and a sampling port, as shown in Fig. 1. An electrolyte solution is $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ (60 μmol), 1,3-di(*tert*-butyl)imidazoline chloride (SIt-BuHCl, 180 μmol), PhOH (30 mmol), sodium phenoxide (PhONa, 0.5 mmol) and CH_3CN (40 ml). PhONa functions as an electrolyte and a promoter for the DPC formation [16]. The solution was dried using molecular sieves 3A, and content of impurity water in the solution was kept under 50 ppm. Dry CO (1 atm) passing through a cold trap (197 K) was introduced into the electrolyte solution. The Au/graphene + VGCF anode was sandwiched between two glassy carbon plates (current collector, $5 \times 20 \times 1 \text{ mm}$) and suspended in the solution. Galvanostatic electrolysis of the solution was conducted under galvanostatic electrolysis from 1 to 5 mA for 3 h at 298 K by use of an HZ-5000 electrochemical instrument system (Hokuto Denko Co.).

Product analyses

Products in the electrolysis solution (DPC, etc.) were identified and quantified by gas chromatographic techniques using a Shimadzu GC-2010 [ZB-1capillary column ($0.25 \text{ } \phi \times 30 \text{ m}$), FID detector, He carrier gas] and an Agilent EZ-Chrome with a SS420X module. Products in gas phase (CO , CO_2 and H_2) were analyzed by an online gas chromatograph (GL-Science GC-323), CO_2 and CO analysis; Porapak-Q column ($4 \text{ } \phi \times 2 \text{ m}$), TCD detector, He carrier gas, H_2 analysis; activated carbon column ($4 \text{ } \phi \times 2 \text{ m}$), TCD detector, Ar carrier gas.

In this study, homogeneous Pd^{2+} electrocatalyst was used for carbonylation of PhOH. According to our previous reports [17], DPC formation consisted of two different reaction paths, stoichiometric carbonylation and electrochemical carbonylation. The stoichiometric DPC formation finished within 10 min (Eq. 1). CO_2 was also stoichiometrically formed until 60 min (Eq. 3). In electrolysis condition, $\text{Pd}^0(\text{L})$ was oxidized to $\text{Pd}^{2+}(\text{L})$ at the anode (Eq. 2) and DPC was produced after 10 min (Eqs. 1, 2). CO_2 was also electrochemically produced after 60 min (Eqs. 1, 3). The current efficiencies to DPC and CO_2 formation were calculated kinetic slopes after 10 and 60 min, respectively.

Characterization of Au/carbon

The Au/carbon materials were characterized using transmission electron microscopy (TEM) and X-ray diffraction spectroscopy (XRD). An image of Au particles on graphene was obtained by TEM (JEM-2010F (JEOL) microscope equipped with a detector (Genesis, EDAX) for energy-dispersive X-ray spectroscopy). The crystal structure of the Au particle was studied by XRD analysis (MiniFlex 600/TISS (Rigaku) diffractionmeter using a Cu-K α radiation).

Results and discussion

As mentioned in the introduction, the Au/carbon + VGCF anodes were applied for the electrochemical carbonylation of PhOH catalyzed by the homogeneous Pd (in situ *Si*-Bu) electrocatalyst in this work. The AC, XC72, KB_{JD} and graphene-1, -2, -3 materials were used as a carbon support. The XRD spectra of Au/carbon materials are indicated in Fig. 2. All the diffraction peaks observed in the Au/carbon were assignable to Au metal and graphite structure. Diffraction lines at $2\theta = 38, 44, 67, 78, 82,$ and 98° corresponded to the crystal planes of (111), (200), (220), (311), (222), and (400) facets of the face-centered cubic structure of Au metal, respectively. Diffraction peaks at $2\theta = 27^\circ$ corresponded to graphite (002). The XRD spectra indicated that Au species on carbon surface were present as Au metal and (111) plane was the major orientation in all the Au/carbon materials.

Specific surface areas of carbon supports and the average crystalline sizes of Au calculated from (111) plane using Scherer's equation are indicated in Table 1. The average crystalline sizes of Au on AC, XC72, KB_{JD} and graphene-3 supports were

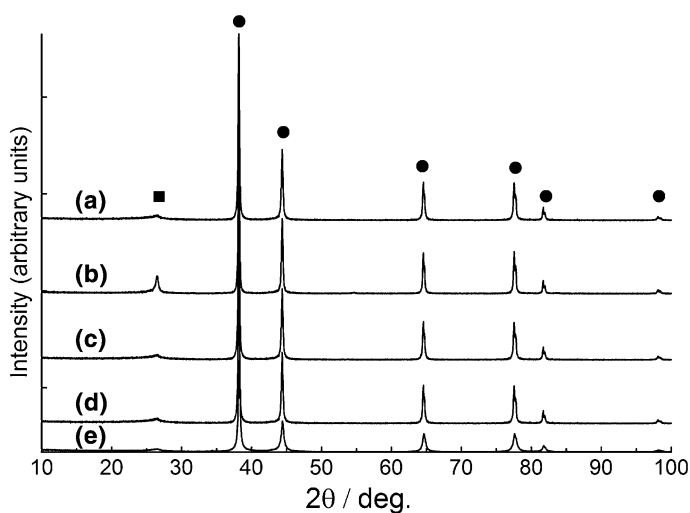


Fig. 2 XRD spectra of Au/carbon materials, *a* Au/XC72, *b* Au/KB_{JD}, *c* Au/AC, *d* Au/graphene-3, *e* Au/graphene-3 (NaBH₄). Au metal: circle and graphite: square

Table 1 Electrochemical carbonylation of PhOH by Pd (in situ Si*r*-Bu) electrocatalyst at Au/carbon anode

Entry	Anode	Surface area of support/m ² g ⁻¹	Crystalline size of Au/nm	Product yield/ μ mol		CE (%) ^e		
				DPC		CO ₂		
				Stoichio. ^c	E. Chem. ^d	Stoichio. ^c	E. Chem. ^d	
1	Au wire	–	–	34.9	44.4	15.3	7.6	64
2	Au/AC ^a	1420	57	22.0	18.4	23.4	8.8	33
3	Au/XC72 ^a	238	55	35.8	46.2	19.2	9.5	66
4	Au/KBJD ^a	1105	54	33.5	45.2	17.2	7.5	65
5	Au/graphene-1 ^a	342	78	30.3	22.0	19.2	9.4	40
6	Au/graphene-2 ^a	471	70	33.0	27.9	19.4	4.8	50
7	Au/graphene-3 ^a	711	56	32.9	46.8	18.1	7.6	69
8	Au/graphene-3(NaBH ₄) ^b	711	26	32.7	48.9	17.6	4.7	72

PdCl₂(MeCN)₂: 60 μ mol, Si*r*-BuHCl: 180 μ mol, PhOH: 30 mmol, PhONa: 0.5 mmol CH₃CN: 30 ml, Galvanostatic electrolysis: 1 mA, P(CO): 101 kPa

^a Au loading: 25.0 wt%

^b Au loading: 10.0 wt%

^c Stoichiometric yield

^d Electrochemical yield

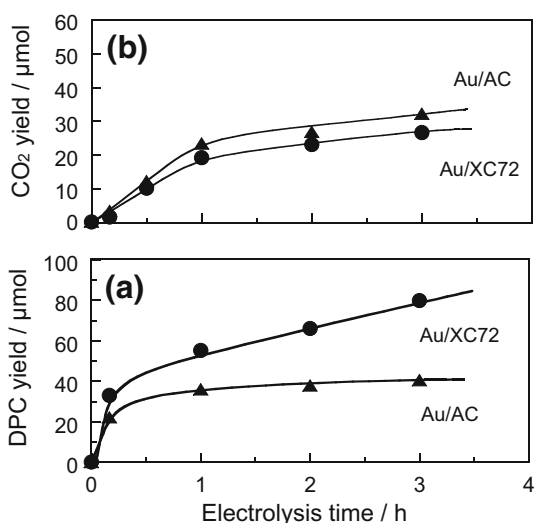
^e Current efficiency

almost the same (54–57 nm). In the case of graphene supports, the average crystalline size decreased with increasing in the specific surface areas. As described in the experimental section, the Au/carbon materials were prepared using the same conventional impregnation method and reduction as H_2 . The preparation method may be a primary factor to decide the crystalline size of Au. On the same nature of carbon surface of graphene materials, the surface area may be secondary factor to decide the crystalline size of Au.

Electrochemical carbonylation of PhOH using the Pd (in situ *SI*-Bu) electrocatalyst at the Au/carbon + VGCF anodes was carried out under galvanostatic condition at 1 mA. Figure 3 shows the time courses of (a) DPC and (b) CO_2 formation by the electrochemical carbonylation of PhOH using the Au/XC72 + VGCF and Au/AC + VGCF anodes. At the beginning of the reaction, within 10 min the rapid formation of DPC by the stoichiometric formation with initial Pd^{2+} (in situ *SI*-Bu) was observed. After 10 min, the DPC yield linearly increased with the electrolysis time at the Au/XC72 + VGCF anode. Thus, the electrochemical formation rate and the current efficiency of DPC were calculated from the slope after 10 min. On the other hand, an increase in DPC yield after 10 min was small for the Au/AC + VGCF anode. With respect to CO_2 formation, the stoichiometric formation was slow and continued for 60 min. It was confirmed that $PdCl_2(CH_3CN)_2$ catalyzed the formation of DPC and CO_2 because the products were not formed without $PdCl_2(CH_3CN)_2$. In order to confirm the role of Au/carbon, a VGCF anode without Au was used for the carbonylation. In this case, only 3 μmol of DPC and 1 μmol of CO_2 were electrochemically formed, which indicated the Au/carbon accelerated the electrochemical formations.

The Au/carbon anodes evidently affected the electrochemical formation of DPC; therefore, other carbon supports were applied for the electrochemical carbonylation. The stoichiometric and electrochemical yields of DPC and CO_2 and the DPC current efficiency at the Au/carbon anodes are summarized in Table 1. In addition, results at

Fig. 3 Time courses of DPC and CO_2 formation by 1 mA galvanostatic electrolysis at 298 K. $PdCl_2(MeCN)_2$: 60 μmol , *SI*-BuHCl : 180 μmol , PhOH : 30 mmol, PhONa: 0.5 mmol CH_3CN : 30 ml, $P(CO)$: 101 kPa



the Au wire anode were also indicated at entry 1 in Table 1. The stoichiometric yields of DPC using the anodes (entry 1, 3–7) were very similar, except for the Au/AC + VGCF anode (entry 2). On the other hand, the electrochemical yields of DPC strongly depend on the Au anodes. The Au/XC72 + VGCF (entry 3), Au/KB_{JD} + VGCF (entry 4) and Au/graphene-3 + VGCF (entry 7) anodes showed high electrochemical DPC yields as well as that at the Au wire anode. The Au/AC + VGCF (entry 2), Au/graphene-1 + VGCF (entry 5) and Au/graphene-2 + VGCF (entry 6) anodes showed low DPC yields. The stoichiometric and electrochemical yields of CO₂ were not large and did not depend on the Au anodes. The current efficiency of DPC strongly depended on the Au anodes. The Au/XC72 + VGCF, Au/KB_{JD} + VGCF, Au/graphene-3 + VGCF and Au wire anodes showed high current efficiencies, corresponding to the electrochemical DPC yields.

As described above, the Au/XC72 + VGCF, Au/KB_{JD} + VGCF and Au/graphene-3 + VGCF anodes were suitable for the DPC formation, especially the Au/graphene-3 + VGCF anode would be effective. The Au/AC + VGCF anode could not be effective for the DPC formation because the high adsorption capability of AC might have an influence on the stoichiometric yield. In addition, it is likely that poor conductivity of AC decelerated the electrochemical reaction. Except for the Au/AC + VGCF anode, the relativities of Au anodes of the DPC formation at Au anodes seem to be related to the average crystalline sizes of Au. Very similar sizes of Au crystalline were observed in entries 3, 4, and 7, and their electrochemical DPC yields and DPC current efficiencies were similar. On the other hand, larger Au crystalline sizes on graphene-1 and graphene-2 anode were observed and their carbonylation activities were inferior activities for the DPC formation.

Among the Au/carbon materials prepared by the impregnation method and reduction with H₂ (entry 2–7), the Au/graphene-3 + VGCF anode was suitable for the electrochemical carbonylation of PhOH to DPC catalyzed by Pd (in situ Si*t*-Bu) electrocatalyst. The effect of Au loading on the electrochemical carbonylation was studied and 1.0, 5.0, 10.0, 15.0, and 25.0 wt% Au/graphene-3 were prepared. Figure 4 shows (a) the electrochemical yields of DPC and CO₂, (b) the stoichiometric yields of DPC and CO₂ and their current efficiencies as a function of Au loadings on the graphene-3 support. In the case of 0 wt% of Au, a small yield of DPC was electrochemically formed at the graphene-3 + VGCF anode. When the Au loading on graphene-3 was increased from 1.0 to 10.0 wt%, the electrochemical DPC yield linearly increased. The high electrochemical DPC yield of 46.9 μmol and current efficiency of 70 % were obtained at 10.0 wt% loading. When the Au loading was increased more than 10.0 wt%, the electrochemical DPC yield and current efficiency did not increase. The stoichiometric yields of DPC and CO₂ also did not depend on the Au loadings. On the other hand, the electrochemical CO₂ yields did not depend on the Au loadings and were low values.

These experimental facts strongly suggest that smaller Au particles on carbon is effective for the electrochemical DPC synthesis and promotes the oxidation of Pd (in situ Si*t*-Bu) electrocatalyst. The stoichiometric reactions are independent of the anodes. The 10.0 wt% Au loading is enough to obtain high yield and current efficiency of DPC. Hereafter, the electrochemical carbonylation using the Au (10.0 wt%)/graphene-3 + VGCF anode was studied.

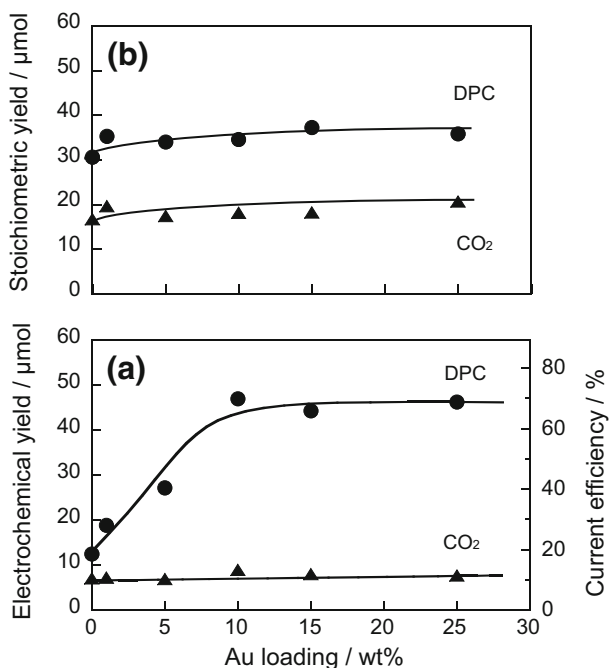


Fig. 4 Effects of Au loading of the anode on electrochemical carbonylation of PhOH by Pd (in situ SIr-Bu) electrocatalyst. **a** Electrochemical yields of DPC and CO₂ and current efficiency of DPC and **b** stoichiometric yields of DPC and CO₂. Reaction conditions are the same as in Table 1, except for Au loadings

As mentioned above, among 10.0 wt% Au/graphene-3 materials, smaller crystalline size of Au was favor for the DPC formation. We tried to prepare a smaller crystalline size of Au on the graphene-3 supported by using a chemical reduction method. 10.0 wt% Au/graphene-3 was prepared using a NaBH₄ reductant [10]. This material was abbreviated as Au/graphene-3(NaBH₄). The XRD spectrum of Au/graphene-3(NaBH₄) was shown in Fig. 2e. The diffraction peaks were assigned to Au metal. The average crystalline size of the Au was 26 nm, which is a half of the Au/graphene-3 reduced with H₂, as abbreviated Au/graphene-3(H₂).

Figure 5 shows TEM images of the 10 wt% Au/graphene-3(H₂) and 10.0 wt% Au/graphene-3(NaBH₄). The EDS analysis in the TEM images showed that the black spots correspond to Au. In both of the TEM images, we could observe graphene sheets and numerous Au nanoparticles. Particle sizes observed in Au/graphene-3(H₂) were larger than that in Au/graphene-3(NaBH₄). The distribution of Au particles in Au/graphene-3(H₂) was from 20 to 140 nm, while that in Au/graphene-3(NaBH₄) was from 4 to 75 nm. The difference in average particle size of Au in TEM images is in accordance with the average crystalline size of Au evaluated from XRD spectra.

The results of electrochemical carbonylation of PhOH catalyzed by Pd (in situ SIr-Bu) electrocatalyst at the Au/graphene-3(NaBH₄) + VGCF anode were

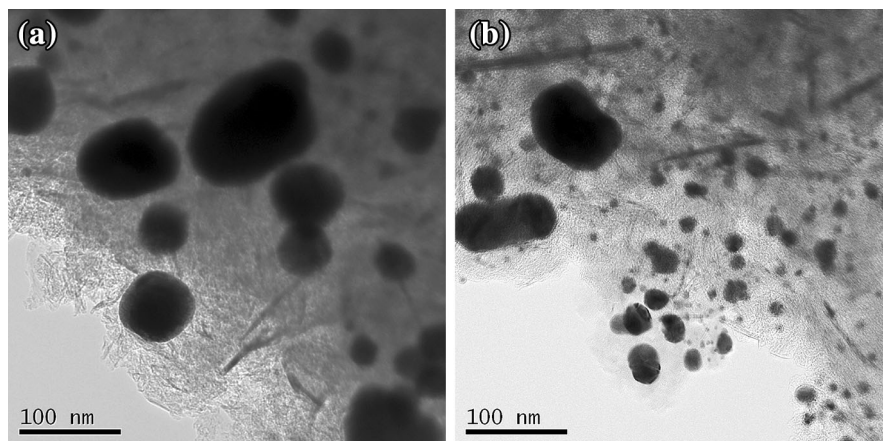


Fig. 5 TEM images for **a** 10 wt% Au/graphene-3(H₂) and **b** 10 wt% Au/graphene-3(NaBH₄)

indicated at entry 8 in Table 1. The yield of DPC and the current efficiency of DPC formation were slightly higher than that of the Au/graphene-3(H₂) + VGCF anode at entry 7. In addition, the Au/graphene-3(NaBH₄) + VGCF anode was washed with acetonitrile after electrolysis, and the washed Au/graphene-3(NaBH₄) + VGCF anode was reused for the electrochemical carbonylation using fresh electrolysis solutions. As a result, the same DPC and CO₂ yields were obtained at the second run. The Au/graphene-3(NaBH₄) + VGCF anode can be reused for the carbonylation and is stable. The advantage of the Au/graphene-3(NaBH₄) + VGCF anode was small to compare with the Au/graphene-3(H₂) + VGCF anode at 1 mA galvanostatic electrolysis. To clarify reactivity of the Au/graphene-3(NaBH₄) anode, the electrochemical carbonylation of PhOH catalyzed by Pd (in situ *SI*-Bu) electrocatalyst was conducted at higher electrolysis currents of 2, 3, and 5 mA. Figure 6 shows (a) electrochemical yield of DPC and CO₂ and (b) current efficiency of DPC and CO₂ as functions of electrolysis current at the Au/graphene-3(NaBH₄) + VGCF, Au/graphene-3(H₂) + VGCF and Au wire anodes. At 1 mA, the electrochemical DPC yields of the Au/graphene-3(NaBH₄) + VGCF, Au/graphene-3(H₂) + VGCF and Au wire anodes were 48.9, 46.8, and 44.4 μmol, respectively. When electrolysis current was increased to 2, 3, and 5 mA, the electrochemical DPC yield increased linearly in all the anodes, as shown in Fig. 6a. The highest DPC yield of 118.3 μmol was obtained using the Au/graphene-3(NaBH₄) + VGCF anode. The reactivities of the anodes were Au/graphene-3(NaBH₄) > Au/graphene-3(H₂) > Au wire. The current efficiency of DPC formation at the Au/graphene-3(NaBH₄) + VGCF was very good at 1 mA; however, current efficiency linearly decreased with the electrolysis current, as shown in Fig. 6b. The current efficiency at the Au wire and Au/graphene-3(H₂) + VGCF anodes also decreased with current. A higher current efficiency of 45 % was obtained using the Au/graphene-3(NaBH₄) + VGCF anode at 5 mA. On the other hand, the electrochemical CO₂ yield and the current efficiency of CO₂ did not depend on the electrolysis currents. The sum of current efficiency of DPC and CO₂

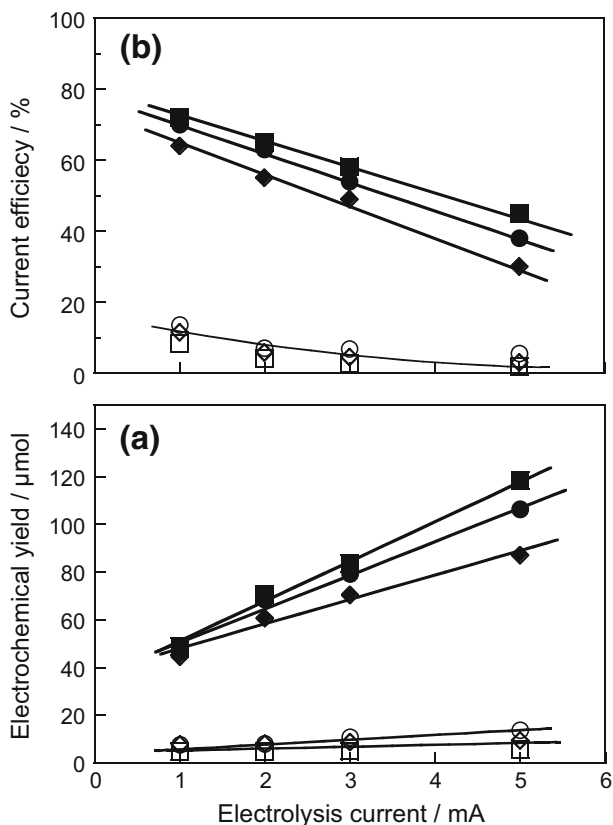


Fig. 6 Effects of electrolysis current on electrochemical carbonylation of PhOH by Pd (in situ Si*t*-Bu) electrocatalyst, **a** current efficiency of DPC and CO₂ and **b** electrochemical yields of DPC and CO₂ Au wire (DPC: filled diamond, CO₂: open diamond), Au/graphene-3(H₂) + VGCF (DPC: filled circle, CO₂: open circle) and Au/graphene-3 (NaBH₄) + VGCF (DPC: filled square, CO₂: open square)

was 47 % at the Au/graphene-3(NaBH₄) anode at 5 mA. Other byproducts could not be detected. Use of the remaining current could not be revealed.

As described above, the current efficiency at 5 mA was not enough; however, the Au/graphene-3(NaBH₄) + VGCF anode was most superior for the DPC formation among the anodes tested. If smaller Au particles on graphene-3 are prepared, a higher current efficiency and yield of DPC would be accomplished at high electrolysis currents.

Conclusions

The electrochemical carbonylation of PhOH to DPC catalyzed by Pd (in situ Si*t*-Bu) electrocatalyst using the Au/carbon anodes (carbon: AC, XC72, KB_{JD} and graphene-1, -2, -3) was studied at galvanostatic electrolysis conditions. The most

effective carbon support for the DPC formation was graphene-3, though the average crystalline sizes of Au on AC, XC72, KB_{JD}, graphene-3 were very similar (54–57 nm). Effects of Au loading and reduction method of Au/graphene-3 on the DPC formation were studied and 10.0 wt% Au/graphene (NaBH₄) material was superior. This material was characterized by XRD and TEM analyses and Au crystalline size of 26 nm and small particles were observed. At sever electrolysis condition of 5 mA, a fairly good current efficiency of 45 % was obtained for the DPC formation. These data propose that graphene-3-supported Au particles of a few nanometer material will be an effective anode, which accelerates electrochemical oxidation of Pd⁰(in situ SI \bar{t} -Bu) and achieves selective formation of DPC at higher electrolysis currents.

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