

Sonochemical Synthesis of Conducting Polymer-Metal Nanoparticles Nanocomposite

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Metal nanoparticles (Me-NPs), which have a high specific surface area and a high fraction of surface atoms to volume atoms, have been studied extensively due to their unique physicochemical characteristics such as catalytic activity, optical properties, electronic properties, and magnetic properties. [1]

On the other hand, ultrasound can generate acoustic cavitations, which is the formation and violent collapse of micro bubbles or gas cavities within a liquid. The collapse of the cavities generates the energy for chemical and mechanical effects. [2] The temperature and pressure generated from the collapse in water have been estimated to be over 5000 K and 1000 atm, respectively, which is high enough to dissociate water molecules into primary hydrogen radicals ($H\bullet$) and hydroxyl radicals ($OH\bullet$) in cavitation bubble. [3] These active species also can drive chemical reactions. For instance, ultrasound offers a very attractive method for the synthesis of Me-NPs. In addition, polymer synthesis using ultrasound has been reported previously. [4]

Meanwhile, it was reported that gold nanoparticles-polyaniline composite was prepared using H_2O_2 for both reduction of $HAuCl_4$ and oxidation of aniline in same aqueous medium by chemical method. [5] Hydrogen peroxide (H_2O_2) is formed by the recombination of hydroxyl radicals ($OH\bullet$) during the sonolysis of aqueous solution. These facts indicate that one-step syntheses of nanoparticles and polymer in the form of composite can be possible in aqueous solution using ultrasonic irradiation. With this motivation, we have combined the two sonochemical synthetic methods to obtain the conducting polymer/Me-NPs nanocomposite.

$HAuCl_4$ was dissolved in distilled water to make 0.25 mmol dm^{-3} solutions in the absence and presence of 10 mM pyrrole, and sodium dodecyl sulfate (SDS) (1.25 mmol dm^{-3}) was added as a stabilizer. The solution containing SDS was placed in a water bath. Because the local heating produced by the cavitation also influences on the solution temperature, the temperature of the water bath was held at 278 ± 0.5 K during sonication. Ultrasonic irradiation was performed with a collimated 20 kHz beam from a ceramic transducer with a titanium amplifying horn (13 mm Φ , Branson Sonifier 450D) directly immersed in the solution and operated with an input power of 30 W. The colloidal suspensions were analyzed using UV-vis spectrometer and transmission electron microscopy (TEM).

Figure 1 shows the UV-vis spectra of change during ultrasonic irradiation. Before the irradiation, the $HAuCl_4$ solution containing pyrrole and SDS shows valence-to-conduction band transition at 800 nm (1.5 eV) as shown in Figure 1(a). In addition, the absorption band of zerovalent Au-NPs was also observed at ca 530 nm (Figure 1a). This fact suggests that $AuCl_4^-$ ion was reduced to some extent in the absence of ultrasonic irradiation. By ultrasonic irradiation, the absorbance of Au-NPs at 530 nm was blue shift with an increasing the irradiation time and a new absorption band was observed at ca. 462 nm, and its intensity was increased with an increasing the time. The absorption band at 462 nm could be assigned as $\pi-\pi^*$ transition of polypyrrole (PPy), but no absorption band due to charge carriers, i.e. polarons at 685 nm or bipolarons at 978 nm, was present. This means that the surface of the composite entirely consists of polypyrrole molecules and the core of gold atoms, but PPy formed on Au-NPs was not doped during the polymerization.

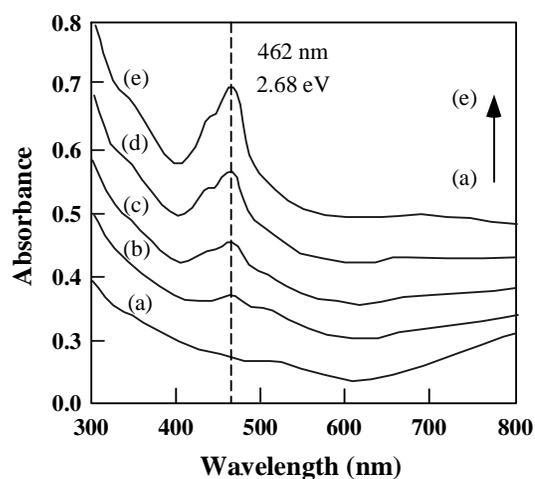


Figure 1. UV-vis absorption spectra change during ultrasonic irradiation to an aqueous solution of $HAuCl_4$ (0.25 mM)-pyrrole (10 mM) in the presence of 1.25 mM SDS at 25 °C. Curves (a)-(e) refer to the spectra of the sample irradiated by ultrasound for 0, 1, 2, 3, and 4 hrs respectively.

The formation of the colloidal dispersions of PPy/Au-NPs nanocomposite clusters was also confirmed by TEM. Figure 2 shows the TEM images of PPy/Au-NPs nanocomposite suspensions corresponding to 4 hrs ultrasonic irradiation. TEM revealed that small Au-NPs dispersed in PPy matrix and the average diameter of PPy/Au-NPs was 15 nm.

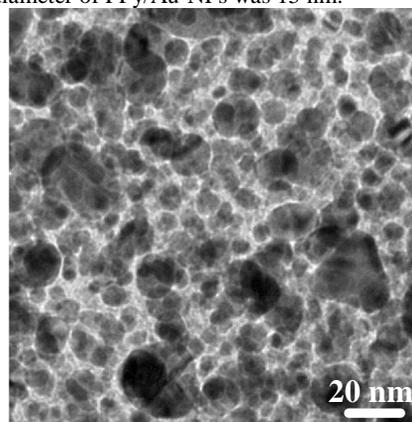


Figure 2. TEM images of PPy/Au-NPs nanocomposites prepared by ultrasonic irradiation.

The results on the electron micrographs as well as the UV-vis spectra suggest that the dispersions prepared by one-step synthesis are not mixture of the Au-NPs and PPy but composed of the PPy/ Au-NPs composite clusters.

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