Review Paper

Nanoparticles Synthesis and Modification using Solution Plasma Process

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Abstract Across the most industry, the demand for nanoparticles is increasing. Therefore, many studies have been carried out to synthesize nanoparticles using various methods. The aim of this paper is to introduce an industry-applicable as well as financially and environmentally effective solution plasma process. The solution plasma process involves fewer chemicals than the traditional kit, and can be used to replace many of the chemical agents employed in previous synthesis of nanoparticles into plasma. In this study, this process is compared to the wet-reaction process that has thus far been widely used in the most industry. Furthermore, the solution plasma process has been classified into four different types (in-solution, out of solution, direct type, and remote type), according to its plasma occurrence position and plasma types. Thus, the source of radicals, nanoparticle synthesis, and modification methods are explained for each design. Lastly, unlike nanoparticles with hydrophilic functional groups that are made inside the solution, a nanoparticle synthesis and modification method to create a hydrophobic functional group is also proposed.

Keywords: Solution Plasma, Nanoparticle, Wet-reduction

I. Introduction

Numerous materials are used in each industry according to their characteristics such as hardness, flexibility, and conductivity. However, materials with higher measurements and more complex characteristics are currently in demand. Research on nanoparticles is thus being carried out to meet such various demands from different industry. Different physical and chemical processes are used to synthesize these nanoparticles [1-11]. In terms of physical methods, sputtering and ball-mill are used. [1-4]. Sputtering is suitable to make nanoparticles with materials that have a high melting points, yet the collection of nanoparticles is difficult and dispersion among nanoparticles is troublesome due to aggregation. While ball-milling is a relatively simple method, the shape of the resulting nanoparticle is irregular and its size control is inefficient. Chemical methods are used to synthesize nanoparticle in gaseous or liquid condition [5-11]. Nanoparticle synthesis in gaseous condition includes methods such as vapor-phase hydrolysis and Chemical vapor deposition (CVD). Although these methods can be used to manufacture and synthesize various nanoparticles, they require high temperatures and harmful chemicals are generated in large quantities [5-7]. Therefore, the wet-reduction process is used across the most industry. Wet-reduction process is applicable for large

quantity production, and is thus preferred [8]. To synthesize nanoparticles in liquid condition, many toxic chemicals such as reducing agents and dispersant agents are needed [9-12]. When a reducing agent is not sufficient, nanoparticle Ostwald ripening occurs, and excess or insufficient dispersant creates aggregation and inefficient size control. Since the types and sizes of synthesizable materials are selected according to various process conditions such as precursors, solvent, stabilizer, reducing agent, and temperature, the experiment conditions must be set considering the resulting material and its desired size.

Table 1 shows a summary of the nanoparticles obtained by wet reduction without plasma according to conditions such as precursor, solvent, reducing agent, and materials [13-27]. To manufacture high-quality nanoparticles, the appropriate selection of various materials is important from wider options than the solvent, reducing agent, polymer stabilizer, and precursor introduced in Table 1. When choosing a solvent and polymer stabilizer, phenomena such as the coil-up of the polymer stabilizer inside the solvent need to be considered [60,61].

As shown in Table 1, wet-reduction process allows the manufacture of nanoparticles in different experimental conditions. The wet-reduction process always requires toxic chemicals such as precursors, solvents, stabilizers, and reducing agents [10-30]. However, globally, a non-toxic green process is required, thus processes involving fewer chemicals or no chemicals need to be developed. Since the solution plasma process (SPP) can supply

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Table 1. Nanoparticles obtained by wet reduction without plasma

Material	Precursor	Solvent	Stabilizer	Reduction method	(°C)	Average size (nm)	Ref
Ru	RuCl ₃	EG	PVP	L-ascorbic acid KBr	100~175	6~18	13
Pt	H ₂ PtCl ₆	Water	PVA	Formic acid	RT	3~60	14
Ag	AgNO ₃	Water	NIPAM AAAc	NaBH ₄	RT	8~80	15
Pt/Fe	Pt(acac) ₂ Fe(acac) ₃	EG	TGA	NaBH ₄	RT	5~6	16
Sn	Na ₂ SnO ₃	Ethanol	PPI PAMAM	CO ₂		3-3.5	17
Ag/Au	AgNO ₃ HCl ₄ Au	Water	PVP	PVP	70	~20	18
Mn/Zn/Fe	Zn(NO ₃) ₂ Mn(NO ₃) ₂ Fe(NO ₃) ₃	Water	TEG	NaAc	RT	2~8	19
Pb/Sn	Pd(NH ₄) ₂ Cl ₄ SnCl ₂	Ethanol	Cretic Acid	KOH	RT	5	20
Ag	AgNO ₃	Water		Chitosan	95	5~7	21
Fe	Fe(OEt) ₂	THF	THF	NABEt ₃ H	67	10-100	22
Ni	Ni(acac) ₂	HDA	HDA	NaBH ₄	160	3.7	23
Mg	[CH ₃ (CH ₂) ₃] ₂ Mg	THF		Lithium	60	8-40	24
Au	HCl ₄ Au	Water		Na ₃ C ₆ H ₅ O ₇	28	12	25
Ag/Au	AgNO ₃ HCl ₄ Au	Water	CRD	CRD NaOH	RT	5-15	26
Cu	CuSO ₄	Water	NPEI	AA		2.5	27
Cu	CuSO ₄	Water	SDS PDADMAC	SDS	RT	50-70	28

ethylene glycol (EG), N-isopropylacrylamide (NIPAM), allylacetic acid (AAAc), sodium acetate (NaAc), triethylene glycol (TEG), oxygen reduction reaction (ORR), Cobalt(II) phthalocyanine (PcCo), N,N-dimethyl formamide (DMF), ascorbic acid (AA), hexadecylamine (HDA), Curdlan (CRD), polyethyleneimine (BPEI), sodium dodecyl sulfate (SDS), Poly-diallyldimethylammonium (PDADMAC).

electrons through plasma instead of a reducing agent, the reducing agent can be replaced [59]. Furthermore, nanoparticle fabrication is also possible by using an as a precursor [50]. Additionally, the electrode can replace the stabilizer [59]. Since less toxic chemicals are used, SPP can be considered an environmentally friendly process [62]. Not only does it substitute various chemicals, it can also induce chemical reactions at a low temperature [63]. The aim of this paper is to introduce such SPP with its many abovementioned advantages.

II. Solution Plasma Process

1. Solution plasma module

Professor Tomohiro Akiyama of Hokkaido University explained 41 types of modules used in SPP [30]. In this current work, those 41 types of solution plasma modules are divided into four groups as shown in Fig. 1. In case of Figs. 1(a) and 1(b), plasma is discharged outside the solution. [30-39] Figs. 1(c) and 1(d) show the in-solution process, where the plasma is not exposed to the atmosphere and directly affects the solution [39-43]. In Figs. 1(a) and 1(c), plasma is created outside of the solution [30-32]. Fig. 1(c) shows the introduction of remote type plasma to the solution [39-41]. Figs. 1(b) and 1(d) show the direct

Figure 1. Summary of solution plasma process modules.

plasma created inside or outside of the solution [30,33-38,42-43]. While many other types of modules exist apart from those shown in Fig. 1, all these modules can be divided and classified according to their plasma type and whether the plasma is affected by the atmosphere.

As shown in Figs. 1(a) and 1(b), atmospheric plasma is affected by humidity, oxygen, and nitrogen in the atmosphere, as well as by its process gas and solvent [44-46]. However, as shown in Figs. 1(c) and 1(d), atmospheric

cases shown in Figs. 1(c) and 1(d), unlike those in Figs. 1(a) and 1(b), the electrode part is not exposed to the atmosphere; thus, active species that are expected to be generated with the reaction with atmosphere can be ignored during the process.

3. Generation of active species in solvent

When plasma is irradiated on the solution surface as shown in Figs. 1(a) and 1(b), active species or ions are created on the solution surface, as shown in Fig. 3 [58]. This is the SPP mechanism of the cases in Figs. 1(a) and 1(b). As shown in Figs. 1(a) and 1(b), the active species and ions are not only made from the solution but also directly affect the inside of the solution [41]. Furthermore, in the case of Fig. 1(b), the electrode material also directly affects the solution internally due to sputtering [50]. As stated, the active species generation mechanism differs between the in-solution and out-of-solution processes.

The dissociation of plasma shown in Fig. 3(a) explains the chemical reaction when plasma is irradiated on an H₂O surface. Not only is H₂O dissociated into many radicals including H and OH by the plasma, but nitrogen in the air can also dissociate and form products. Furthermore, the generation of HNO₂ and NHO₃ from the reaction with the OH radical with the reaction products such as NO and NO₂ formed with nitrogen has been reported [84]. When plasma irradiation occurred on the surface of water, the chemical species generated by the reaction between the atmosphere and the plasma discharge layer are included. However, when plasma irradiation occurred inside a solvent other than water, such as phenol or amino acid, entirely different chemical species and organic materials are generated [32,85]. Fig. 4 shows a mimetic diagram describing the way in which plasma changes phenol into benzoquinone, resorcinol, catechol, hydroxyl-1,4-benzoquinone, hydroquinone, and hydrogen peroxide [85]. It has been reported that different radicals and OH active species made from plasma change

the phenol solvent into other organic materials. Table 2 shows the change of amino acid after oxidation, hydroxylation, dehydrogenation, hydroxylation, nitration and dimerization [32]. Fig. 3, Fig. 4, and Table 2 show that the solution plasma and solvent undergo chemical reaction to make chemical species, radicals, and reaction products. Therefore, the type of solvent is important in SPP for nanoparticle synthesis or surface modification. It is crucial to determine the chemical species that is generated by the solvent and its plasma irradiation. This is because when nanoparticle synthesis is carried out inside the solution, the chemical species made by plasma in the solvent modifies the surface

Figure 4. Chemical reaction of phenol solvent by the plasma.

Table 2. Oxidation of amino acids by plasma

Amino acid	Hydroxylation	Dehydrogenation	Hydroxylation and nitration	Dimerization
Tyrosine	O		O	
Phenylalanine	O		O	
Tryptophan	O			
Cysteine	O			O
Methionine	O			
Proline	O			
Histidine	O			
Lysine	O	O		
Arginine	O	O		
Glutamine	O			
Glutamic acid	O			
Valine	O	O	O	
Leucine	O	O	O	
Isoleucine	O	O	O	

of the nanoparticles [41,83].

III. Nanoparticle Manufacture and Modification

1. Plasma reduction

Table 3 shows a summary of the nanoparticles synthesized using SPP. Many metals such as Ag, Au, Cu, Ni, and Ti are synthesized using SPP. Furthermore, for some of the precursors shown in Table 3, it can be seen that the electrodes themselves are used as the precursors. The precursors are obtained from the electrode because nanoparticles are fabricated when electrodes are sputtered at a nano-size in the solution [50]. The differences between the wet-reaction process and SPP can be observed by comparing Table 1 and Table 3. The wet-reaction process requires precursors, stabilizers, and reducing agents, while SPP sometimes requires none of these [50,69,81]. Alternatively, although the precursor chemical agents are used, stabilizers are used in minimal amounts and reducing

agents are never required in any of the solution plasma processes [64-81]. Even though it is not stated in Table 1, a few hours is required for the completion of the wet-reaction process. However, as shown in Table 3, SPP is completed in a few minutes. Through comparison between Table 3 and Table 1, it is observed that chemicals are not used in SPP as its precursors mainly use water as the solvent and most of the processes do not use stabilizers. It can be understood that the differences in the process conditions between the wet-reaction process and SPP is the different nanoparticle synthesis region, reaction time, and reaction mechanisms [59,67,78].

2. Solution plasma synthesis and modification

As shown in Table 3, many materials can be synthesized or modified using SPP. SPP mechanism involves dissociation of solvent by the plasma and resulting radicals reduce the metal ions (precursors). Furthermore, the radicals generated by the plasma can also directly reduce

Table 3. Nanoparticles synthesis using solution plasma process

Material	Precursor	Solvent	Stabilizer	Reduction method	Time (min)	Type (Fig 1.)	Average size (nm)	Ref
Ag	AgNO ₃	Ethanol	PVP	Plasma jet	2	(a)	30	64
Ag	AgNO ₃	Water	Fructose	Microplasma	15	(b)	5~35	65
Ag	AgNO ₃	Water		Solution plasma	10	(d)	8~16	66
Ag	AgNO ₃	DMF	PAN	Atmospheric plasma	3	(b)	3~7	68
Ag/Au	Electrode	Water:HNO ₃		Microplasma	5	(b)	~10	69
Ag/Au	AgNO ₃ HAuCl ₄	Water	SDS	Dc glow discharge	10	(a)	10~30	67
Au	Electrode	Liquid N ₂		Solution plasma	1	(d)	1~2	50
Au	HAuCl ₄	Water	SDS	Solution plasma	7	(d)	150	70
Au	HAuCl ₄	dodecane	AOT	Solution plasma	10	(d)	4~12	71
Au	HAuCl ₄	Water		Microplasma	2	(b)	20~30	72
Au	HAuCl ₄	Water		Microplasma	10	(b)	5	73
Au	HAuCl ₄	Water		Microplasma	15	(b)	32~36	74
Au	HAuCl ₄	Water		Solution plasma	30	(d)	20	75
Cu	CuCl CuCl ₂	[BMIm]dca		Microplasma	30	(b)	2~10	76
Ni	NiCl ₂	Water		Solution Plasma	10	(d)	20	77
Ni	Electrode	Water		Microplasma	6	(b)	100	78
Ti	TiCl ₃	Water		Arc Plasma	10	(a)	10~100	79
Pt	H ₂ PtCl ₆	Water		Ac Plasma	5	(b)	2~5	80
Ag	AgNO ₃	Water	PVP	Microwave plasma	1.5	(c)	4.5	39
Pt	H ₂ PtCl ₆	Water	PVP	Microwave plasma	1.5	(c)	2	39
Fullerene	Electrode	Toluene		Pulsed plasma	5	(d)	7	81

Polyacrylonitrile (PAN), N,N-dimethylformamide(DMF), sodium bis(2-ethylhexyl)sulfosuccinate (AOT), 1-butyl-3-methylimidazolium dicyanamide ([BMIm]dca).

Figure 5. A schematic model of reaction mechanisms for the gold nanoparticles synthesis by plasma-induced liquid chemistry [82].

Figure 6. Schematic diagram of PEDOT:PSS in water being coated on the nanoparticle surface by plasma [83].

the metal ions [67,70-81]. Fig. 5 shows a mimetic diagram of the reduction of the precursor's metal ion to metal when plasma is irradiated above the solution [82].

However, the solvent itself plays an important role. The surface of the nanoparticles change, depending on the solvent [83]. As shown in Fig. 6, if the solvent contains PEDOT:PSS, the nanoparticles inside the solution can be modified by the plasma. Fig. 7 shows the modification of the nanoparticle surface inside the solution by the plasma [83]. When the module is the same as that shown in Figs. 1(c) and 1(d), the modification of nanoparticle surface is directly affected by the plasma, as shown in Fig. 8 [41]. Fig. 8 shows that plasma has a direct impact on the nanoparticles by using the gases that cannot be generated from the solvent. In most SPP, it is difficult to distinguish whether the nanoparticles are affected by the radical from the solvent or the radicals from the plasma. This is because during the plasma irradiation, it is difficult to distinguish whether the surface of nanoparticles is modified by the

Figure 7. PEDOT:PSS in water is used as a surface source for modification of nanoparticle by plasma [83].

Figure 8. Schematics diagram showing ions made from solution plasma process by plasma having direct impact on nanoparticles. (a) decomposition of solvent. (b) direct impact.

plasma or by the active species and ions generated in the solution. Most researchers used solvents with -OH functional groups and used Ar, He, O₂, and air as the process gases when irradiating the plasma; the generated OH radicals then modify the nanoparticles [86-89]. Due to the OH radicals, the modified nanoparticles have hydrophilic characteristics [92,93]. However, OH radicals are also formed in plasma. Therefore, it is difficult to distinguish with certainty whether the change in nanoparticle characteristics is due to the plasma or the solvent. When nanoparticles are synthesized or modified inside the solution using a plasma jet, it is only possible to make nanoparticles hydrophilic because of the OH radicals from the solvent. However, by controlling the solvent mixture or gas for plasma, nanoparticles can also be made hydrophobic.

3. Comparison between wet-reaction and solution plasma synthesis

Fig. 9 shows the nanoparticle synthesis region regarding

Figure 9. Comparison of wet-reaction process and solution plasma process. (a) nanoparticle synthesis using wet-reaction process (b) nanoparticle synthesis using in-solution direct type plasma (c) nanoparticle synthesis using out of solution direct type plasma.

	Module	Method	Ref
(a) Direct reaction of plasma		He/SF ₆ is used as the plasma process gas to modify the particles inside the solution. F anion of SF ₆ can modify the particles inside the solution hydrophobically.	[41]
(b) PFOA solution		When perfluorooctanoic acid is used as solvent when plasma is irradiated in the solution, F anion is synthesized.	[55-57]
(c) Liquid N ₂		Even though direct plasma is synthesized inside the solution using Liquid N ₂ as the solvent, OH group is not made.	[50]

Figure 10. Methods for hydrophobic nanoparticle synthesis or modification.

the wet-reaction and SPP. The wet reaction shown in Fig. 9(a) requires solvents, precursors, stabilizers, and reducing agents. General nanoparticle synthesis is then carried out [10-30]. In Fig. 9(b), the nanoparticles are synthesized only between the electrodes and only solvent is thus required [50,69,81]. Here, nanoparticles are generated or grown only in the plasma discharge region. Furthermore, since an electrode can act as a precursor and, although nanoparticle aggregation can occur outside the plasma discharge region, the growth is not possible [50,69,81]. Fig. 9(c) shows the inside of the solution which can be subdivided into three regions. At Region A, precursors are synthesized into nanoparticles and grown due to the reduction of plasma. Region B involves neither synthesis nor growth.

Nanoparticle contact occurs in Region C [78]. When the size of the nanoparticles in Region A is compared to that of the nanoparticles shown in Regions B and C, the nanoparticles in Region A are about 50nm and the size of the nanoparticles in Regions B and C is 150 nm. This shows that synthesis and growth only occur in Region A [78]. As stated earlier, many differences have been identified between wet-reaction and SPP. By comparing Table 1 and Table 3, SPP is more environmentally friendly and faster than the wet-reaction.

4. Hydrophobic modification of nanoparticles using Solution Plasma Process

Solutions in most of the SPP have the –OH functional

group [15-26,41,53,54] (Refer to Table 1). Regardless of the types of module used from Fig. 1, if the solvent has an OH group, OH is generated in the solution. These OH functional groups attach to the nanoparticles formed inside the solution or to the modified nanoparticles to make the particles hydrophilic [41,53-54]. When SPP is used, most of the particles are made hydrophilic or are hydrophilically modified. Methods shown in Fig. 10 can be used to manufacture or modify nanoparticles hydrophobic without OH group.

However, the methods shown in Fig. 10 cannot completely control the OH groups. Fig. 10(a) can hydrophobically modify the nanoparticles inside the solution, but cannot perfectly block the generation of the OH group [41]. Furthermore, in the case shown in Fig. 10(b), the F anions are formed inside the solution; the OH group is thus still formed even though particles can be made hydrophobic. Fig. 10(c) shows the only method in which the OH group is not created, although nanoparticles cannot be chemically modified to be hydrophobic. Fig. 10(a) shows the in-solution remote plasma type shown in Fig. 1(c). When the module shown in Fig. 10(a) is changed into an out-of-solution remote plasma type, the particles inside the solution are hydrophobically modified [41].

IV. Conclusions

Many unknown factors remain concerning the mechanism of SPP. In this paper, Modules that have been used in solution plasma process so far is classified with four different methods. The criteria of this classification is plasma discharge region and plasma type. The four groups are remote plasma / out of solution, remote plasma / in solution, direct plasma / out of solution and direct plasma / in solution. When it is classified as direct plasma / in solution, nanoparticles can be synthesized using metals sputtered from the electrode without precursors. The radicals and electrons that reduce precursors are generated by the plasma inside the solvent or directly from the plasma itself. Previously, it was believed that electrons and radicals generated in the plasma reduce the precursor by chemical reaction of the solvent from the plasma. However, some studies have suggested that plasma directly affects the nanoparticles. In the in-solution process, solvent and process gas can also affect the nanoparticles. In addition to hydrophilic treatment, studies have been carried out on hydrophobic nanoparticle synthesis and modification. Originally, nanoparticles possess hydrophilic functional groups due to the solvent; however, the change in solvent and process gases (in-solution process) can synthesize nanoparticles with hydrophobic functional groups. When the usage ratios of the chemical agent were compared with those for wet-reaction processes, it was found that the usage ratio of the chemical agent is greatly decreased. From the many journals published so far, it is

found that SPP is an environmentally friendly process that has faster chemical reaction than the previous processes. Lastly, because the nanoparticle synthesis process can decrease many chemical agents other than the toxic agents, it leads to a cost reduction, and thus is suitable for all industries.

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