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LETTERS

"Single" Pd(0) Atom Encapsulated in Multiporphyrin Arrays as a Highly Efficient Heterogeneous Catalyst

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Well-defined "single" Pd(0) atoms were encapsulated in Pd-mediated multiporphyrin arrays and used as a catalyst. Compared with the Pd(0) nanoparticles prepared from dilute K_2PdCl_4 solution, the encapsulated Pd(0) atoms showed much higher catalytic activity for photoinduced hydrogen evolution.

Palladium-catalyzed reactions such as hydrogen production, hydrogenation, and the Heck reaction have attracted much attention because of their importance to clear energy development and organic synthesis applications.[1,2] Although many Pd(0)-based catalysts are well established, catalyst separation and enhancement of catalytic activity are still large challenges and continue to be the focus of intense research. Over the last three decades, several elegant approaches have been explored to overcome the limitation of catalyst separation, for example, aqueous and fluorous biphase catalysis,[3] reactions in supercritical media,[4] and catalyst immobilization onto solid supports.[5] However, for biphase catalysis including immobilized Pd(0) particles, particle size often plays an important role in catalytic activity since hydrogen or organic molecules interacting with small palladium clusters is a strong function of cluster size.[6] To achieve a highly active palladium catalyst, recently many palladium nanoparticles have been prepared and used as an efficient catalyst.[7]

We present here a novel methodology to prepare an encapsulated Pd(0) single atom in multiporphyrin arrays to be used in catalyzing hydrogen production. We have previously reported the preparation of Pd-mediated multiporphyrin arrays at the air−water interface and directly on solid supports.[8] Multilayers of the multiporphyrin arrays, especially those directly assembled on the solid supports, showed a well-defined chemical structure and high thermal and chemical stability and were expected to a possibility for practical applications. In the present work, the linkage, the Pd^{2+} ion, in the multiporphyrin arrays was reduced by H_2 in water, which results in well-separated Pd(0) atoms in the organized ultrathin films (Scheme 1). The porphyrin that was used for the assembly was zinc-5,10,15,20-tetra(4-pyridyl)-21*H*,23*H*-porphine (ZnTPyP). Experimental details on the preparation of multilayers can be found in our previous paper.[8d]

The encapsulated Pd(0) atoms were used as a catalyst for photoinduced hydrogen evolution with zinc-5,10,15,20-tetra(4-methylpyridyl)-21*H*,23*H*-porphine tetrakis(methochloride) (ZnTMPyP) as a photosensitizer, ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid, disodium salt (EDTA) as an electron donor, and methyl viologen (MV^{2+}) as an electron carrier.[9] To evaluate the catalytic activity of the present Pd(0) atoms, we compared the hydrogen evolution rate with the use of Pd(0) nanoparticles under the same experimental conditions. These Pd(0) nanoparticles were prepared by reducing 0.02 mM and 0.2 mM K_2PdCl_4 aqueous solutions with H_2 gas.[10] Figure 1 shows two photographs obtained from field emission scan electron microscopy (FESEM) that indicate that the average particle sizes are about 20−30 and 40−50 nm, respectively.

For the H_2 evolution measurement with encapsulated Pd(0) atoms as a catalyst, the glass plates with one to four layers of Pd−ZnTPyP multiporphyrin arrays were assembled and reduced

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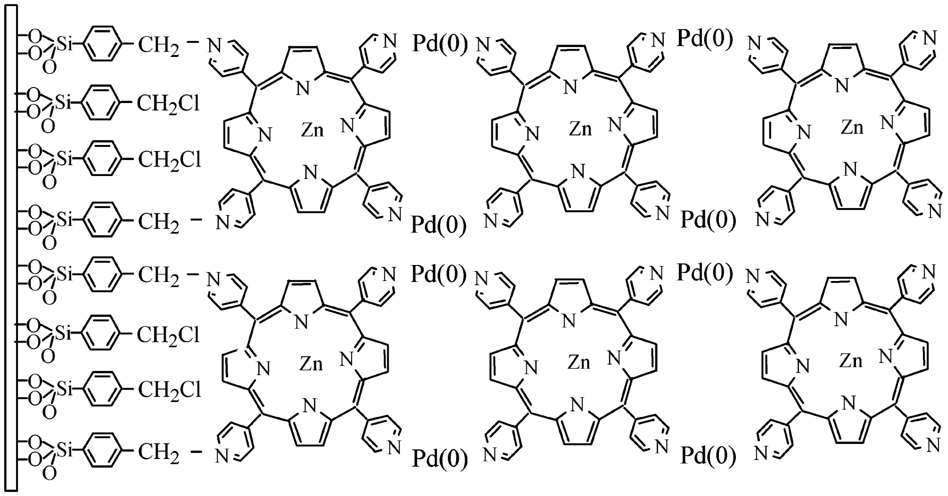
SCHEME 1: Schematic Illustration of Encapsulated Pd(0) Atoms in the Multiporphyrin Arrays



by H_2 gas in water. A hydrogen electrode was used to detect the hydrogen concentration produced. As an example, Figure 2 shows a plot of hydrogen concentration versus illumination time with a piece of Pd(0)-encapsulated multiporphyrin layer-coated glass as a catalyst. An almost linear increase in the hydrogen evolution was recorded under illumination. The hydrogen evolution rates were calculated according to the hydrogen concentration 20 min after illumination, and the obtained data are summarized in Tables 1 to 3.

To obtain the hydrogen evolution rate per nanogram of Pd(0), the surface coverage of Pd(0) was calculated according to the

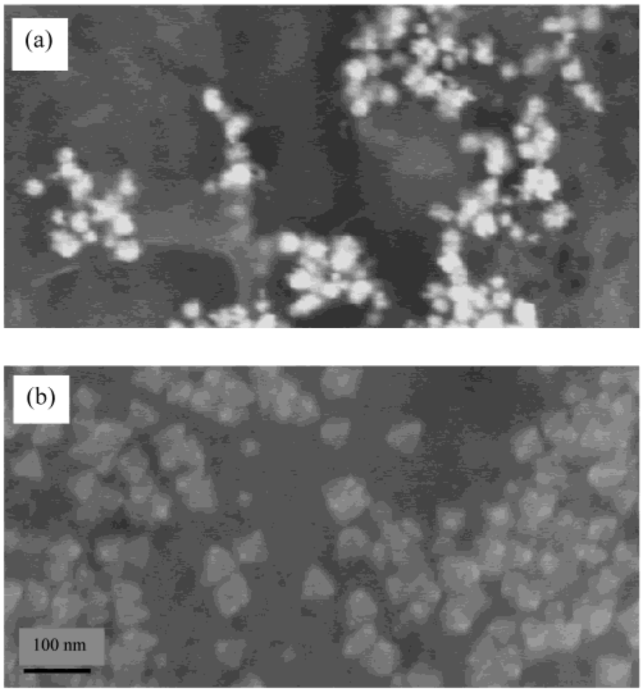


Figure 1. FESEM images of Pd(0) nanoparticles prepared from (a) 0.02 mM and (b) 0.2 mM K_2PdCl_4 solution.

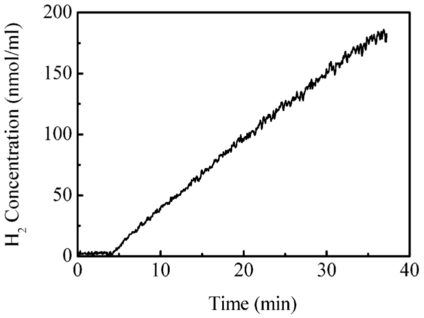


Figure 2. Plot of hydrogen concentration vs illumination time. The reaction was preformed in a 10 mM tris-HCl buffer (pH 7.4) containing 0.2 mM ZnTMPyP, 15 mM EDTA, 1 mM MV^{2+}, and a piece of glass coated with encapsulated Pd(0) atoms.

TABLE 1: Hydrogen Evolution Rate with the Encapsulated Pd(0) Atoms as a Catalyst

layer numbers	quantity of Pd(0) atoms on glass surface (ng)[a]	H_2 evolution rate (nmol mL^{-1} min^{-1})	H_2 evolution rate per nanogram of Pd(0) (pmol mL^{-1} min^{-1} ng^{-1})
1	18.4	1.97	110
	49.8	5.18	100
	66.7	6.04	91
2	44.4	4.01	90
	88.0	9.00	102
	163	12.2	75
3	63.8	4.70	74
	145	9.25	64
	244	20.4	84
4	75.1	7.40	98
	175	17.3	99
	372	32.7	88

[a] Estimated from the glass area used and the surface density of Pd in the multiporphyrin arrays.

TABLE 2: Hydrogen Evolution Rate with Pd(0) Nanoparticles Prepared from 0.02 mM K_2PdCl_4 as a Catalyst

quantity of Pd(0) (ng)	H_2 evolution rate (nmol mL^{-1} min^{-1})	H_2 evolution rate per nanogram of Pd(0) (pmol mL^{-1} min^{-1} ng^{-1})
65	1.30	20
195	1.42	7.3
650	2.34	3.6
1300	3.89	3

TABLE 3: Hydrogen Evolution Rate with Pd(0) Nanoparticles Prepared from 0.2 mM K_2PdCl_4 as a Catalyst

quantity of Pd(0) (ng)	H_2 evolution rate (nmol mL^{-1} min^{-1})	H_2 evolution rate per nanogram of Pd(0) (pmol mL^{-1} min^{-1} ng^{-1})
650	2.16	3.3
1950	2.90	1.5
6500	4.93	0.76
13000	9.25	0.71

surface coverage of ZnTPyP in the multiporphyrin monolayer, 2.4×10^{-10} mol/cm[2,8d], and the composition of Pd−ZnTPyP multiporphyrin arrays (molar ratio of Pd to ZnTPyP, 2:1). The data are summarized in Table 1. The hydrogen evolution rate per nanogram of Pd(0) nanoparticles was also calculated, and the data are listed in Tables 2 and 3.

A comparison of the data in Table 1 with those in Tables 2 and 3 reveals the following important features. First, the encapsulated Pd(0) atoms show that the average hydrogen evolution rate per nanogram of Pd(0) is around 100 pmol mL^{-1} min^{-1} ng^{-1} whereas that of the Pd(0) nanoparticles is in the range of 0.2−20 pmol mL^{-1} min^{-1} ng^{-1}. That is, the encapsulated Pd(0) atoms are of much higher catalytic activity than the Pd(0) nanoparticles. Considering the size of the nanoparticles, we can find that the catalytic activity decreases as the size of the nanoparticles increases. This is agreement with Li et al.'s results in which higher catalytic activity was observed for smaller Pd(0) nanoparticles in the Suzuki reaction.[6c] For Pd(0) in the assembled films, Pd(0) atoms are well-separated by porphyrin macrcycles, thus we can suppose that these Pd(0) atoms are like single atoms, which may be the "smallest particles" and an ideal catalyst. Second, the hydrogen evolution rate is almost in proportion to the amount of Pd(0) when the encapsulated Pd(0) multilayer was used as a catalyst (Table 1) whereas only a slight increase was recorded when increasing amounts of Pd(0) nanoparticles were used (Tables 2 and 3). As a consequence, the hydrogen evolution rate per nanogram of Pd(0) remains constant with increasing amounts of encapsulated Pd(0) atoms (Table 1) whereas it decreases greatly for the nanoparticles (Tables 2 and 3). This decrease should not be due to the limit of the reactants since the amounts of EDTA, ZnTMPyP, and MV^{2+} are much larger than that of Pd(0) nanoparticles. The constant hydrogen evolution rate is another advantage of the encapsulated Pd(0) catalyst.

In summary, we have demonstrated that single Pd(0) atoms encapsulated in the ultrathin organized multiporphyrin arrays are of high catalytic activity—even higher than that of the Pd(0) nanoparticles. Because the encapsulated Pd(0) atoms are immobilized on the glass surface, the catalyst separation is much easier. These features indicate that the present encapsulated, well-separated metals may be developed as efficient and easily controlled catalysts.

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References and Notes

(1) (a) Gao, J. S.; Arunagiri, T.; Chen, J. J.; Goodwill, P.; Chyan, O. *Chem. Mater.* **2000**, *12*, 3495−3500. (b) Winkler, K.; de Bettencourt-Dias, A.; Balch, A. L. *Chem. Mater.* **2000**, *12*, 1386-1392. (c) Shah, N.; Panjala, D.; Huffman, G. P. *Energy Fuels* **2001**, *15*, 1528−1534. (d) King, R. B.; Bhattacharyya, N. K.; Wiemers, K. D. *Environ. Sci. Technol.* **1996**, *30*, 1292−1299. (e) King, R. B.; Bhattacharyya, N. K.; Smith, H. D.; Wiemers, K. D. *Environ. Sci. Technol.* **1997**, *31*, 984−992. (f) Jaramillo, T. F.; Ivanovskaya, A.; McFarland, E. W. *J. Comb. Chem.* **2002**, *4*, 17−22.

(2) (a) Amatore, C.; Jutand, A. *Acc. Chem. Res.* **2000**, *33*, 314−321. (b) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009−3066. (c) Hierso, J. C.; Feurer, R.; Kalck, P. *Chem. Mater.* **2000**, *12*, 390−399. (d) Farthing, C. N.; Kočovský, P. *J. Am. Chem. Soc.* **1998**, *120*, 6661−6672. (e) Koizumi, T.; Sakamoto, J.; Gondo, Y.; Endo, T. *Macromolecules* **2002**, *35*, 2898−2902.

(3) (a) Bergbreiter, D. E.; Osburn, P. L.; Wilson, A.; Sink, E. M. *J. Am. Chem. Soc.* **2000**, *122*, 9058−9064. (b) Rocaboy, C.; Gladysz, J. A. *Org. Lett.* **2002**, *4*, 1993−1996.

(4) (a) Ohde, H.; Wai, C. M.; Kim, H.; Kim, J.; Ohde, M. *J. Am. Chem. Soc.* **2002**, *124*, 4540−4541. (b) Hancu, D.; Green, J.; Beckman, E. J. *Ind. Eng. Chem. Res.* **2002**, *41*, 4466−4474. (c) Hancu, D.; Beckman, E. J. *Ind. Eng. Chem. Res.* **1999**, *38*, 2833−2841.

(5) (a) Liu, J.; Alvarez, J.; Ong, W.; Roman, E.; Kaifer, A. E. *Langmuir* **2001**, *17*, 6762−6764. (b) Okitsu, K.; Yue, A.; Tanabe, S.; Matsumoto, H. *Chem. Mater.* **2000**, *12*, 3006−3011. (c) Ebitani, K.; Fujie, Y.; Kaneda, K. *Langmuir* **1999**, *15*, 3557−3562.

(6) (a) Efremenko, I.; German, E. D.; Sheintuch, M. *J. Phys. Chem. A* **2000**, *104*, 8089−8096. (b) Fayet, P.; Kaldor, A.; Cox, D. M. *J. Chem. Phys.* **1990**, *92*, 254−261. (c) Li, Y.; Boone, E.; El-Sayed, M. A. *Langmuir* **2002**, *18*, 4921−4925.

(7) (a) Chechik, V.; Crooks, R. M. *J. Am. Chem. Soc.* **2000**, *122*, 1243−1244. (b) Li, Y.; El-Sayed, M. A. *J. Phys. Chem. B* **2001**, *105*, 8938−8943. (c) Lu, P.; Teranishi, T.; Asakura, K.; Miyake, M.; Toshima, N. *J. Phys. Chem. B* **1999**, *103*, 9673−9682. (d) Rahim, E. H.; Kamounah, F. S.; Frederiksen, J.; Christensen, J. B. *Nano Lett.* **2001**, *1*, 499−501. (e) Li, Y.; Hong, X. M.; Collard, D. M.; El-Sayed, M. A. *Org. Lett.* **2000**, *2*, 2385−2388.

(8) (a) Qian, D. J.; Nakamura, C.; Miyake, J. *Langmuir* **2000**, *16*, 9615−9619. (b) Qian, D. J.; Nakamura, C.; Miyake, J. *Thin Solid Films* **2001**, *397*, 266−275. (c) Qian, D. J.; Nakamura, C.; Miyake, J. *Chem. Commun.* **2001**, 2312−2313. (d) Qian, D. J.; Nakamura, C.; Ishida, T.; Wenk, S.-O.; Wakayama, T.; Takeda, S.; Miyake, J. *Langmuir* **2002**, *18*, 10237−10242.

(9) Qian, D. J.; Wenk, S.-O.; Nakamura, C.; Wakayama, T.; Zorin, N.; Miyake, J. *Int. J. Hydrogen Energy* **2002**, *27*, 1481−1487.

(10) Henglein, A. *J. Phys. Chem. B* **2000**, *104*, 6683−6685.