Supercritical CO₂ as a Solvent for Synthesis of Nanoporous Materials

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Nanoporous platinum, silica, and titania have been made using activated carbon templates in a supercritical solvent. Precursors were dissolved in supercritical carbon dioxide and attached to an activated carbon template. After the activated carbon in the sample coated with materials was removed by calcination or oxygen plasma treatment, samples faithfully that replicated not only macroscopic shape (e.g., fiber, powder, granule) but also porous structure on the nanometer scale were obtained. In addition, we confirmed that such a faithful reflection in the nanoscale structure is realized only by use of a supercritical fluid as a solvent, in comparison with impregnation in a liquid.
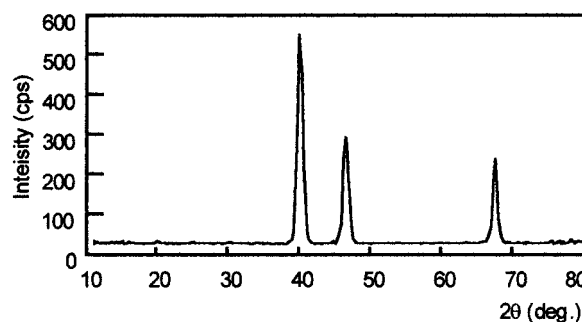
Introduction

In a conventional coating process using a liquid solvent, the high viscosity of the liquid prevents penetration into narrow gaps. Even when gaseous phases under their critical temperatures are used, they capillary condense in fine spaces. The use of supercritical fluids is greatly focused on their physicochemical properties. They have low viscosities and high diffusivities. In addition, they never condense to the liquid phase when they are pressurized. The solubility can be controlled by changing temperature and pressure or by adding entrainers. Thus, supercritical fluids are expected to carry effective amounts of precursors into small spaces.

Several studies have focused on deposition[1-3] or impregnation[4-11] using supercritical fluids. Although wood,[4] ceramics,[5,6,10] or polymers[7-11] have been used as a substrate during impregnation using supercritical fluids, they have only macropores.

We have demonstrated that precursors of metal or metal oxides are impregnated into activated carbon with micro- and mesopores as a template by using supercritical carbon dioxide and that nanoporous materials are obtained after the activated carbon template is removed by calcination or oxygen plasma treatment.[12-14] In the present work, the advantage of using a supercritical fluid as a solvent for replication of the nanoscale structure and shape of the template will be demonstrated. In addition, supercritical fluids will be shown to be an effective solvent for chemical reactions such as sol–gel reactions in nanospaces.

Experimental Section

The metal or metal oxide precursor, along with the entrainer, was placed in a stainless steel vessel (50 mL). A stainless steel cage with 1 g of activated carbon template was placed in the vessel. The activated carbon template was not in contact with the precursor and entrainer in the liquid phase. The closed vessel was filled with CO₂ and heated in an oil bath. The treatment conditions are shown in Table 1. After treatment in the

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Figure 1. XRD patterns of platinum sample treated in oxygen plasma after treatment in the supercritical fluid.

supercritical fluid, the recovered samples were calcined in air flow at 873 K for 6 h. Activated carbon was also removed by oxidation in oxygen plasma at 453 K (at maximum). For comparison, samples were prepared without supercritical solvents. They were soaked in liquid precursor [tetraethyl orthosilicate (TEOS)] or liquid solvent with precursor (acetone with platinum acetylacetonate or 2-propanol with titanium isopropoxide).

TGA patterns were collected on a Rigaku Thermoplus TG8120 thermogravimetric analyzer. The temperature was increased at a rate of 2 K/min, and the samples were heated to 1273 K in air flow. X-ray diffraction spectra were recorded on a Rigaku RINT-2000 instrument with Cu Kα radiation. Nitrogen sorption isotherms were obtained at 77 K on a Quantacrome AUTOSORP-1-MP. Scanning electron microscope (SEM) observations were performed using a JEOL JSM-890 scanning electron microscope. Transmission electron microscope (TEM) images were obtained on a JEOL transmission electron microscope.

Results and Discussion

Nanoporous Platinum. The X-ray diffraction pattern of platinum sample oxidized in plasma after the impregnation of platinum acetylacetonate in supercritical fluids is shown in Figure 1. In Figure 1, three characteristic peaks corresponding to (110), (200), and (220) peaks for metallic platinum can be observed. No XRD peaks from the activated carbon template can be observed in the XRD pattern for the platinum sample.

Table 1. Sample Preparation Conditions in Supercritical Solvents

	precursor	entrainer	temp (K)	pressure (MPa)	time (h)
platinum	Pt(acetylacetonate)$_2$, 0.5 g	acetone, 5 mL	423	32	2
silica	tetraethylorothosilicate, 3 mL	none	393	26	2
titania	titanium isopropoxide, 5 mL	isopropranol, 5 mL	423	32	24
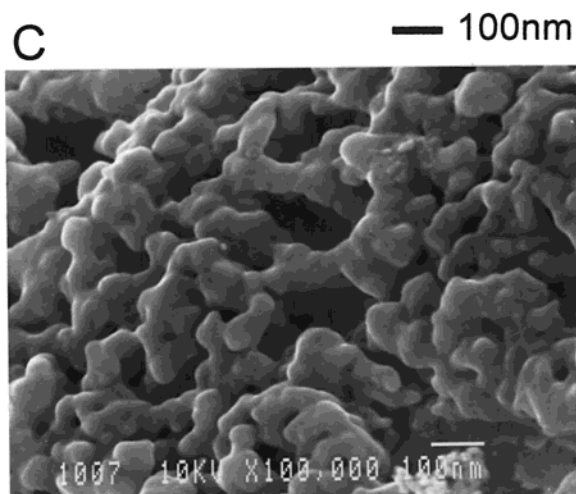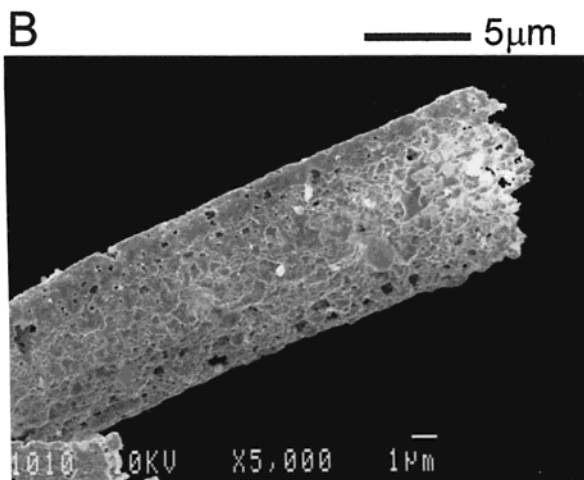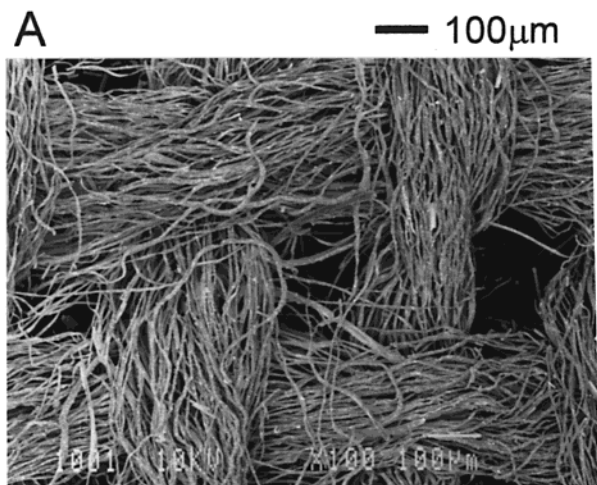
Figure 2. Scanning electron microscopy (SEM) images of platinum sample treated in oxygen plasma after treatment in the supercritical fluid.

The crystalline size of the platinum metal calculated from the half widths of these three peaks from the platinum metal was estimated to be ca. 10 nm.
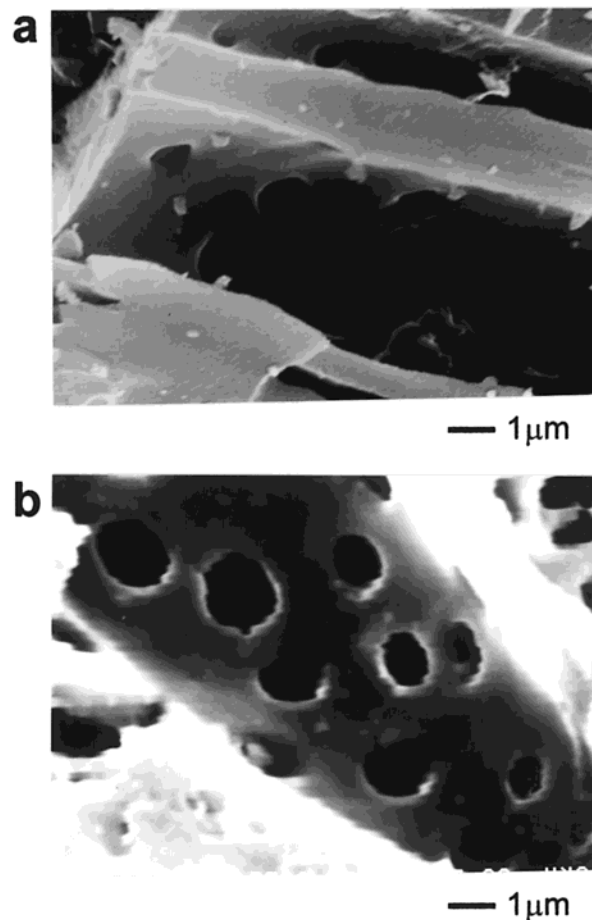
Figure 3. Scanning electron microscopy (SEM) images of (a) activated carbon from palm nutshell GC-2 and (b) silica sample calcined in air at 873 K after treatment in the supercritical fluid.
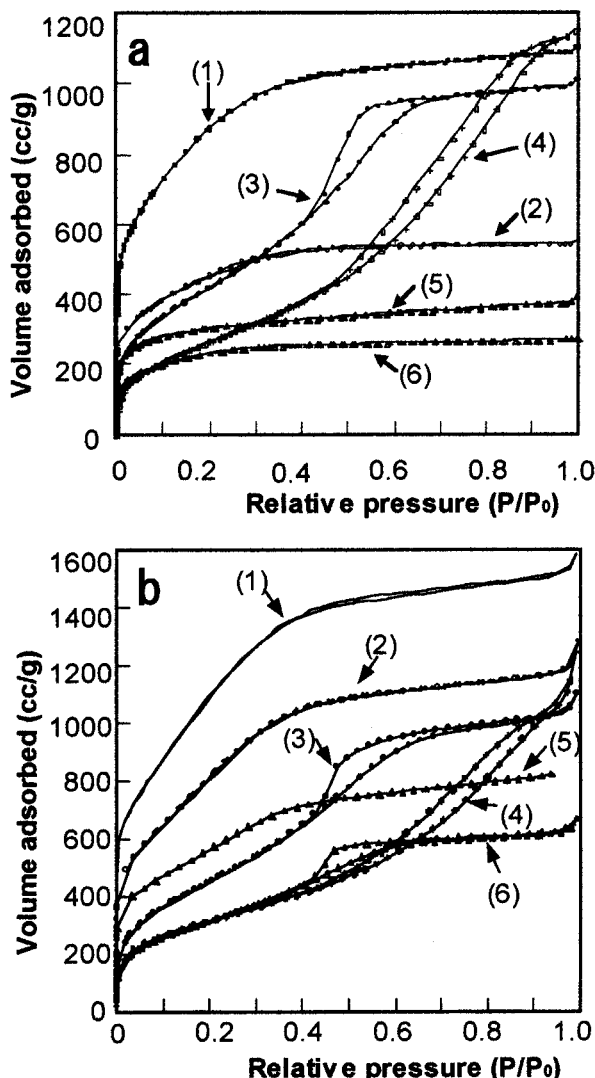
TGA results for the platinum sample oxidized in plasma after treatment in the supercritical fluid shows that the weight loss between 423 and 1273 K in air flow is less than 3 wt %. This confirms that no activated carbon template is left in the platinum sample.

SEM images of the platinum sample are shown in Figure 2. The cloth and fibrous shape of activated carbon is replicated in the platinum sample. Platinum fibers consist of fused particles that are 20−80 nm in diameter.

The BET surface area of the platinum sample determined from nitrogen adsorption isotherms is 47 m^2/g. This value is twice as large as that for platinum black.

Pt precursors were carried into pores of activated carbon in the impregnation process in SCFs. These precursors would be partly reduced to Pt metal after reaction with adsorbed water molecules or functional units on the surface of the activated carbon. During the treatment in oxygen plasma, the sample was heated to 453 K (at maximum), so the Pt precursors would be reduced to Pt metal.
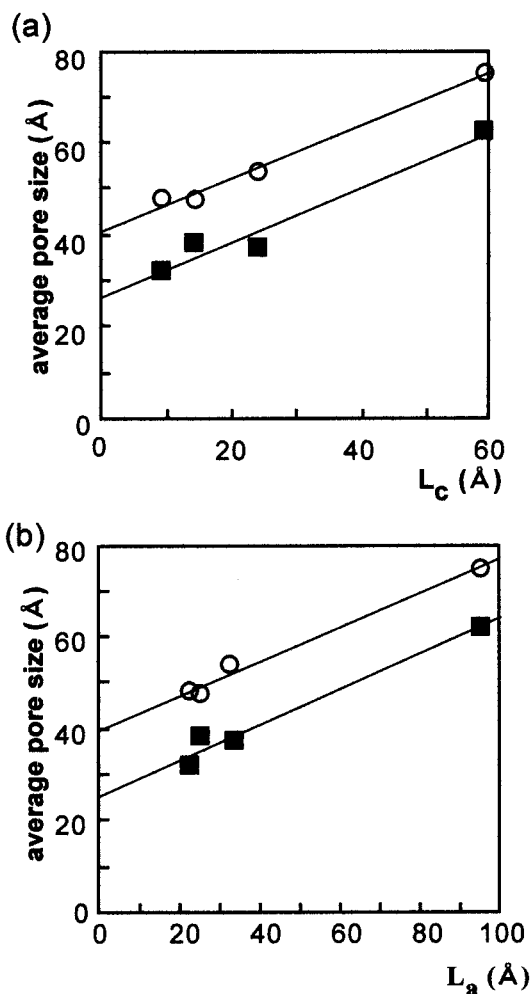
Nanoporous Silica. The plant structure of the activated carbon template from palm nutshell (Takeda Pharm. Chem. Co. Ltd., GC-2) can be replicated in a silica sample calcined in air after impregnation of

Figure 5. Relations between the size of the crystallites of the activated carbon along the *a* axis L_a and the *c* axis L_c and the average pore size of the silica samples after removal of the activated carbon by calcination in air (■) or in oxygen plasma (○).

Figure 4. (a) Nitrogen adsorption−desorption isotherms for (1) activated carbon fibers A-20, (2) A-20 coated with silica in supercritical CO_2, (3) sample after removal of A-20 by calcination in air from silica-coated A-20 in supercritical CO_2, (4) sample after removal of A-20 by calcination in oxygen plasma from silica-coated A-20 in supercritical CO_2, (5) A-20 coated with silica immersed in liquid silica precursor, tetraethlorthosilicate (TEOS), and (6) sample after removal of A-20 by calcination in air from silica-coated A-20 in liquid TEOS. (b) Nitrogen adsorption−desorption isotherms for (1) activated carbon powders M-30, (2) M-30 coated with silica in supercritical CO_2, (3) sample after removal of M-30 by calcination in air from silica-coated M-30 in supercritical CO_2, (4) sample after removal of M-30 by calcination in oxygen plasma from silica-coated M-30 in supercritical CO_2, (5) M-30 coated with silica immersed in liquid silica precursor, tetraethlorthosilicate (TEOS), and 6) sample after removal of M-30 by calcination in air from silica-coated M-30 in liquid TEOS.

tetraethyl orthosilicate (TEOS) in supercritical fluids, as shown in Figure 3.

Nitrogen adsorption−desorption isotherms of silica samples prepared using activated carbon fibers with smaller pores (Osaka Gas Chem. Co. Ltd., A-20) and activated carbon powders with larger pores (Osaka Gas Chem. Co. Ltd., M-30) are shown in Figure 4. The shape of the isotherm for activated carbon fibers A-20 is identical to that for microporous materials [Figure 4a (1)]. The total pore volume decreases after the sample is coated with silica in supercritical fluids [Figure 4a (2)]. This is due to the filling of part of the micropores of the activated carbon. The pore volume increases after

removal of the activated carbon template by calcination in air or oxidation in plasma [Figure 4a (3), (4)]. A hysteresis between the adsorption and desorption isotherms beyond $P/P_0 = 0.4$ indicates the existence of mesopores in the Barret−Joyner−Hallender with pore sizes of 3.8 and 4.8 nm in the samples calcined in air and oxidized in plasma, respectively. The pore volume decreased significantly after the sample was soaked in TEOS [Figure 4a (5)]. The silica sample soaked in TEOS has a small amount of surface area even after removal of the activated carbon template. No manifested uptake indicating the existence of micropores or mesopores can be observed in the isotherm for the silica sample [Figure 4a (6)]. It is assumed that silica products cover only the entrances of the pores in the activated carbon template and that they do not fill deeply into the pores, resulting in an extensive reduction in the pore volume of the sample soaked in liquid TEOS and small pore volume in the silica sample after removal of the activated carbon.

A small adsorption−desorption hysteresis in the isotherm for activated carbon powders M30 can be seen [Figure 4b (1)]. Although the total pore volume decreases because of the treatment in supercritical fluids [Figure 4b (2)], the amount of decrease is not as significant as that for BW-103 or A-20. After the activated carbon is removed, hystereses in the isotherms are observed for the silica samples, and the total pore

Table 2. Characterization Data for Nanoporous Materials

material	activated carbon template	method for removal of activated carbon template	BET surface area (m^2/g)	total pore volume (cc/g)	structure
platinum	BW103	treatment in oxygen plasma	47	0.07	metal
silica	A-20	calcination in air at 873 K	984	1.57	amorphous
	A-20	treatment in oxygen plasma	733	1.80	amorphous
	M30	calcination in air at 873 K	1377	1.71	amorphous
	M30	treatment in oxygen plasma	889	1.93	amorphous
titania	A-20	treatment in oxygen plasma	387	0.68	anatase

volumes are almost the same as those for the silica-coated sample using supercritical fluids. The hysteresis is also observed for the silica sample prepared by the immersion method in liquid TEOS [Figure 4b (6)].

The structure of activated carbon is thought to be elucidated by Franklin's view of pregraphitic carbon.[15] The porous structure of activated carbon is composed of randomly stacked graphene crystallites. The crystallite sizes along with a axis L_a and c axis L_c are calculated from the half width of the (10) and (002) lines in the XRD patterns. The relations between the crystallite sizes L_a and L_c of the activated carbon template and the pore sizes of the silica samples calcined in air or oxidized in plasma after silica coating in supercritical fluids are shown in Figure 5. As the crystallite sizes L_a and L_c increase, the pore size of the silica samples increases, as seen in Figure 5. They are on the same order of magnitude (nanometer). The actual sizes of the structural units of activated carbon would be a little larger than that estimated from the XRD results because disordered structures and functional units are included in the activated carbon. The pore sizes of the silica samples calcined in air are a little smaller than those of the silica samples oxidized in plasma. In the oxidation in plasma, samples are heated to 453 K at the maximum. Rearrangement in the silica structure during removal of the activated carbon template in the plasma would be less than that in the calcined samples. The microscopic structures of the activated carbon template are reflected in the silica samples oxidized in plasma more faithfully than in the calcined silica samples.

Schematic drawings of nanoscale casting in supercritical fluids (NC-SCF) are shown in Figure 6. The porous structures of the activated carbon template are composed of randomly stacked graphene crystallites (Figure 6a). Silica precursor dissolved in supercritical CO_2 is carried into pores and hydrolyzed into a silica network through reactions with adsorbed water and functional units on the surface of the activated carbon template (Figure 6b). The pores with sizes corresponding to the sizes of carbon crystallites of the activated carbon template remain in the silica samples after removal of the activated carbon template (Figure 6c).

Nanoporous Titania. The structure and fibrous shape of the activated carbon template was replicated in titania samples after removal of the activated carbon template, as for nanoporous platinum or silica.

The sample oxidized in plasma or calcined in air at 873 K for 6 h after impregnation of titanium isopropoxide in SCFs shows characteristic X-ray diffraction peaks that correspond to peaks for anatase. The sample oxidized in plasma shows broad peaks for anatase, whereas sharp peaks are observed for the calcined sample.

The TGA results for the titania sample oxidized in plasma or calcined in air shows that weight loss between 473 and 1273 K in air flow is less than 4 wt %. This confirms that no activated carbon template is left in the titania samples.
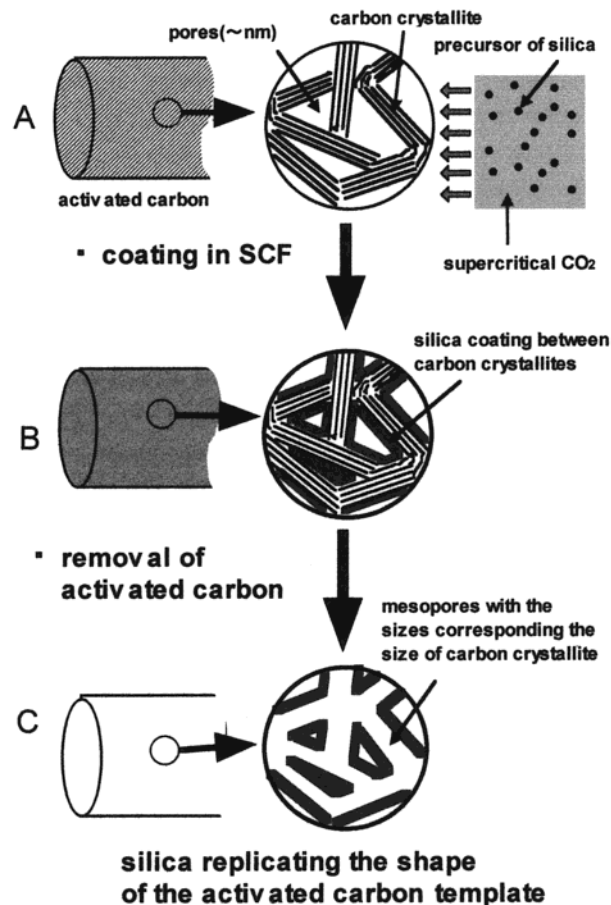
Figure 6. Possible mechanistic pathway for the formation of silica replicas.

The domain size of the titania samples after the activated carbon template is removed by oxidation in plasma is 5−15 nm, as observed in TEM images.

The BET surface area of the titania sample oxidized in plasma was as high as 387 m^2/g, as estimated from nitrogen sorption results.

Characterization data for the nanoporous materials are summarized in Table 2. Silica samples calcined in air or oxidized in plasma after being coated with silica in supercritical fluids have mesopores in the size range corresponding to the size of the carbon crystallites of the activated carbon templates. In the platinum or titania coating process in supercritical fluids, precursors are carried into pores of the activated carbon and partly hydrolyzed on the surface of the activated carbon through reactions with adsorbed water and functional units. During removal of the activated carbon template, hydrolyzed precursors are crystallized into platinum metal or titania anatase. Rearrangements due to crystallization result in less accurate replication than is found silica samples. Platinum or titania samples have no mesopores in the size range corresponding to the size of the carbon crystallites of the activated carbon tem-

plates. However, hydrolyzed precursors are dispersed on the surface of the activated carbon templates so highly that the surface areas of platinum or titania samples are still high even after the activated carbon template is removed.

The platinum sample worked as a catalyst for CO oxidation. A nitrogen carrier stream (3300 mL/min) containing 1% of CO, 1% of H_2, and 7.5% of O_2 was introduced into a reaction tube in which 13.3 mg of platinum sample had been placed. The sample was heated to 773 K at 12 K/min, and 50% of the CO was converted to CO_2 at 475 K.

Conclusion

Nanoporous materials have been synthesized using activated carbon templates in supercritical solvents. The results suggest the great advantage of supercritical fluids for fabrication of ceramic or metal replicates of templates with complex structures, such as activated carbon. This process denoted "Nanoscale Casting using Supercritical Fluids (NC-SCF)" can be applied to the synthesis of not only nanoporous ceramics but also nanoporous metals. This process is expected to be a versatile route to functional ceramics (adsorbents, photocatalysts, capacitors, solar cells, etc.) and catalysts (synthesis of carriers, impregnation of precious metals, or promoter) whose structures can be skillfully controlled through the choice of templates.

Acknowledgment

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