Repeated self-assembly process to produce three-dimensional inverse opal structure for catalysts

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Abstract

This study aims to apply self-assembly process of particles to fabrication of inverse opal structure which improves the performance of catalyst. The process consists of two steps dip-coating. The first one is fabrication of sacrificial silica particles of 1 or 2 μm diameter. The second one is fabrication of silver nano-particles for catalyst. After these processes, silica particles were dissolved to fabricate inverse opal or porous structures. Optimal process condition is discussed as well as the verification of catalyst.

1 Introduction

Catalyst structure should have wide surface area while keeping the easiness of the media flow around the structure. Inverse opal is one of the candidates for such structures. Thus, this paper proposes an application of self-assembly process to produce Ag nano-particles inverse opal structure which has pores in three-dimensional packed structure.

2 Procedure to produce inverse opal structure

Figure 1 shows schematic image of repeated dip-coating process to fabricate inverse opal structure. Dipping and extracting a substrate from suspension that contains fine particles, packed structure can be assembled [1, 2]. The number of layers can be changed from monolayer to multilayer by changing the process conditions. Repeating this process with different suspension containing smaller particles, smaller particles fill the vacant space between the particles assembled beforehand. The important point is that catalyst particles can be selectively allocated to the contact area of larger particles as described later. Dissolving the larger particles, inverse opal structure made of smaller particles can be obtained. The larger particles are completely removed during the process, thus, they should be called sacrificial particles.

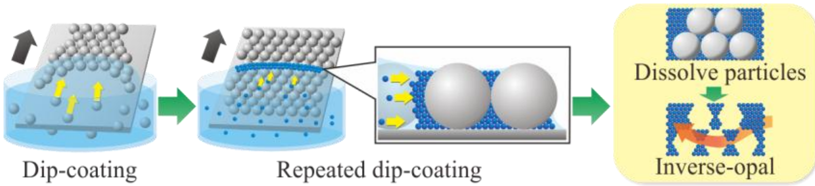
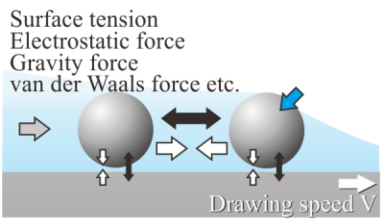


Figure 1: Schematic of repeated dip-coating process to produce inverse opal structure

3 Assembly of sacrificial particles – first dip-coating –

Close-packed structure is necessary at the first coating process because the contact area between the particles becomes opening for the media flow. However, particles in solution are affected by various forces during the assembly process. Figure 2 shows interactions between particles and particle-substrate. Easily controllable parameters in the process are electrostatic force and drawing speed. The electrostatic force can be changed by adding solvent of specific pH. Typical conditions are shown in table in the figure. Silica particles were used as sacrificial particles.



Sacrifice particles	SiO_2 1, 2 μm
Particles concentration	1 wt%
Solvent	Phosphate buffer
Solvent pH	5.8 ~ 7.0
Solvent concentration	0.1~0.01 M
Drawing speed V	10 ~ 200 μm/s
Drawing angle	30 ~ 90 degrees

Figure 2: Interactions between particles and particle-substrate

Figure 3 shows the various cases of assembled particles. Upper left figure shows the case of low solvent concentration and high pH. Particles formed islands with packed structure. In contrast, upper right figure shows the case of high concentration and low pH. Particles formed multi-layer structure. It is found that electrostatic repulsion force can be controlled by changing the combination of solvent concentration and pH. Lower left figure shows the case of fast drawing speed. Particles formed island due to fast evaporation speed. It was found that particles can be assembled on the substrate in various forms by tuning drawing speed and suspension condition.

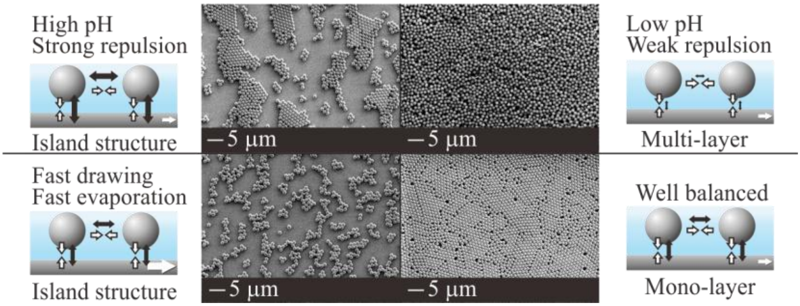
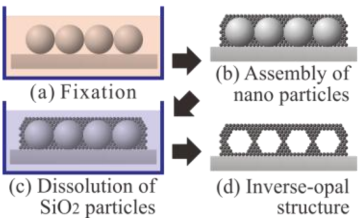


Figure 3: Schematic and SEM photos of sacrificial particles assembly

4 Fabrication of catalyst structure – second dip-coating –

Figure 4 shows the detailed procedure to fabricate inverse opal structure together with tabulated conditions. Sacrificial particles were fixed to the substrate producing chemical bond with soaking in hydrochloric acid. After the second dip-coating of nano-silver particles for catalyst, silica particles were dissolved by soaking the structure in hydrofluoric acid.



Nano particles	Ag 10 nm ~
Fixing solution	Hydrochloric acid
Fixation time	30 min
Drawing speed	5 μm/s
Drawing angle	90 degrees
Solvent for dissolution	Hydrofluoric acid
Dissolution time	~ 30 s

Figure 4: Procedure for Ag inverse-opal structure

Figure 5 shows the results of inverse opal structure fabrication. The left SEM photo shows the structure fabricated using ϕ1μm silica particle monolayer. It is found that pores of approximately 1 μm spacing were fabricated. Structural defect is attributable to defects in assembly of sacrificial particles. The right SEM photo shows the case of SiO_2 2 μm in multilayer. The pores with 2 μm spacing were confirmed. Opening of the structure near the contact area between sacrificial particles can be observed.

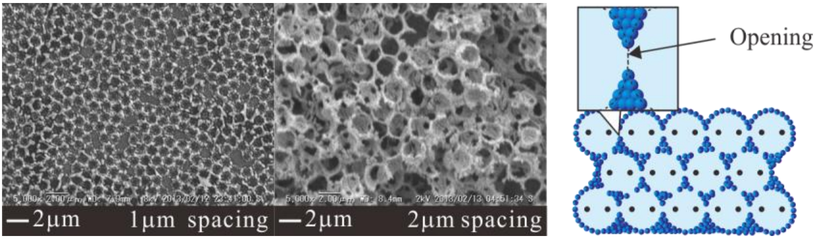


Figure 5: SEM photos of Ag inverse opal structure

We have applied this kind of structure to a gas sensor [3]. Assembled structures of SnO_2 particles work as gas sensor for ethanol for example by changing electric resistance between them according to the concentration of nearby gas molecules. Inverse opal structures were produced by evaporating sacrificial polystyrene particles. In this case, different size of polystyrene particles were mixed to produce fractal structure. In addition, platinum nano-particles were added as catalyst to promote reaction on the SnO_2 surface. The platinum particles were allocated selectively near the contact area between the neighboring SnO_2 particles due to the meniscus force in the assembly process. The sensitivity was improved up to four times of that without inverse opal structures.

5 Conclusions and future works

We made clear the condition to fabricate inverse opal structure for catalyst by applying repeated self-assembly of particles with dip-coating.

Future work includes peeling off the inverse opal structure to produce free standing membrane-like catalyst, in addition to verification of catalyst function.

References:

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