

## SIZE UNIFORMING PROCESS OF MINUTE SPHERES BASED ON AXIOMATIC DESIGN

**Hiroaki Rikihisa**

rikihisa.hiroaki@furukawa.co.jp  
 Smart Energy Department  
 Power & System Laboratories  
 The Furukawa electric co., Ltd.  
 6, Yawata-kaigandori, Ichihara, Chiba, Japan 290-8555

**Masayuki Nakao**

nakao@hnl.t.u-tokyo.ac.jp  
 Department of Engineering Synthesis  
 School of Engineering  
 The University of Tokyo  
 Hongo 7-3-1, Bunkyo-ku, Tokyo, Japan 113-8656

### ABSTRACT

Modern micro droplet reactors and nanoparticle processing require uniform minute spheres. They, however, often face difficulty in collecting minute spheres with the same diameter. The difficulty comes from the bottom-up process of growing small seeds, instead of breaking larger ones. The bottom-up process ends up with the byproduct of spheres smaller than the target size due to variation in temperature, pressure, and concentration of the system. Moreover, when the minute sphere size is smaller than the filter pore or the opening of the pipette tip, separating them into different sizes is difficult. One will have a hard time even in selecting out the right sized ones visually. For our study we report with this paper, we set the primary functional requirement to “Produce minute spheres” and the secondary functional requirement to “Homogenize minute spheres” and applied axiomatic design theory to develop a design solution that satisfies the two functional requirements by “suppressing the growth of secondary cores.”

**Keywords:** axiomatic design theory, independence axiom, process control, minute sphere, byproduct core.

### 1 INTRODUCTION

Minute spheres in this paper are spheres or hemispheres with diameters under 1mm. Minute spheres offer a number of advantages in engineering processes; i.e., the large surface area for the same volume makes enzyme particles highly reactive, or the low heat capacity produces chemical field with high heat response. These properties, however, are easily affected with the minute sphere size and often require “uniform size” spheres.

In general, however, when the target sphere size is smaller, supplying spheres with the same diameter is more difficult. One of the main reasons is their bottom-up production process. Bottom-up methods often have the byproduct of cores with diameters smaller than the target. The reason is spatial and timeline based variation in the temperature, pressure, and concentration within the production pool. Also, when multiple cores stick together, they turn into aggregated cores with undesired size. When the target diameter is 1mm or larger, homogenizing uniformity with the sphere size is fairly easy. They can be classified and separated with filters with small pores or hand-picked one by one with pipettes. Separating out minute spheres of smaller

size, however, is in general not easy. Filters with 100nm pores are not in the market and if the minute sphere has active surface, it will stick to the filter surface to hinder the separation process.

In our study, we applied axiomatic design theory and set the primary functional requirement ( $FR_1$ ) to “Produce minute spheres”, “Supply minute spheres” or “Enlarge spheres from seeds or embryo”. And we set the secondary functional requirement ( $FR_2$ ) to “Homogenize minute spheres”, “Select minute spheres” or “Sort minute spheres into same size”.

In the next Section 2, we will derive a method to suppress the growth of minute spheres with off-target sizes to satisfy the two functional requirements of  $FR_1$  and  $FR_2$  without relying on filtering or hand-picking. In Section 3, we apply the method to the design of a method to maintain micro droplet size, and in Section 4, to designing a particle control system for copper nanoparticles.

### 2 METHOD FOR SUPPRESSING OFF-TARGET SIZED PARTICLES

The design equation for our system is equation (1).

$$\begin{bmatrix} FR_1: \text{Produce minute spheres} \\ FR_2: \text{Homogenize minute spheres} \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \begin{bmatrix} DP_1 \\ DP_2 \end{bmatrix} \quad (1)$$

$DP_1$  is the design parameter to satisfy  $FR_1$  about our target primary cores.  $DP_2$  is the design parameter to satisfy  $FR_2$  about the byproduct secondary cores. We selected our  $DP_1$  and  $DP_2$  following the independence axiom so that the system is uncoupled with both  $a_{12}$  and  $a_{21}$  being 0, or at least one is zero so the system is decoupled [Suh, et al., 2001].

We can make  $a_{12}$  and  $a_{21}$  go to zero by selectively removing the byproduct secondary cores if we select filtering or hand-picking for  $DP_2$ . As we discussed above, however, there are hardly any filters or pipettes that work for minute spheres. Applying other bottom-up methods for  $DP_1$  would allow smaller new cores to generate one after another and the diameter distribution would never converge to the target size ( $a_{21} \neq 0$ ).

So for our study, we assigned a way of suppressing the core generation to  $DP_1$ . The suppression cancels the growth and the sphere diameter distribution does not expand ( $a_{21} \rightarrow 0$ ).

If, however, we apply growth suppression to the entire system, the chamber that produces all, that is target primary cores and byproduct secondary cores, is the same and it would suppress the growth of byproduct secondary cores ( $a_{12} \rightarrow 0$ ), however at the same time, the production of target primary cores would also be suppressed ( $a_{11} \rightarrow 0$ ). To avoid this tradeoff, we developed a mechanism to selectively suppress the growth of byproduct secondary cores but not the target primary cores ( $a_{12} \rightarrow 0$ , but at the same time,  $a_{11} \neq 0$ ).

From the above discussion, we derived the following guidelines for our  $DPs$ :

- Guideline 1 for  $DP_1$ : Suppressive generation of all spheres
- Guideline 2 for  $DP_2$ : Selectively suppressive growth against secondary cores

In the following sections, we report our findings from applying these guidelines, derived from axiomatic design theory, to a couple of processes. If we can find design solutions that resolve past problems, the guidelines will be proved effective. The two processes are "maintaining micro droplet size" for liquid and the "copper nanoparticle production" for solid. Analogically speaking, these guidelines can apply to a policy of developing countries. The government decides the suppressive birth control and financial support for poor people in order to make all people happy.

### 3 MAINTAINING MICRO-DROPLET SIZE

#### 3.1 PROCESS DESIGN

Combinatorial experiments have the need for devices with multiple droplets arranged in a lattice array on an open substrate [Kim, et al., 2012]. With the micro droplet defining the field of chemical reaction, its small size allows small quantity of reagent or blood sample with shorter reaction time proportional to the square of the size ratio. Also, preparing the micro droplets on an open substrate makes the injection of a variety of reagents easier. From the above guidelines, we set the design equation for handling micro droplets on an open substrate as following equation (2):

$$\begin{pmatrix} FR_1: \text{Produce micro droplet} \\ FR_2: \text{Homogenize micro droplets} \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} DP_1: \text{Wet droplets with spray} \\ DP_2: \text{Dry secondary droplets with electrolysis} \end{pmatrix} \quad (2)$$

If we hold the micro droplets on an open dry substrate, evaporation would shrink the droplet size. So, we set  $DP_1$  to "Wet all droplets with spray" on open dry substrate. This solution, however, would result in condensing seeds for micro droplets in areas that are "not reserved" for the experiment, i.e, byproduct secondary droplet's cores. To avoid forming unwanted droplets, we set  $DP_2$  to decompose the byproduct secondary droplet's cores by electrolysis. The target primary droplets are sitting on reserved seats that that are masked and they do not reduce in size ( $a_{21} \rightarrow 0$ ). In other words,  $DP_1$  cancels out the effect of evaporation with humidification to

maintain the target primary droplets diameter, and  $DP_2$  eliminates byproduct secondary droplet's cores with electrolysis and the target primary droplets continue to keep the target diameter ( $a_{12} \rightarrow 0$ , but at the same time,  $a_{11} \neq 0$ ).

Another  $DP_1$  would be to add liquid for the amount evaporated using a pipette and maintain the target primary droplets diameter so that  $FR_1$  and  $FR_2$  are both satisfied. This solution, however, would cause cross contamination among cores with the pipette, thus, is unwanted for a combinatorial device. Also, adding humidity and removing the byproduct secondary droplet's cores with a pipette is another conceptual design solution, however, searching for byproduct secondary droplet's cores with a microscope and removing them with a constantly shivering pipette is not an easy task. And the smaller the size of the droplet is, the larger contamination to the droplet from the impurities on the opening of the pipette tips have.

#### 3.2 EXPERIMENT

We built an electrochemical device shown in Figure 1. Two electrode films (Carbon nano tube 13wt%, PolyVinylidene DiFluoride 33wt%, 1-Butyl-3-methylimidazolium Tetrafluoroborate 54wt%) sandwich an electrolyte film (PolyVinylidene DiFluoride 40wt%, 1-Butyl-3-methylimidazolium Tetrafluoroborate 60wt%) in between. The surface was masked with a lattice array of circles where electrolysis could not reach across; they were the "reserved seats" for target primary cores.

We produced this device by first preparing the three layer sandwich, covering one side with porous fluorine resin for hydrophobic treatment, attaching hydrophilic polyimide resin stages and then placing target primary cores on the stages. The cores were not "placed" one by one, but the whole structure was submerged under the solution and then lifting the structure formed a target primary core on each hydrophilic stage. The experiment proceeded by humidifying the whole structure while decomposing the byproduct secondary cores with electrolysis.  $DP_1$  performed a 30 second spray of mist for every 3 minutes in dry air. The mist volume measured 2mL/hour over a roughly 30cm square plane. The environment was open with a 0.5m/sec wind, thus, without the spray, the cores would have reduced their sizes by evaporation.  $DP_2$  applied 4V step voltage to the device from the beginning of the experiment.

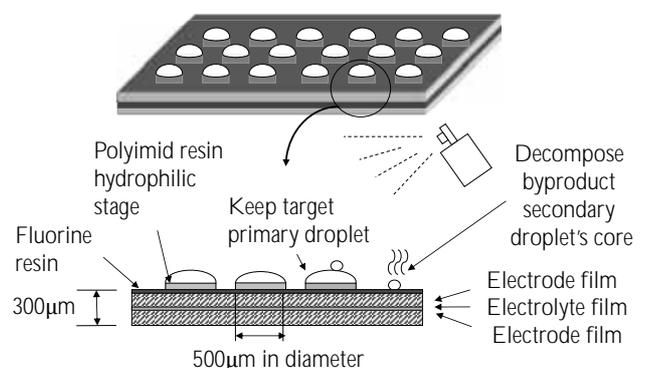
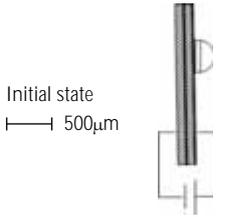
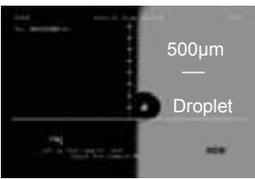
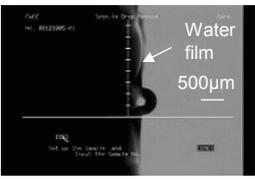
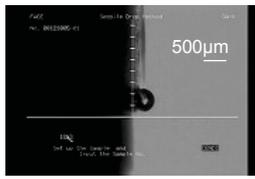
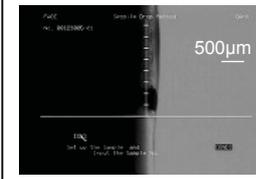
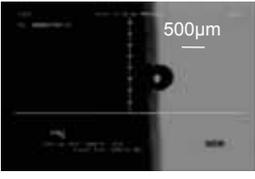
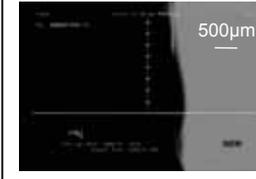
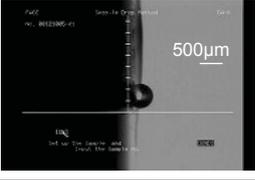
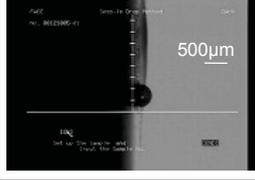
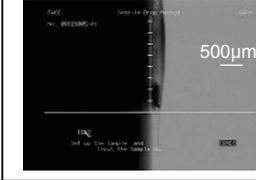


Figure 1. Cross section of the electrochemical device.

Table 1. Results of the first case (Humidification and Electrolysis).

Condition	DP <sub>1</sub> : Wet with spray	Results FR <sub>1</sub> on primary droplet	Interference of DP <sub>1</sub> for FR <sub>2</sub>	Initial state 500µm	Mid state 500µm	End state 500µm
	DP <sub>2</sub> : Dry with electrolysis	Results FR <sub>2</sub> on byproduct droplet	Interference of DP <sub>2</sub> for FR <sub>1</sub>			
1	Yes	Satisfied: Survived more than 60 min.	No interfered $a_{21} = 0$			
	Yes	Satisfied: Evaporated immediately after generation.	No interfered $a_{12} = 0$			
2	No	Unsatisfied: Evaporated in 4min. 50sec.	No interfered $a_{21} = 0$			
	Yes	Satisfied: No generation. (Incidentally placed water film for this case was evaporated.)	No interfered $a_{21} = 0$			
3	Yes	Unsatisfied: Aggregated with secondary core into a large droplet	Interfered $a_{21} \neq 0$ Droplet grew			
	No	Unsatisfied: Aggregated with primary core into a large droplet.	No interfered $a_{12} = 0$			
4	No	Unsatisfied: Evaporated in 7 min. 40 sec.	No interfered $a_{21} = 0$			
	No	Satisfied: No generation.	No interfered $a_{21} = 0$			

### 3.3 RESULTS

We ran cases with both DP<sub>1</sub> (Wet droplets with spray) and DP<sub>2</sub> (Dry secondary droplet's cores with electrolysis), and three reference cases; two with one of the two design parameters missing, and one with both DP<sub>s</sub> missing. Table 1 shows the results. The time the target primary micro droplet maintained its size on stage is the average of 4 measurements. The substrate was held vertically for observation. The photographs show the actual particles during the experiment.

As Table 1 shows, only with Condition 1, the micro droplet on its stage kept the same diameter even after 60 minutes into the experiment and byproduct secondary droplets did not grow. In other words, DP<sub>1</sub> and DP<sub>2</sub> designed with the guidelines satisfied FR<sub>1</sub> and FR<sub>2</sub>. As the target primary droplet survived and the secondary droplet's cores evaporated, the experimental result agreed, at least, with the original design equation. Condition 2, without spray, evaporated the primary target micro droplet in less than 5 minutes; FR<sub>1</sub> was not satisfied. For this particular Condition 2, we placed a film of water away from the target primary micro droplet. The water film disappeared as the experiment proceeded demonstrating that electrolysis decomposed water as well as byproduct secondary micro droplets. Condition 3,

without DP<sub>2</sub> electrolysis, formed byproduct secondary micro droplets around the target primary droplet, and they aggregated to form a large aggregate droplet. The resulting large droplet diameter violated FR<sub>2</sub>; DP<sub>2</sub> interfered FR<sub>1</sub>. Condition 4 ran without both the humidification DP<sub>1</sub> and electrolysis DP<sub>2</sub> to evaporate the target primary micro droplet in less than 8 minutes, thus, did not meet FR<sub>1</sub>.

## 4 PRODUCTION OF COPPER NANO-PARTICLE

### 4.1 PROCESS DESIGN

Wiring technology using metal slurry inkjet requires uniform size copper nanoparticles in the ink for smaller gaps between slurry particles, thus, higher conductivity. Reduction of copper ions with non-electrolytic plating within a solution added with high-polymer electrolyte like polyvinylpyrrolidone (PVP) produces copper nanoparticles.

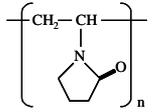
This copper nanoparticle process, however, fails to control the particle size because the non-uniform process parameters like temperature or concentration result in late generation of byproduct secondary cores that grow after target primary cores are formed. Furthermore, surface active

## Size uniforming process of minute sphere based on axiomatic design

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Table 2. Composition of Material for copper nanoparticle production.

Name	Formula	Amount
Polyvinylpyrrolidone (PVP)		5mM/mL
Sodium tetrahydroborate	$BaH_4 \cdot NaOH$	30mM/mL
Copper acetate	$Cu(CH_3COO)_2$	15mM/mL
Water	$(H_2O)$	(500mL)

nano-sized particles adhere to particle size classifier walls and filters to hinder their classification. We then set the design equation (3) to the following from the above guidelines.

$$\left( \begin{array}{l} FR_1: \text{Produce nanoparticles} \\ FR_2: \text{Homogenize nanoparticles} \end{array} \right)$$

$$= \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \left( \begin{array}{l} DP_1: \text{Suppressive generation of nanoparticles} \\ \text{by suppressor (Na}^+) \\ DP_2: \text{Selectively growth of secondary cores} \\ \text{with wide active surface area per} \\ \text{volume (CuOH}_2\text{)} \end{array} \right) \quad (3)$$

We chose a suppression method to add sodium ion to the above solution. The method canceled the Cu growth to keep the distribution of particle diameters under control ( $a_{21} \rightarrow 0$ ), i.e., adding sodium hydroxide where PVP was present suppressed the growth of both the target primary cores and byproduct secondary cores ( $a_{11} \rightarrow 0$ ,  $a_{12} \rightarrow 0$ ) [Nishimura, et al., 2010], [Hirayama, 2013]. Table 2 shows the composition of the solution. It had 30mM/mL of sodium ion at minimum, and when we ran a control case without the sodium ion, the reaction itself no longer took place.

To lessen the effect of target primary core suppression, we controlled the initial core production to small size so byproduct secondary cores would be selectively suppressed. PVP and sodium ions react with the very surface of cores and smaller byproduct secondary cores have larger surface area per volume. Then particles with smaller diameters are subject to stronger effect of growth suppression than those with larger diameters ( $a_{12} \rightarrow 0$ ,  $a_{11} \neq 0$ ). To keep the core size small, we applied classical core generation theory that keeping the degree of supersaturation low will produce smaller size cores. So, we used copper hydroxide with smaller copper ion solubility compared to copper acetate to keep the degree of supersaturation low. Figure 2 sketches the difference of copper nanoparticle generation with copper acetate and copper hydroxide. Copper hydroxide can make smaller embryos. Using copper hydroxide for the material, byproduct secondary core generation proceeds with that of target primary cores, however, secondary cores are strongly suppressed to leave just the primary cores in the solution.

## 4.2 EXPERIMENT AND RESULTS

The initial copper reduction process proceeded with sodium borohydride solution dripping in the solution. To wait for the copper to complete reacting with the sodium borohydride, we stirred the solution at room temperature while sending nitrogen into the solution. Then we poured the additional sodium hydroxide in the solution before generating the copper cores. To wait for the copper to complete reacting with the sodium borohydride, we stirred the solution at room temperature while sending nitrogen into the solution.

After we produced the copper nanoparticles, we degassed the solution for an hour with nitrogen gas at 10 degrees Celsius for preventing the oxidation. We determined the reaction time by measuring the amount of byproduct hydrogen until it saturated.

Table 3 shows the results of this experiment. We tried the reference case of no  $Na^+$  for  $DP_1$ , however, as we explained above, the conditions resulted in no reaction. Condition 3 was the conventional process condition which still produced copper nanoparticles to meet  $FR_1$ , however, with an average diameter of 14.6nm with a standard deviation of 3.6nm.

When we used copper hydroxide to reduce the initial core size with lower degree of supersaturation (Condition 1), the average nanoparticle diameter dropped to 11.0nm to still satisfy  $FR_1$  and it additionally satisfied  $FR_2$  with a smaller standard deviation of 2.8nm. The experimental result agreed, at least, with the original design equation.

To further improve  $FR_1$ , we added sodium borohydride after the process and as Conditions 2 and 4 show, both cases of copper acetate and copper hydroxide gave longer reaction times of factors 1.5 to 1.7. These conditions resulted in larger nanoparticle diameters of 23.4nm and 19.1nm to meet  $FR_1$  and, however, the standard deviation values also grew to 4.2nm and 4.5nm. The longer reaction time let the small number of target primary cores to grow larger and resulted in degrading  $FR_2$ .

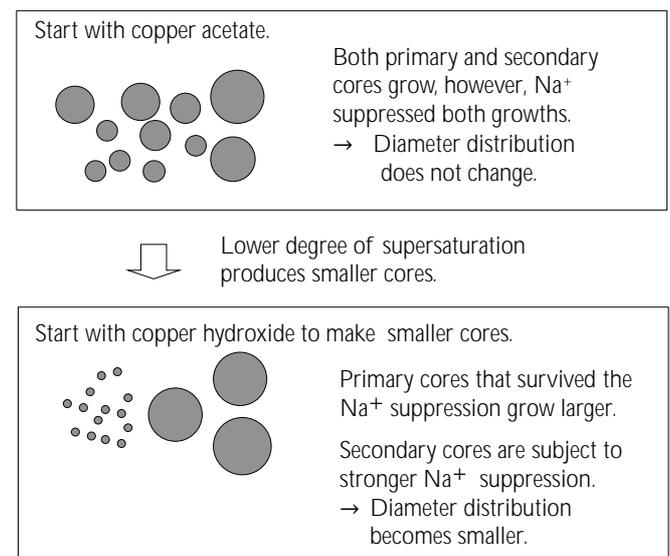
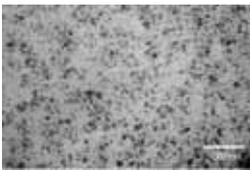
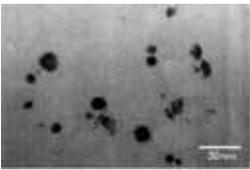
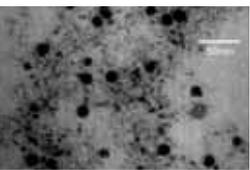
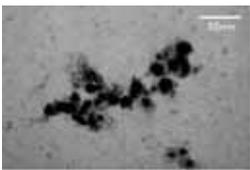


Figure 2. Growth and suppression of primary and secondary cores.

Table 3. Copper nanoparticle average diameter and reaction time.

Condition	DP <sub>1</sub> (Na <sup>+</sup> ) (mM/ ml)		DP <sub>2</sub> (CuOH)	Particle photo ┆ 50nm	Reaction time(min)	FR <sub>1</sub> Average diameter (nm)	FR <sub>2</sub> Standard deviation (nm)	Interference of DP <sub>1</sub> for FR <sub>2</sub>
								Interference of DP <sub>2</sub> for FR <sub>1</sub>
1	NaOH	0	Copper hydroxide		45 min	Acceptable 11.0 nm	Satisfied 2.8	→ 0
	BaH <sub>4</sub> NaOH	30						→ 0 Making the degree of supersaturation lower
2	NaOH	30	Copper hydroxide		70 min	Satisfied 23.4 nm	Unacceptable 4.2	≠ 0 Making reaction time longer
	BaH <sub>4</sub> NaOH	30						→ 0 Making the degree of supersaturation lower
3	NaOH	0	Copper acetate		10 min	Acceptable 14.6 nm	Acceptable 3.6	→ 0
	BaH <sub>4</sub> NaOH	30						≠ 0 Making the degree of supersaturation larger
4	NaOH	30	Copper acetate		17min	Acceptable 19.1 nm	Unacceptable 4.5	≠ 0 Making reaction time longer
	BaH <sub>4</sub> NaOH	30						≠ 0 Making the degree of supersaturation larger

In comparing results, we took several photographs for measurement and the average diameter change with copper hydroxide was 11.0nm to 23.4nm, while, that for copper acetate was 14.6nm to 19.1nm. When we used copper hydroxide, the degree of supersaturation was low and the active surface area of per volume of secondary cores was wide. As a result, the interference of DP<sub>2</sub> for FR<sub>1</sub> (a<sub>21</sub>) was small. The long reaction time of 70 minutes for copper hydroxide, compared to 17 minutes with copper acetate, caused the target primary cores to grow huge.

### 5 DISCUSSION

As we showed in Section 3 and 4, the design guidelines of setting DP<sub>1</sub> to growth suppression and DP<sub>2</sub> to selective application to byproduct secondary cores are applicable to designing minute spheres. These design guidelines are also

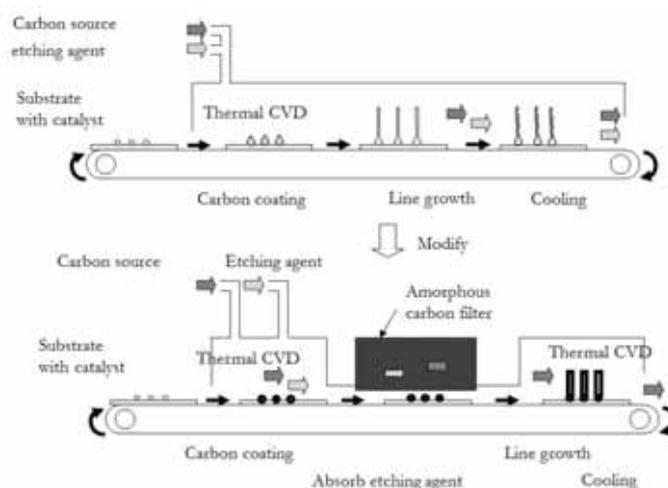


Figure 3. Sketch of CNT production process.

applicable to minute linear structures that start from minute spheres and grow in one direction.

For example, in designing carbon nanotubes (CNT), adding a small amount of water as etching agent for  $DP_1$  suppresses the overall reaction [Yamada, et al., 2008]. If we introduce the etching agent water to both the upstream process of coating carbon to the catalyst and the downstream process of linearly growing the tube, we can suppress the generation of byproduct core amorphous carbon, however, at the same time, we will end up introducing flaws to the target primary core CNT itself by etching it. We can then apply the guidelines to this design to reach the following design equation(4):

$$\begin{matrix} \left[ \begin{array}{l} FR_1: \text{Supply CNTs} \\ FR_2: \text{Homogenize CNTs} \end{array} \right] \\ \\ = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \left[ \begin{array}{l} DP_1: \text{Suppressive generation by etchant} \\ \quad \text{(H}_2\text{O)} \\ DP_2: \text{Selectively flawless growth under} \\ \quad \text{etchant free condition.} \\ \quad \text{(Amorphous carbon filter)} \end{array} \right] \end{matrix} \quad (4)$$

Figure 3 shows our design with DP2 of applying the etching agent only to the upstream process and an amorphous carbon filter to the downstream process to absorb the etching agent. The etchant free condition of the downstream process can produce flawless CNTs. Although still in the prototyping stage, it promises to satisfy both  $FR_1$  and  $FR_2$ .

## 6 CONCLUSION

We applied axiomatic design to derive the design guidelines for producing minute spheres with a uniform diameter, i.e.,  $FR_1$  is to produce minute spheres and  $FR_2$  is to keep the sphere diameter uniform. The design solution we reached were  $DP_1$  to suppress the particle growth for the entire system and  $DP_2$  to apply the suppression selectively to byproduct secondary cores. This solution provides the design guideline for uniform minute sphere generation. We demonstrated the effect of this guideline with two designs; one for maintaining micro-droplet size and the other for copper nanoparticle diameter control.

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