Sonochemical Synthesis of Inorganic–Organic Hybrid Nanocomposite Based on Gold Nanoparticles and Polypyrrole

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Colloidal dispersions of hybrid nanocomposite composed of gold nanoparticles (Au-NPs) and polypyrrole (PPy) were prepared by a sonochemical method, in which gold ion and pyrrole monomer in an aqueous solution were reduced and oxidized, respectively, by ultrasonic irradiation in the presence of poly(*N*-vinyl-2-pyrrolidone) (PVP).

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 because of their unique physicochemical characteristics such as catalytic activity, optical properties, electronic properties, and magnetic properties.[1–3]

On the other hand, ultrasound can generate acoustic cavitations, which is the formation and violent collapse of microbubbles or gas cavities within a liquid. The collapse of the cavities generates the energy for chemical and mechanical effects.[4] 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•) and hydroxyl radicals (OH•) in cavitation bubble.[5,6] These active species also can drive chemical reactions. For instance, ultrasound offers a very attractive method for the synthesis of Me-NPs, and the advantages of this method include a rapid reaction rate compared with chemical synthesis and the ability to form very small Me-NPs.[7–10] In addition, polymer synthesis using ultrasound has been reported previously. Kruus et al. studied the polymerization of nitrobenzene and methylmethacrylate as well as other monomers.[11,12]

Meanwhile, Selvan et al. reported that gold/polypyrrole composites have been prepared using both solution-phase and vapor-phase polymerization in inverse micelles in toluene.[13] Sarma et al. 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.[14] Hydrogen peroxide (H_2O_2) is formed by the recombination of hydroxyl radicals (OH•) during the sonolysis of aqueous solution. These facts indicate that one-step synthesis 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 Au-NPs/PPy nanocomposite. In this article, we report a successful preparation of a Au-NPs/PPy nanocomposite using ultrasonic irradiation.

$NaAuCl_4 \cdot 2H_2O$ was dissolved in distilled water to make 0.05 mmol dm^{-3} solutions in the absence and presence of 10 mM pyrrole, and PVP (0.25 mmol dm^{-3}) was added as a stabilizer. The $NaAuCl_4 \cdot 2H_2O$ solution containing PVP was placed in a water bath. Because the local heating produced by the cavitation also depends 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 Shimadzu 1600 UV–vis spectrometer. Transmission electron microscopy (TEM) images were recorded with a Hitachi H-8100 Electron Microscope, operating at 200 kV.

The UV–vis absorption spectrum of Au-NPs prepared by ultrasonic irradiation in the absence of pyrrole monomer was investigated. The absorbance of $AuCl_4^-$ complexes appears approximately at 311 nm. The absorbance of $AuCl_4^-$ complexes at 311 nm was disappearing in the presence of ultrasound as shown in Figure 1B. The color of solution was changed from colorless to pale pink during the reaction. It means that $AuCl_4^-$ ion was reduced by hydrogen radials (H•) produced by acoustic cavitation.

To investigate the formation of the Au-NPs/PPy nanocomposites, ultrasound irradiated $NaAuCl_4 \cdot 2H_2O$ (0.05 mmol dm^{-3}) aqueous solution containing pyrrole (10 mM) and PVP

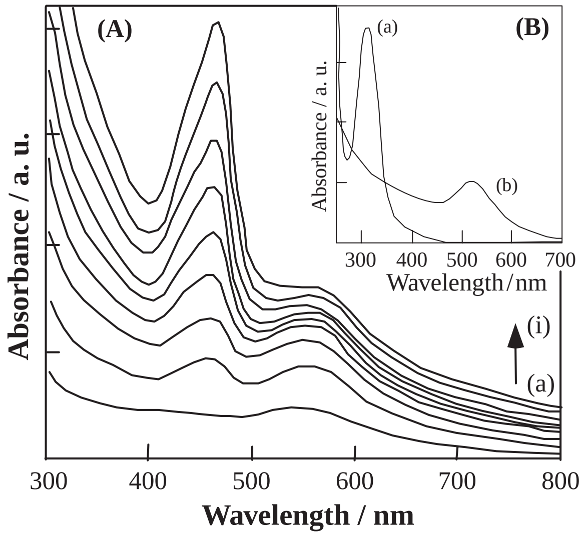

Figure 1. (A) UV–vis absorption spectra change during the reaction of $NaAuCl_4 \cdot 2H_2O$ (0.05 mM) aqueous solution containing pyrrole (10 mM) and of 0.25 mM PVP at 25 °C. Curves (a)–(i) refer to the spectra of the sample irradiated by ultrasound for 0, 30, 60, 90, 120, 150, 180, 210, and 240 min, respectively. (B) UV–vis absorption spectra obtained for (a) $NaAuCl_4 \cdot 2H_2O$ (0.05 mM) solution and (b) corresponding Au-NPs solution.

(0.25 mmol dm^{-3}) as a stabilizer. Figure 1A shows the UV–vis spectra of change during the formation of Au-NPs/PPy nanocomposite. Before the irradiation, the $NaAuCl_4 \cdot 2H_2O$ solution containing pyrrole and PVP shows absorption band of zerovalent Au-NPs at 530 nm, which is caused by plasmon resonance as shown in Figure 1A. This fact suggests that $AuCl_4^-$ ion was reduced to some extent in the absence of ultrasonic irradiation. In fact, Henry at el. reported that polypyrrole/gold colloids could be prepared using a redox reaction between chlorauric acid ($HAuCl_4$) as an oxidant and pyrrole monomer as a reductant.[15] However, a further change in the absorption was never observed in our experiment even after standing for a few hours in the absence of ultrasonic irradiation. In the presence of ultrasonic irradiation, the absorbance of Au-NPs at 530 nm was red-shifted with an increasing the irradiation time and a new absorption band was observed at ca. 462 nm, and its intensity was increased with increasing the time. The absorption band at 462 nm could be assigned to π–π^* transition of polypyrrole, but no absorption band due to charge carriers, i.e., polarons at ca. 685 nm or bipolarons at ca. 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.

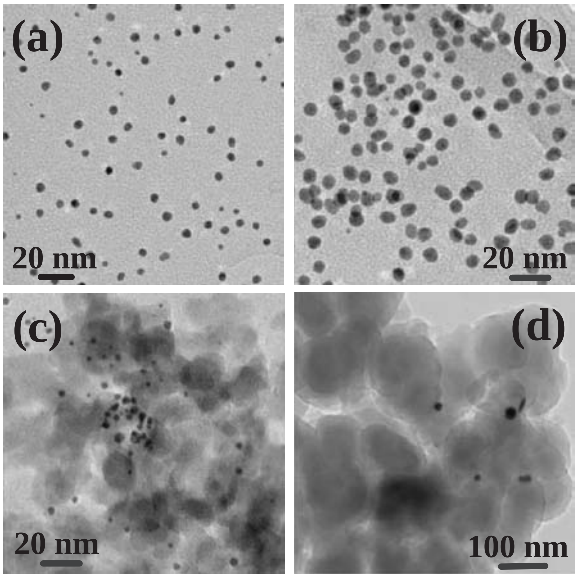

Figure 2. TEM images of Au-NPs/PPy nanoparticles taken from different ultrasonic irradiation time in aqueous solution: (a) 0 min, (b) 30 min, (c) 120 min, and (d) 240 min. The TEM samples were obtained by dropping the solutions onto carbon-coated copper grids placed on a filter paper for rapid removal of the liquid.

The formation of the colloidal dispersions of Au-NPs/PPy nanocomposite was also examined by TEM. Figure 2 shows the TEM images of Au-NPs/PPy nanocomposite obtained for different ultrasonic irradiation time. Figure 2a shows the Au-NPs formed without sonication. The average diameter was 5 nm. In the presence of ultrasound, the Au-NPs particles grow up about 8 nm and polypyrrole was formed on the Au-NPs surface (Figures 2b–2d). TEM revealed that the PPy formed on the Au-NPs and thickness of PPy increased with increasing ultrasonic irradiation time. 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 Au-NPs/PPy composite clusters.

On the other hand, the reaction step for the formation of Au-NPs/PPy nanocomposite under ultrasonic irradiation can be expected a sequence of reaction of the formation of polypyrrole on the Au-NPs surface. One is reduction of $NaAuCl_4 \cdot 2H_2O$ by ultrasonic irradiation, the other is oxidation of pyrrole by H_2O_2 which is formed by the recombination of hydroxyl radicals (OH•) during the sonolysis of an aqueous solution. Hence, as described the above, Au-NPs/PPy composite can be formed via a redox reaction between $AuCl_4^-$ and pyrrole monomer regardless of ultrasonic irradiation. Therefore, it can be also considered that the formation of the nanocomposite was accelerated in the presence of ultrasonic irradiation. The analysis of nanocomposite properties composed of conducting polymer and metal nanoparticles is currently being carried out and results will be presented elsewhere.

It has been reported that gold nanoparticles/polypyrrole nanocomposite have been obtained by means of ultrasonic irradiation. The formation of PPy on the surface of Au-NPs is conformed by UV–vis and TEM. The formation of Au-NPs/PPy nanocomposites depends on the ultrasonic irradiation time. The PPy layer formed on the surface of Au-NPs depends on the power of ultrasound (not shown here).

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