Preparation of π-conjugated polymer-protected gold nanoparticles in stable colloidal form

Yong Zhou, Hideaki Itoh, Takashi Uemura, Kensuke Naka* and Yoshiki Chujo*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto, 606-8501, Japan. E-mail: ken@chujo.synchem.kyoto-u.ac.jp

Received (in Cambridge, UK) 17th January 2001, Accepted 21st February 2001

π-Conjugated polymer-protected gold nanoparticles of narrow size distribution in stable colloidal form have been prepared *via* reduction of $HAuCl_4$ by a π-conjugated poly(dithiafulvene) having electron donating properties.

Recently, hybrid systems consisting of inorganic nanoparticles with π-conjugated polymers as supporting matrices were found to display various interesting characteristics, particularly in the areas of dielectric properties, energy storage, catalytic activity, and magnetic susceptibility. The reason is that π-conjugated polymers as one-dimensional semiconductors have the advantage of being easy to process to form large-area devices. Their energy gaps and ionization potentials can readily be tuned by chemical modification of the polymer chains. The process of charge transfer at the contact between a metal nanoparticle and an organic (or polymeric) semiconductor plays an important role in many areas of technology.[1] The electronic structure of the polymer chain strongly influences the characteristic of the metal nanoparticles.[2,3]

This communication describes the first example of stable colloidal forms of nanocomposites consisting of metal nanoparticles protected with a π-conjugated polymer. Reduction of metal ions by the π-conjugated polymer leads to metal nanoparticles with the resulting oxidized polymer protecting the metal nanoparticles. It has already been reported that reduced forms of polymers such as polypyrrole and polyaniline are converted to the respective oxidized forms with simultaneous *in situ* reduction of metal ions, Pd(II) and Au(III) to their elemental forms.[4–6] However, these composites could not be dispersed in any solvents. Here we used a π-conjugated polymer containing the strong electron-donating dithiafulvene unit in the main chain, which was synthesized recently by our group.[7] We found that gold colloidal particles were formed with narrow size distribution *via* reduction of $HAuCl_4$ by the π-conjugated poly(dithiafulvene) (PDF). The oxidized polymer then protected and stabilized the gold nanoparticles.

In a typical preparation of π-conjugated polymer-protected gold nanoparticles, PDF† (5.44 mg, 2.86×10^{-5} mol by repeating unit) was dissolved in 5 ml of a dimethyl sulfoxide (DMSO) solution of $HAuCl_4$ (5×10^{-6} mol). The reaction mixture was stirred for 24 h at room temperature. The reaction mixture changed gradually from yellow to purple with stirring. A similar solution in the absence of PDF was also stirred for 24 h at room temperature. The solution remained yellow. These results indicate the reduction of $HAuCl_4$ to gold nanoparticles by PDF. The resulting DMSO solution of the polymer-protected gold nanoparticles was stable without precipitation for more than a month at room temperature under air. The sample showed film-forming properties when the DMSO solution was cast onto a glass slide.

Fig. 1(a) shows a transmission electron microscopy (TEM) image of the produced π-conjugated PDF-protected gold nanoparticles, which was deposited on a grid from a DMSO solution. It can be seen that spherical gold nanoparticles were produced with narrow size distribution and high dispersion. The histogram of the size distribution is shown in Fig. 1(b), which was obtained directly from an enlarged TEM image by counting 300 particles. The average size of the particles was 6 nm.

Fig. 2 shows the UV–VIS absorption spectrum of the PDF-protected gold nanoparticles in DMSO. An absorption band appears at 550 nm. It can be concluded that the band results from the surface plasmon resonance of the gold nanoparticles. A π–π* transition absorption band of PDF was observed around 400 nm.[7] The surface plasmon resonance band of gold colloids is calculated theoretically to be at 510–525 nm in an aqueous system.[8] It is clear that the absorption band of the PDF-protected gold nanoparticles was strongly red shifted compared with the theoretical value. It is well known that, for spherical

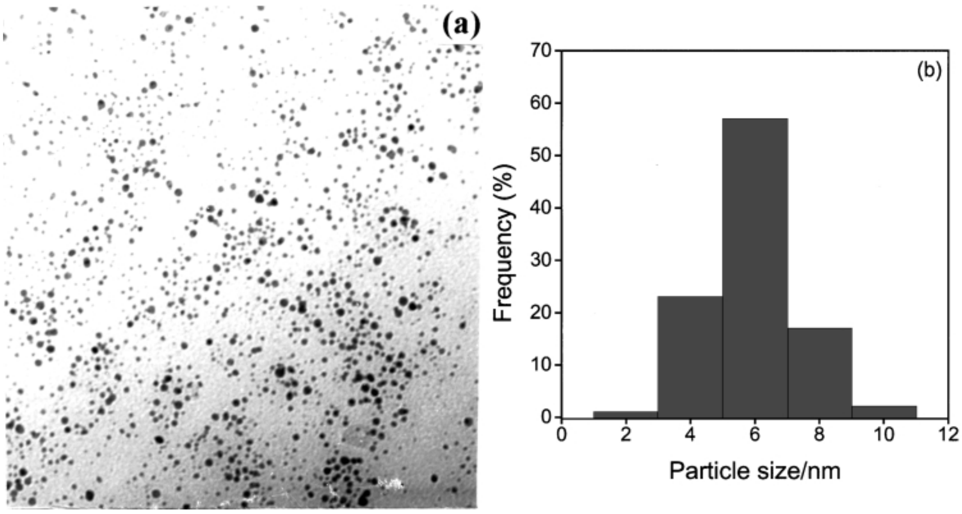

Fig. 1 (a) TEM image of the π-conjugated PDF-protected gold nanoparticles; (b) Histogram of the size distribution of the π-conjugated PDF-protected gold nanoparticles.

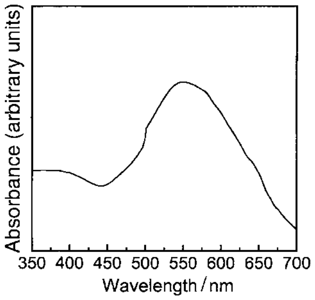

Fig. 2 UV–VIS absorption spectrum of the PDF-protected gold nanoparticles in DMSO.

colloidal metals of size 3–20 nm, there is not a strong dependence of the absorption spectrum on particle size.[8] This is because, for particle sizes below *ca.* 20 nm diameter the quadrupole and higher-order term in the Mie summation become significant.[9] In the present case, since the gold nanoparticles were of average size 6 nm, the red shift was not due to the size effect. However, the surrounding medium affects the absorption peak position of the metal nanoparticle by varying the interface conditions.[10] In this case, to study the influence of DMSO on the surface plasmon resonance band of the gold colloid, we used $NaBH_4$ as the reducing reagent and polyvinylpyrrolidone (PVP) as the protecting polymer for reduction of $HAuCl_4$ in DMSO. The absorption band of the gold nanoparticles of size 14 nm produced by this system was located at *ca.* 520 nm *i.e.* with no red shift. These results indicate that the red shift originated from the influence of the oxidized PDF. When protected by the oxidized PDF, the work function of the gold particle will decrease compared to that *in vacuo*, which lowers the energy of the surface resonance state,[11] leading to the red shift of the absorption band.[12]

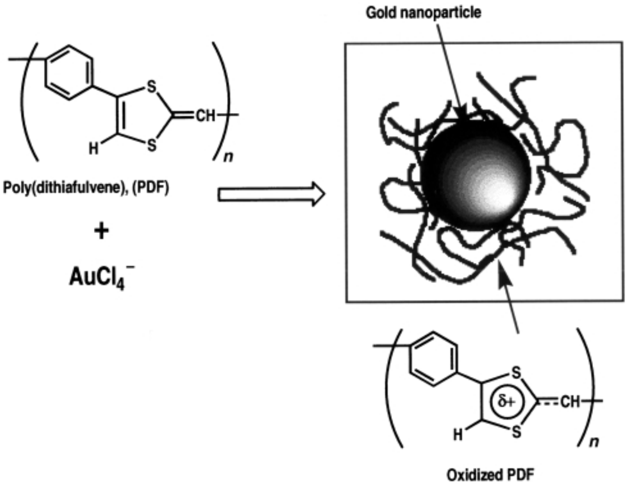

Fig. 3 Schematic illustration of the formation of the PDF-protected gold nanoparticles.

In conclusion, π-conjugated polymer-protected gold nanoparticles of narrow size distribution have been prepared in stable colloidal form *via* reduction of $HAuCl_4$ by the π-conjugated electron-donating PDF. Formation of the gold nanoparticle by the π-conjugated PDF is schematically shown in Fig. 3. The oxidized π-conjugated PDF induced a strong red shift of the absorption spectrum of the gold nanoparticles.

We thank Dr M. Tsujii, Dr S. Yamamoto and Professor T. Fukuda (Kyoto University) for the TEM micrographs. We also thank Dr T. Sato (Kyoto University) for helpful discussions.

Notes and references

† PDF was prepared from 1, 4-diethynylbenzene according to our previous report.[7] The number-average molecular weight (M_n) of PDF used here was 5440 as determined by ^1H NMR spectroscopy.

1 J. C. Scott and G. G. Malliaras, *Chem. Phys. Lett.*, 1999, **299**, 115.
2 K. V. Sarathy, K. S. Narayan, J. Kim and J. O. White, *Chem. Phys. Lett.*, 2000, **318**, 543.
3 T. Hertel, E. Knoesel, M. Wolf and G. Ertl, *Phys. Rev. Lett.*, 1996, **76**, 535.
4 S. W. Huang, K. G. Neoh, C. W. Shih, D. S. Lim, E. T. Kang, H. S. Han and K. L. Tan, *Synth. Met.*, 1998, **96**, 117.
5 K. G. Neoh, K. K. Tan, P. L. Goh, S. W. Huang, E. T. Kang and K. L. Tan, *Polymer*, 1999, **40**, 887.
6 S. W. Huang, K. G. Neoh, E. T. Kang, H. S. Han and K. L. Tan, *J. Mater. Chem.*, 1998, **8**, 1743.
7 K. Naka, T. Uemura and Y. Chujo, *Macromolecules*, 1999, **32**, 4641.
8 J. A. Creighton and D. G. Eadon, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 3881.
9 M. Kerker, *The Scattering of Light and Other Electromagnetic Radiation*, Academic Press, New York, 1969, p. 38.
10 S. Underwond and P. Mulvaney, *Langmuir*, 1994, **10**, 3427.
11 M. Wolf, E. Knoesel and T. Hertel, *Phys. Rev. B*, 1996, **54**, R5295.
12 N. Sandhyarani and T. Pradeep, *J. Mater. Chem.*, 2000, **10**, 981.