A NOVEL DISCHARGE TECHNIQUE FOR NOBLE.METAL NANOPARTICLES

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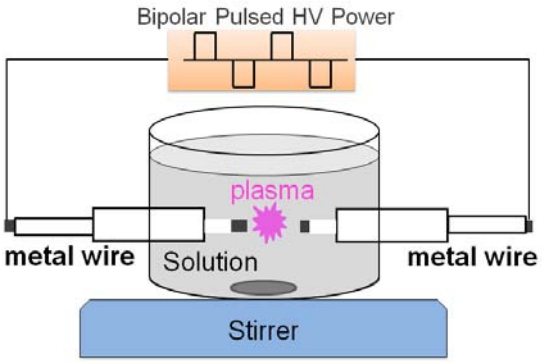
Introduction

Ultrafine noble metal nanoparticles exhibit size-dependent photonic and electric properties that are of interest for applications such as biosensors, catalyst for chemical and fuel cells, optics, and electronics. Gold particles show a highly active catalyst for many reactions and intrinsic magnetic polarization when the sizes decrease to a few nanometers. Various synthesis methods were carried out to get noble metal nanoparticles such as chemical approaches and vacuum metal-vapor-condensation techniques. However, high-purity, size controllable and high-dispersibility nanoparticles have not been achieved. Recently, *Solution plasma* processing defined by non-equilibrium plasma in solutions, provides us a novel reaction field with highly excited energy state. Clean nanoparticles without any impurity were successfully synthesized due to the strong reduction potential of the generated radicals [1-3]. The advantage of this method is the operation in an open system under atmospheric pressure. In the present study, we addressed a novel and one-step route for high-efficient synthesis of noble metal nanoparticles from their metal wire electrodes by *solution plasma sputtering*.

Experimental

Materials: Metal wires (such as Au, Pt) with the diameter of 1.0 mm (Aldrich, 99.9%) were used as an electrode. Pure water and ethanol were selected as a solvent.

Experiment: The schematic diagram of experimetal setup of *solution plasma sputtering* technique was shown in scheme 1. The gap between the electrodes maintained at 0.3 mm during discharging time. Plasma was generated using a high voltage pulsed DC power supply. *Characterization*: The optical property of nanoparticles in water/ethanol was detected by an ultraviolet spectrophotometer UV-3600 (UV-Vis, Shimadzu**,** Japan) in the range of 200–800 nm. The shape and microstructure of gold clusters were observed in annular dark field scanning TEM (ADF-STEM) and high resolution TEM (HR-TEM) in JEM-2500SE (JEOL, Japan) operated at 200 kV.



Scheme 1. Schematic diagram of the experimental setup by *solution plasma sputtering*.

Results and Discussion

Gold nanoparticles formed simultaneously with *solution plasma sputtering* in a solution. The TEM and typical HR-TEM images of as-prepared gold nanoparticles are shown in Fig.1. Almost all of gold nanoparticles shaped with spherical morphology were formed in water and ethanol. High-resolution TEM image show all of nanoparticles have well crystalline structure, judging by the well-defined lattice fringes. It is well known that a surface plasmon resonance band near 520 nm originated from the gold nanoparticles was detected easily. Fig.2 shows the UV-Vis absorbance spectra of gold nanoparticles in water and ethanol, respectively. The intensity of surface plasmon resonance band became stronger with the increasing discharge time. The results indicated the number amount of gold nanoparticles increased with the discharge times. However, when the discharge in ethanol is kept for 1.5 min, only broaden and weak intensity of surface plasmon resonance band was detected. By comparison with the solution color from the inset photograph, the gold nanoparticles in water is detected by the appearance of typical red color, gold

nanoparticles in ethanol is purple color. These results clarified that the surface plasmon resonance of gold nanoparticles was affected by dielectric constant of solvent.

And well-crystalline and spherical platinum nanoparticles were also fabricated by solution plasma sputtering (Fig.3). The formation mechanism of metal nanoparticles was hypothesized as the follows. When the pulsed voltage was supplied, gas phase began to form due to the Joule heating. Once increasing up to the breakdown voltage, sputtering discharge became visible. The gold electrodes pair is continuously bombarded by the produced energetic particles in the plasma region. Along with the bombardment of highly energetic plasma particles, metal atoms were ejected from the solid electrodes pair's tip, and with the plasma expanded in the solution due to the enormous difference in the temperature and pressure between plasma and the surrounding medium. The expanded plasma particles were quickly condensed. Finally, the plasma lost its expansive driving force, resulting in the formation of smaller gold nanoparticles.

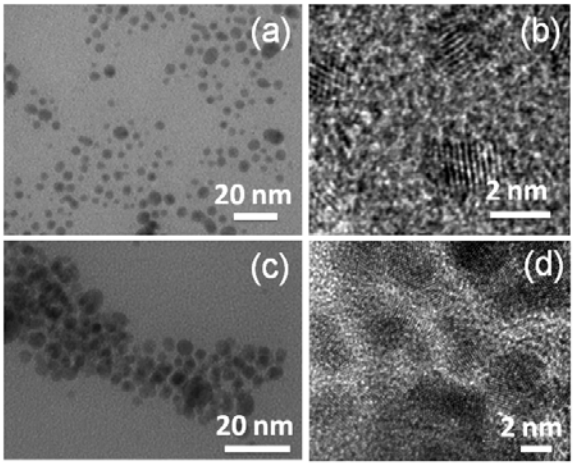


Fig.1. TEM (a, c) and typical HR-TEM images (b, d) of gold nanoparticles. (a, b) and (c, d) for samples prepared in water and ethanol medium, respectively.

Conclusion

Well-crystalline clean gold and platinum nanoparticles with spherical morphology were successfully fabricated via a valuable one-step route from metal electrodes wire by *solution plasma sputtering* in water or ethanol at atmospheric pressure. The plasma provides a novel reaction field with highly energetic state for the formation of metal nanoparticles in the solution medium. Rapid energetic radicals' bombardment, atom vapor diffusion, plasma expansion and medium condensation resulted in the formation of metal nanoparticles. The *solution plasma sputtering* will have potential application in future in the design and mass preparation of various multifunctional metal nanoparticles. These nanoparticles will find a very useful application among the various fuel cell systems.

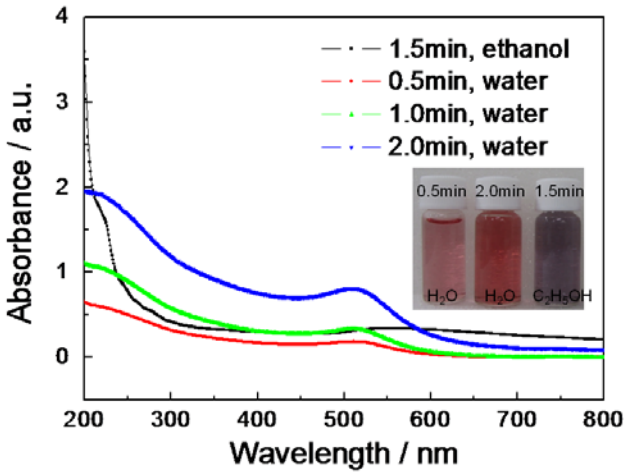


Fig.2. The UV-vis absorbance spectra of gold nanoparticles in water and ethanol, respectively. Inset is a photograph of gold nanoparticles solutions.

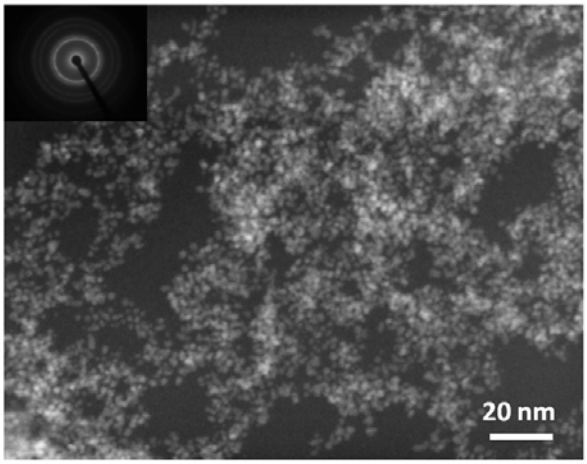


Fig. 3. A DF-TEM image of Pt nanoparticles prepared by *solution plasma sputtering*. Inset is the SAED pattern.

References

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