Multicomponent Nanoparticles Synthesis in Solution Plasma for ISPC25 21-26 May 2023, Kyoto, Japan

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Abstract: The double layers discharge in the solution plasma system was designed. The plasma was generated in the top layer which was cyclohexane. A plasma-liquid interface was formed and the multicomponent nanoparticles were produced based on the electron transfer reaction. High-resolution transmission electron microscopy was utilized to confirm the surface morphology. A functionalized core-shell structure was found, and multicomponent nanoparticles were the core with carbon as the shell. The synthesized material was expected to conduct the carbon dioxide reduction in photocatalytic or plasma-catalytic reactions.

Keywords: solution plasma, multicomponent nanoparticles, plasma-liquid interface.

1. Introduction

The loaded highly dispersed multicomponent nanoparticle catalysts can be used in electrochemical oxidation reactions of alcohols, carbon-carbon coupling reactions, olefin hydrogenation reactions, liquid-phase oxidation reactions of alcohols, and so on. Due to its good catalytic properties, it has attracted much attention from many researchers in industry and scientific research. However, this research field is still facing the problem of how to achieve the preparation of loaded catalysts with uniform particle size, highly monodisperse, or multi-component nanoparticles with controlled composition. This is because it seriously determines the catalytic activity, stability, and resistance to poisoning and sintering. The solution plasma with a pin-to-pin electrode is a typical configuration and various precursors, e.g., cyclic or chain structure, of the raw molecules have been applied for the synthesis of different products. The SPP can induce several unique reactions at the interfaces (e.g., plasma–liquid, and gas–plasma), due to electric discharge, which causes a dielectric breakdown of the liquid similar to an "opening zipper". This phenomenon results in the generation of strong shock waves, ultraviolet, various active radicals, and high-energy electrons. In addition, the SPP has the advantages of fast chemical reactions with a simple experimental system, inexpensiveness, short-time operation, and easy recovery of products at the same time [1]. Duo to the solution plasma has low-temperature reaction field properties. It has typical advantages in the synthesis of nanoparticles as well as graphene materials.

Conventional thermal plasmas, such as arc plasmas, have reaction field temperatures of up to 6000 K. The chemical reaction processes are controlled by thermodynamics at the molecular-atomic level. In other words, the reaction process is concerned with collision-induced energy exchange, i.e., the entropy-governed reaction process. The utilization of thermal plasma allows the modulation of the shape of carbon materials, such as tube- or sphere-shaped products, which are more common in previous reports. Solution plasma is a glow discharge mode. In the plasma reaction field, the electrons have high reactivity, and their temperature reaches 5000 K in general. However, the heavy particle temperature remains basically at room temperature. Their chemical reactions also occur at the molecular-atomic level, but the reaction process is controlled by kinetics. The reaction process is concerned with the collision-induced electron exchange, i.e., the enthalpy-governed reaction process. The same modulation of the carbon products in terms of shape changes, such as sheet- or sphere-shaped products, could be obtained using solution plasma. In addition, the solution plasma has been utilized for various industrial applications such as nanomaterials synthesis, surface treatment, and so on. In the conventional pin-to-pin electrode system for nanomaterial synthesis, the plasma phase and plasma-liquid interface phase were mixed and resulting in the final product containing various unexpected properties. Based on the previous research, the interaction at the plasma-liquid interface was the main reaction field [2]. However, there is still a lack of direct evidence to prove this conclusion. In this research, a double-layer plasma reaction field was designed, and the phase of plasma and plasma-liquid interface was successfully separated which could purify the final product.

2. Experiment

Figure 1 shows the schematic diagram of the SPP experimental setup. The pin-to-pin electrode system was constructed to do intensive investigation analysis by using a pair of tungsten electrodes (W, φ1.0 mm, Nilaco Co, Japan) covered with ceramic tubes and placed 1 mm apart. The experiment was carried out in a glass container with a volume of 200 ml, and the electrode was placed at the center of the glass reactor. The SPP was driven by a bipolar pulsed power supply (MPS-R06K01C-WP1-6CH, Kurita, Japan) under the condition of a voltage of 1.6 kV, a pulse width of 1.5 μs, and a frequency of 11 kHz. The entire discharge process was carried out with a magnetic stirrer. After the SPP synthesis, the obtained black powder products by vacuum filtration were repeatedly washed to remove the residual organic components by using ethanol and dried at 80 ºC for 8 hours in an oven.

The above layer of the solution plasma system was cyclohexane. The bottom layer was a nitrate solution that was mixed with 15 elements (Fe, Co, Ni, Cr, Y, Ti, V, Cu, Al, Nb, Mo, Ta, Zn, Cd, and Ag). The plasma could be stably generated in the above layer solution which produced the carbon, and the electron transfer reaction could generate in the bottom layer which produces the nanoparticles.

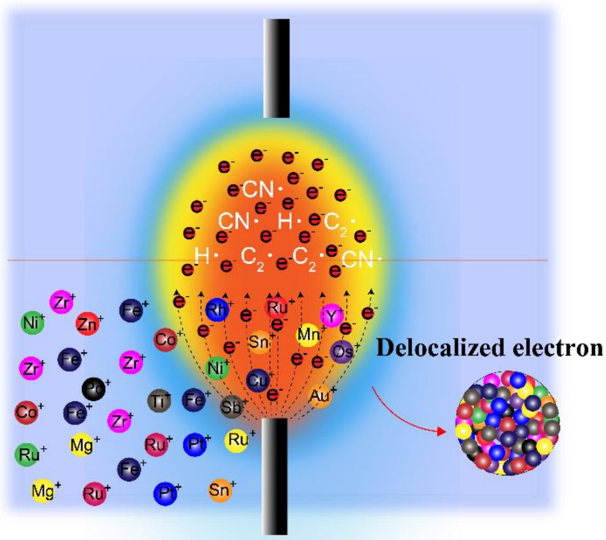

Fig. 1. Schmetic of the electrode system.

3. Result and discussion

The plasma characteristics were observed in space and time. The discharge was first formed at 125 μs on the upper half of the solution, and then plasma spread downstream to the lower half, reaching its maximum intensity and area at 250 μs. At 375 μs, the upper half discharge became weak, while the lower half continued to increase. The spatial scale of the stable discharge reached 3×16 mm, which could be considered as a larger-scale plasma, compared to that of the pin-to-pin system. In addition, the erosion of the metal surface on the electrodes in the criss-cross system was not found after discharge for 15 min. This evidence indicated that the discharge in the criss-cross system had a large scale without excessive energy accumulation.

Transmission electron microscopy (TEM) showed that the micro-scaled graphene structure was obtained and the nano-scaled particles were deposited on the surface of the carbon framework, as shown in Figure 2. Furthermore, the results of energy dispersive X-Ray analysis (EDX) showed that the high entropy multicomponent was successfully generated.

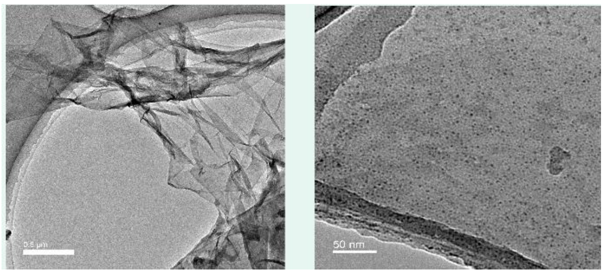

Fig. 2. TEM of the multicomponent particles.

4. Conclusion

The result of this research proved that the interaction of electron transfer reaction at the interface of plasma-liquid was the main field for producing the nanomaterials in the solution plasma process. The synthesized multicomponent particles showed great potential for application in the catalytic reaction.

5. References

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