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Meifang Zhu^a; Xiaqin Wang^a; Kensuke Naka^b; Xingping Zhou^c; Yoshiki Chujo^b

^a State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Material Science and Engineering, Donghua University, Shanghai, P. R. China ^b Institute of Biological Sciences and Biotechnology, Donghua University, Shanghai, P. R. China ^c Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto, Japan

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Self-Organized Nanocomposite of Gold Nanoparticles and π -Electron Organic Molecules

MEIFANG ZHU,¹ XIAQIN WANG,¹ KENSUKE NAKA,²
XINGPING ZHOU,³ AND YOSHIKI CHUJO²

¹State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Material Science and Engineering, Donghua University, Shanghai, P. R. China

²Institute of Biological Sciences and Biotechnology, Donghua University, Shanghai, P. R. China

³Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto, Japan

Aggregates of gold nanoparticles were formed by simple addition of a dithiafulvene derivative (DF) to an acetonitrile solution containing gold ions. The discrete gold nanoparticles in the aggregates were separated by monolayers of oxidized DF. No aggregation was observed with the addition of poly(vinylpyrrolidone) (PVP), which acted as a strong stabilizer and inhibited self-assembly of the gold nanoparticles. DF acted as a reducing agent for gold ions, a stabilizer, and a tether for the resulting gold nanoparticles. Intermolecular S...S interaction and Au–S bonds might be the driving force for the self-assembly of the gold nanoparticles.

Keywords dithiafulvene derivative, reducing agent, stabilizer, tether of gold nanoparticles

Introduction

Development of simple methods for building and patterning of metal nanoparticles into organized structures is a potential route for applications in nanotechnology, since collective properties of the resultant nanostructures are expected to be different from those of the corresponding isolated nanoparticles. Various strategies, i.e., hydrogen bonding (1), π - π stacking (2), covalent bonding (3), and electrostatic attraction (4), have been developed so far to organize nanoparticles into ordered arrays.

Self-organization of nanocomposites from metal nanoparticles and π -electron molecules or polymers is of attractive interest for future nanodevices. Dithiafulvene analogues, including tetrathiafulvalenes (TTF), have been intensively studied to prepare novel low molecular weight and polymeric materials since the discovery of exceptional electric conductivities of their charge transfer complexes (5, 6). Recently, we have

Address correspondence to Xiaqin Wang, State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Material Science and Engineering, Donghua University, Shanghai 200051, P. R. China. E-mail: xqwang@dhu.edu.cn

exploited new methods for preparing nanocomposites of dithiafulvene analogues and metal nanostructures through electron transfer from these molecules to metal ions in solution (7, 8). 2-Benzylidene-4-phenyl-1,3-dithiol (DF) ($E_{\text{pa}} = 0.40$ V vs. Ag/AgCl) (9) has similar redox behavior as TTF ($E_{\text{pa}} = 0.39$ and 0.81 V vs. Ag/AgCl) (10). Herein, we describe the formation of self-assembled gold nanoparticles induced by DF absorbed on the surface of gold nanoparticles. DF played a triple role for the formation of the self-assembly.

Experimental

Preparation of DF

DF was quantitatively synthesized by the treatment of lithium 2-phenylethynethiolate with water in tetrahydrofuran (11). $^1\text{H-NMR}$ (270 MHz, $(\text{CD}_3)_2\text{SO}$): δ 6.73 ($>\text{C} = \text{CH-Ph}$, s, 1H), 7.20 (1,3-dithiole ring proton, m, 1H), 7.30–7.55 (aromatic, m, 10H).

Synthesis of Self-Organized Nanocomposite

A typical preparation of the self-assembled gold nanoparticles was carried out as follows. DF (5.0 mg, 1.86×10^{-2} mmol) was dissolved in 15 ml of acetonitrile (CH_3CN) solution of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (5.0 mg, 1.22×10^{-2} mmol) at room temperature. The color of the solution with DF and $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ changed red within several minutes under vigorous stirring. The solution was quite stable and no large precipitation was observed even after 1 month.

Results and Discussion

The XRD pattern of the product isolated by evaporation of the solvent illustrated the presence of diffraction peaks corresponding to the (111) and other planes of metallic gold. A transmission electron microscopy (TEM) image of the product after the solution was stirred for 0.5 h shows the formation of nearly-spherical aggregates of gold nanoparticles (Figure 1). The discrete nanoparticles separated from each other by DF in an enlarged self-assembly are shown in the inset of Figure 1. The average size of the gold nanoparticles was 4.7 ± 0.8 nm (averaging the sizes of 120 nanoparticles), and the average size for the spherical aggregates was 45.9 ± 9.0 nm (averaging the sizes of 37 aggregates).

When poly(vinylpyrrolidone) (PVP) ($M_w = 40,000$) was added into a solution with the same feed molar ratio as the solution in Figure 1, gold nanoparticles, with an average size of 4.8 nm, were produced and no aggregation was observed by TEM (Figure 2). PVP, a well-known protecting polymer for metal nanoparticles, inhibited the aggregation of the gold nanoparticles.

A surface plasmon resonance band of the gold nanoparticles appeared at 521 nm, in accordance with a theoretical calculation (12). When dimethyl sulfoxide was used as a solvent instead of CH_3CN , the surface plasmon resonance band of the gold nanoparticles also appeared at 521 nm. The aggregation of gold nanoparticles with similar size and shape as in Figure 1 was observed by TEM. Absence of a π -dimer absorption band in the near infrared region ruled out the possibility of π -dimerization of DF radical cations. Furthermore, polar solvents inhibit the formation of the π -dimer of the DF radical cations. These results indicate that electron transfer from DF to gold ions

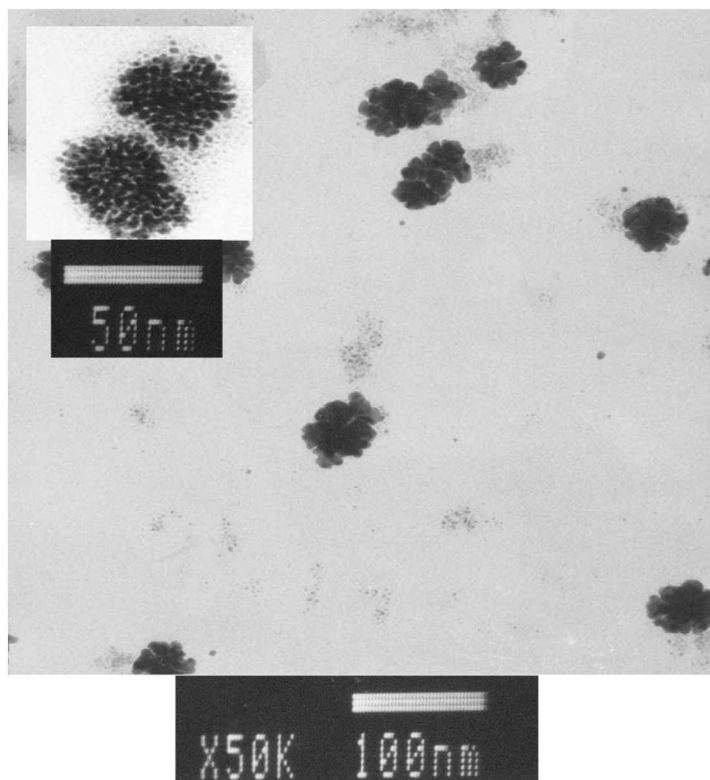


Figure 1. TEM image for the aggregates of the DF-protected gold nanoparticles after 0.5 h reaction. The feed molar ratio of Au and DF was 1:1.53.

yielded self-assembly of the gold nanoparticles with the concurrent formation of metallic gold. The main driving force of the linker-effect of DF for the gold nanoparticles might be Au–S bonding as shown in Figure 3. S–S interaction also contributed to the aggregation (13).

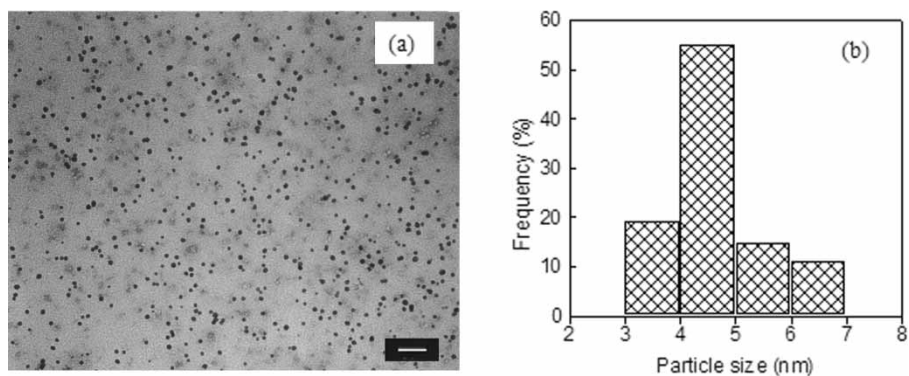


Figure 2. (a) TEM image of the PVP-protected gold nanoparticles (bar: 50 nm), (b) Histogram of the size distribution of the PVP-protected gold nanoparticles.

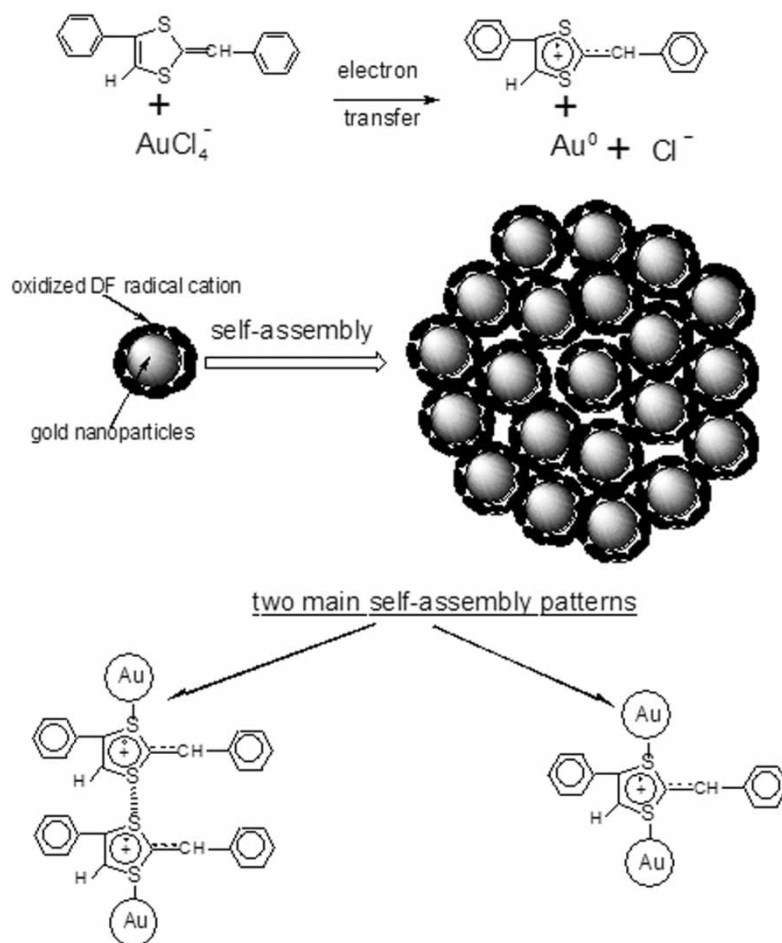


Figure 3. Possible mechanism for the formation of the aggregates derived from the DF-protected gold nanoparticles.

Conclusions

In conclusion, the reducing ability of DF was exploited to prepare spherical aggregates of gold nanoparticles. DF played a triple role, i.e., reducing agent, stabilizer, and tether, of the gold nanoparticles. Intermolecular S...S interaction and Au–S bonds might be the driving force for the self-assembly of the gold nanoparticles. Our current results have opened up a new prospect for self-organized nanocomposites of π -electron organic molecules and metal nanoparticles.

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References

1. (a) Boal, A.K., Lhan, F., Deouchey, J.E., Thurn-Albrecht, T., Russel, T.P., and Rotello, V.M. (2000) *Nature*, 404: 746; (b) Boal, A.K. and Rotello, V.M. (1999) *J. Am. Chem. Soc.*, 121: 4914; (c) Boal, A.K. and Rotello, V.M. (2000) *Langmuir*, 16: 9527; (d) Chen, S. and Kimura, K. (1999) *Langmuir*, 15: 1075.
2. (a) Jin, J., and Iyoda, T., Cao, C., Song, Y., Li, T.J., and Zhu, D.B (2001) *Angew. Chem. Int. Ed.*, 40: 2135; (b) Teranishi, T., Haga, M., Shiozawa, Y., and Miyake, M. (2000) *J. Am. Chem. Soc.*, 122: 4237.
3. Wang, T., Zhang, D., Xu, W., Li, S., and Zhu, D. (2002) *Langmuir*, 18: 8655.
4. Shipway, A.N., Lahav, M., Gabai, R., and Willner, I. (2000) *Langmuir*, 16: 8789.
5. (a) Bryce, M.R. (1991) *Chem. Soc. Rev.*, 2: 355; (b) Hansen, T.K. and Becher, J. (1993) *Adv. Mater.*, 5: 288; (c) Roncali, J. (1997) *J. Mater. Chem.*, 7: 2307; (d) Pittman, C.U., Jr., Liang, Y.-F., and Ueda, M. (1979) *Macromolecules*, 12: 541; (e) Frenzel, S., Arndt, S., Gregorious, M.R., and Müllen, K. (1995) *J. Mater. Chem.*, 5: 1529.
6. (a) Yamamoto, T. and Shimizu, T. (1997) *J. Mater. Chem.*, 7: 1967; (b) Hapiot, P., Salhi, F., Divisia-Blohorn, B., and Müllen, H. (1999) *J. Phys. Chem. A.*, 103: 11221.
7. Wang, X., Naka, K., Itoh, H., Park, S., and Chujo, Y. (2002) *Chem. Commun.*, 1300.
8. Zhou, Y., Itoh, H., Uemura, T., Naka, K., and Chujo, Y. (2002) *Langmuir*, 18: 277.
9. Naka, K., Uemura, T., and Chujo, Y. (1999) *Macromolecules*, 32: 4641.
10. Uemura, T., Naka, K., Gelover-Santiago, A., and Chujo, Y. (2001) *Macromolecules*, 34: 346.
11. Raap, R. (1968) *Can. J. Chem.*, 46: 2251.
12. Creighton, J.A. and Eadon, D.G. (1991) *J. Chem. Soc.: Faraday Trans.*, 87: 3881.
13. (a) Rovira, C. and Novoa, J. (1999) *J. Chem. Eur. J.*, 5: 3689; (b) Hudhomme, P., and Moustarder, S.L., Durand, C., Gallego-Planas, N., Mercier, N., Blanchard, P., Levillain, E., Allain, M., Gorgues, A., and Riou, A. (2001) *Chem. Eur. J.*, 7: 5070; (c) Kobayashi, K., Koyama, E., Kono, C., Namatame, K., Nakamura, K., and Furukawa, N. (2001) *J. Org. Chem.*, 66: 2085.