SHORT PAPER

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Preparation of silver nanostrings and dendrites by a ultraviolet irradiation photoreduction technique at room temperature[†]

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Silver nanostrings and beautiful dendritic supramolecular nanostructures of silver nanoparticles have been prepared by a novel ultraviolet irradiation photoreduction technique at room temperature using hydroxyethyl cellulose (HEC) as a protecting agent.

Keywords: silver nanostrings, dendrites, ultraviolet irradiation photoreduction

Preparation of nanoparticles is a fascinating and important field of applied chemical research.[1,2] Researchers have devoted their energy to the wide field application of nanostructure materials. Nanoparticles of noble metals have intensively studied due to their potential applications in microelectronics,[3,4] and their optical, electronic, and catalytic properties.[5-8] Catalytic reactivity depends on the size and shape of the metal nanoparticles, and therefore the synthesis of well-controlled shapes and sizes of colloidal particles could be critical for their application.[9] The research has demonstrated that the concentration of the stabilising polymer influences the size distribution, stability, and catalytic activity of colloidal particles.[10,11] Another interesting class of colloids generated by very slow UV-reduction is large but thin, platelet-like Au nanocrystallines with triangular or truncated hexagonal shape, the size and homogeneity of which also crucially depend on the type of protective polymer.[13] However, shape control has been much more difficult to achieve. Shape control is an alternative tool for adjusting the optical or catalytic properties.

We now report a novel ultraviolet irradiation photoreduction technique for preparation of silver nanostrings and dendritic supramolecular nanostructures at room temperature. It was found that the concentration of both $AgNO_3$ and hydroxyethyl cellulose (HEC) has a significant effect on the formation and growth of these novel nanostructures.

In a typical preparation procedure, two 20-watt column-like low-pressure mercury lamps (λ=253.7nm) were used as the ultraviolet irradiation source. The solutions containing 1% hydroxyethyl cellulose (average molecular weight, 123 000) and $AgNO_3$ of various concentrations were irradiated for 48 hours in the field of ultraviolet irradiation at room temperature. After irradiation, the photochemically prepared sols were directly investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM) in order to survey clearly the shape of Ag nanoparticles in the solution. The X-ray diffraction pattern was recorded by a Philips PW1710 X-ray diffractometer with Cu Kα irradiation (λ=0.15418 nm). Transmission electron microscopy (TEM) image was taken with a JEM-200CX TEM.

Figure 1 shows the XRD pattern of Ag nanoparticles produced by irradiating the solution containing 1% HEC and 1 mmol/l $AgNO_3$ for 48 hours. It indicates that the as-obtained product belongs to the cubic crystal system on comparison with the reported data (JCPDS 4-0783). The five peaks with 2θ values of 38.1°, 44.4°, 64.5°, 77.4° and 81.5° are homologous with the five crystal planes of 111, 200, 220, 311, 222, respectively. The broadened peak with 2θ values of about 22° corresponds to the phase of HEC.

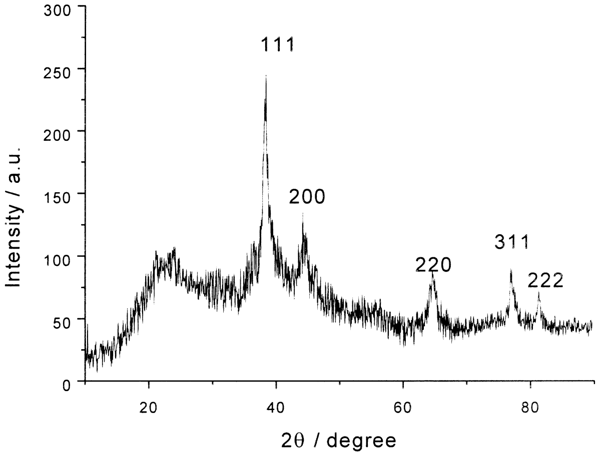

Fig. 1 XRD pattern of Ag nanoparticles produced by irradiating the solution containing 1% HEC and 1 mmol/l $AgNO_3$ for 48 h.

The products were also characterised by TEM. The concentration of $AgNO_3$ was found to play an important role in the formation and growth of the Ag nanoparticles. Figure 2 presents a typical TEM image of the product obtained by irradiating the solution containing 1% HEC and 1 mmol/l $AgNO_3$ for 48 hours. It shows that the Ag nanostrings are about 10–40 nm in diameter, and up to several micrometres in length. The very slow ultraviolet irradiation photoreduction process may favour the formation of the Ag nanostrings.

On increasing the concentration of $AgNO_3$ in the solution, the results indicated that the Ag nanostrings grow thicker and longer. Further observation shows that the produced Ag nanostrings display dendritic growth. The excess of silver in the solution may be favorable for the aggregation and growth into the dendritic structures of the Ag clusters. The TEM image (Fig. 2) shows that many convex areas appeared on the surface of the Ag nanostrings. These convex areas may further develop into dendrites. This proposition was confirmed by further increasing the concentration of $AgNO_3$ in the system. Figure 3 shows the TEM image of the product

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Fig. 2 TEM image of the product obtained by irradiating the solution containing 1% HEC and 1 mmol/l $AgNO_3$ for 48 h.

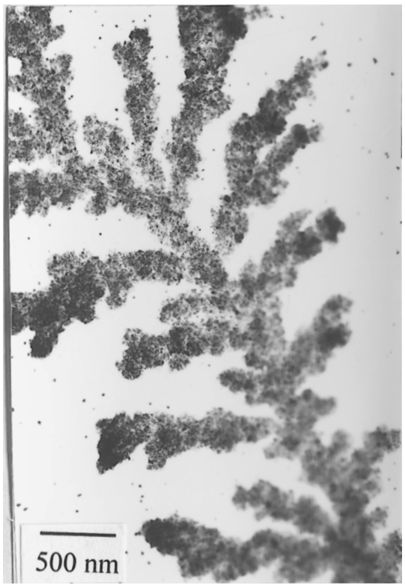

Fig. 3 TEM image of the product obtained by irradiating the solution containing 1% HEC and 50 mmol/l $AgNO_3$.

obtained by irradiating the solution containing 1% HEC and 50 mmol/l $AgNO_3$. Beautiful Ag dendrites were observed. The large supramolecular structure of Ag nanoparticles, abbreviated as DLA (diffusion-limited aggregate),[13,14] represents a very wide variety of growth, in which one particle after the other is formed and then diffuses, sticking to the growing structure. Au-polypyrrole dendritic nanostructures were also observed by Selvan using vapour phase polymerisation of pyrrole onto solution-cast films of block copolymer ionomers.[15]

It was found that the concentration of HEC also plays an important role in the formation of Ag nanostrings. The results confirmed that almost no Ag nanostrings were present in the products if the concentration of HEC was lower than 0.2% in the presence of 1 mmol/l $AgNO_3$, for the same period of irradiation, and that the Ag particles display irregular shapes. Increasing the concentration of HEC in the system is found to be favourable for the formation of the shaped Ag particles. This result of the influence of the concentration of HEC on the shape of the Ag nanoparticles is very similar to that obtained by Ahmadi and coworkers[9], who reported that the ratio of the concentration of the capping polymer material to the concentration of the platinum cations can influence the shapes and sizes of platinum nanoparticles. In the present study, the protecting agent HEC may act as not only as a kind of capping polymer material but also as a kind of soft template. Its presence in the system plays an important role in the formation of the Ag nanostructures. However, the mechanism of the shape-dependent synthesis of colloidal nanoparticles is not yet known and needs to be investigated further.

In summary, Ag nanostrings and beautiful dendritic supramolecular nanostructures of Ag nanoparticles have been prepared by a novel ultraviolet irradiation photoreduction technique at room temperature using HEC as a protecting agent. It was found that the concentrations of both $AgNO_3$ and HEC play a significant role in the formation and growth of the Ag nanostrings and dendrites. These Ag nanoparticles with unusual nanostructures may have important applications in catalysis.

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