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Synthesis of silver dendritic nanostructures protected by tetrathiafulvalene

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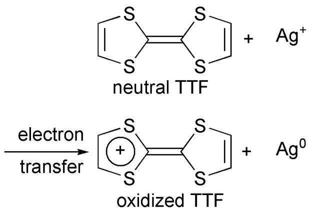
Received (in Cambridge, UK) 2nd April 2002, Accepted 8th May 2002
First published as an Advance Article on the web 17th May 2002

Silver dendritic nanostructures protected by tetrathiafulvalene (TTF) were synthesized *via* reduction of silver ions with TTF in acetonitrile.

In recent years much attention has focused on well-defined nanostructured metals such as nanoparticles, nanorods, and nanowires, because of the influence of their sizes and shapes on their electronic, photonic, and catalytic properties.[1–4] Dendritic nanostructures of noble metals are one type of attractive supramolecular structures. Dendritic fractals are generally observed in non-equilibrium growth phenomena.[5,6] Gold dendritic nanostructures have been prepared by vapour phase polymerization of pyrrole onto solution cast films of polystyrene-block-poly(2-vinylpyridine).[7] Palladium and silver dendritic nanostructures have been prepared by a template method in which the desired materials are encapsulated into the channels or pores of a host.[8] Silver dendrites were observed by ultraviolet irradiation photoreduction technique using PVA as a protecting agent.[9] The presence of nitrilotriacetate or deoxyribonucleic acid also resulted in the formation of silver dendrites with sonoelectrochemical methods.[10,11]

Here we report a preparation of silver dendritic nanostructures with assistance of electron transfer from tetrathiafulvalene (TTF) to silver ions in an organic solvent. Derivatives of TTF act as electron donors and form stable charge transfer complexes with a variety of organic and inorganic acceptor species.[12] However, to our knowledge, the reducing ability of TTF has not been applied to preparing metal nanostructures. Recently, we have reported stable colloidal forms of π-conjugated polymer-protected metal nanoparticles. The reduction of metal ions by π-conjugated poly(dithiafulvene) (PDF) with strong electron donating properties led to metal nanoparticles with the resulting oxidized PDF interacting with metal nanoparticles to form stable hybrid systems.[13] These results motivated us to use TTF as a reducing agent in which the resulting oxidized TTF might protect the elemental metal to form metal nanostructures (Scheme 1).

A typical preparation of the silver dendrites was carried out as follows. In a clean glass container, $AgNO_3$ (3.0 mg, 0.0176 mmol) was dissolved in 25 ml of acetonitrile at room temperature. Then, 3.6 mg (0.0176 mmol) of TTF was added under vigorous stirring at room temperature for 3 days. The initially yellow solution turned into a purple dispersion. In a UV–vis absorption spectrum for the colloidal dispersion, two absorption bands were evident at 436 and 578 nm, both due to cationic TTF.[14] The intensity of these bands increased gradually with the stirring time, indicating the generation of cationic TTF by the redox reaction of TTF with silver ions. The resulting colloidal dispersion was stable without precipitation for more than two weeks. After centrifugation, 1.6 mg of purple product was obtained.



Scheme 1

The XRD pattern of the product showed the presence of diffraction peaks corresponding to the (111), (200), (220) and (311) planes, which indicates the formation of metallic silver. A transmission electron microscopy (TEM) image shows the formation of nanoscale silver dendrites (Fig. 1). The diameter of dendritic nanostructures observed after 21 h reaction was 2.70 ± 0.07 μm. As shown in Fig. 2, spherical particles were observed with narrow size distribution by scanning electron microscopy (SEM). The average particle size was 2.80 ± 0.16 μm, in good agreement with the result from the TEM image. According to an elemental analysis of the isolated product,† the TTF content in the product was 46 wt%. The composition of individual spherical particles was further probed using energy dispersive X-ray (EDX) analysis. The results showed that the contents of

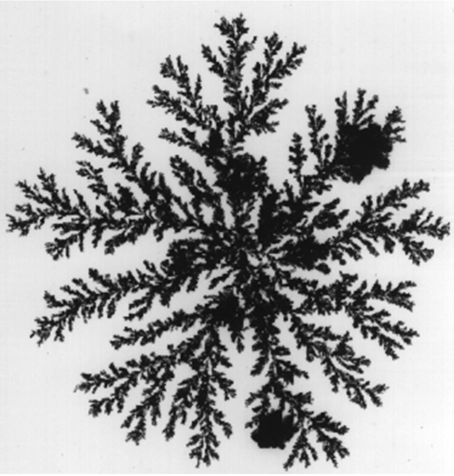


Fig. 1 Transmission electron microscopy image of a silver dendritic nanostructure observed after 21 h reaction.

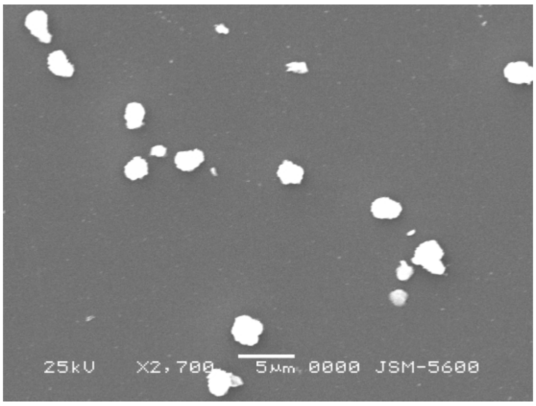


Fig. 2 Scanning electron micrograph of the silver dendrites. The same sample as shown in Fig. 1 was used.

DOI: 10.1039/b203185j

both silver and sulfur elements were uniformly distributed in the particles. These data suggested that the spherical particles consisted of the silver dendrites and TTF. On the basis of the TEM and the SEM images, the silver dendrites were protected by TTF. The oxidized TTF possessed a positive charge and provided electrostatic interaction with the surface of the silver dendrites.

The surface-plasmon resonance of silver nanoparticles did not appear due to the dendritic architecture of silver aggregates compared with the theoretical calculated value of 380 nm in an aqueous system and the reported experimental results at ~410 nm and even longer wavelength as particles became bigger.[15] Some surface-modified nanocolloids did not produce the plasmon absorption band that is characteristic of conventional noble metal colloids. The growth of the silver dendrites *vs*. reaction time was monitored by TEM. Dendritic structures with the diameter of 1.32 ± 0.24 μm appeared after stirring the reaction mixture for 6 h. The size of the dendrites gradually increased with an increase of the reaction time. When a feed molar ratio of TTF to $AgNO_3$ was increased to 1.8, rod-like crystals with diameters of several hundred nanometers and lengths of several micrometers were observed along with the spherical particles by SEM. The rod-like crystals mainly consisted of TTF according to EDX analysis, indicating the formation of a typical charge transfer complex of TTF and metal ions.

Although the growth mechanism of the silver dendrites using TTF is not fully understood, the complex formation of TTF may be a major factor in the formation of the dendrites. In conclusion, silver dendritic nanostructures protected by TTF were prepared *via* redox reaction between TTF and silver ions in solution. TTF acted as both reducing agent and stabilizer. Our current results have provided a new concept for preparing a nanosized composite of metal nanostructures and π-electron organic molecules.

We thank Dr M. Tsujii and Professor T. Fukuda (Kyoto University) for the TEM micrograph. We also thank Dr T. Yazawa and Dr K. Kuraoka (Osaka National Research Institute) for XRD analysis.

Notes and references

† The samples for elemental analysis were isolated by centrifugation and purified by washing with acetonitrile, followed by centrifugation to remove unreacted TTF. This washing process was repeated three times and then the samples were dried in a vacuum oven at room temperature for 48 h.

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