Novel Silver Nanostructures from Silver Mirror Reaction on Reactive Substrates

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Novel silver clusters have been prepared by simply carrying out the silver mirror reaction on certain reactive substrates. Leaflike fractal silver microstructures and perpendicularly aligned silver nanosheets were produced on a commercially available copper foil and sandpaper-rubbed copper foil, respectively. The surface features of copper foils and the chemical state of Cu atoms play important roles in regulating the morphological structures of the resulting silver clusters. Silver nanoclusters with various morphologies ranging from the leaflike to flowerlike hierarchical structures can be produced from the silver mirror reaction on commercially available copper foils after being treated with a dilute aqueous HCl solution under different conditions. The aqueous solution of silver nanosheets shows an optical absorption spectrum with a broad light-scattering peak at about 350 nm, compared to a corresponding surface plasmon absorption band around 430 nm for silver nanoparticles from the conventional silver mirror reaction on glass.

Introduction

The recent development of nanotechnology has opened up novel fundamental and applied frontiers in materials science and engineering. At the nanometer scale, the wavelike properties of electrons inside matter and atomic interactions are influenced by the size and shape (surface) of the material.[1] As a consequence, changes in physicochemical properties (for example, melting points, magnetic, optic, and electronic properties) may be observed through a reduction in size, even without any compositional change.[1] New phenomena, such as the confinement-induced quantization effect, could also occur when the size of materials becomes comparable to the deBroglie wavelength of charge carriers inside.[1] By creating nanostructures, therefore, it is possible to control the fundamental properties of materials through the size/shape effects. This should, in principle, allow us to develop new materials and advanced devices of desirable properties and functions for numerous applications.

Historically, the silver mirror reaction has been and is still being used as an efficient method for preparing thin film coatings of silver nanoparticles.[2] Since glass plates have been being used extensively as the substrate for the silver mirror reaction, almost no attention has been paid to possible influence of the substrate surface on the silver nanostructures thus formed. To our surprise, we have recently observed novel silver nanostructures produced from the classical silver mirror reaction by simply changing the glass plate substrate to certain reactive metal foils. We found that the substrate surface plays an important role in regulating the silver nanoclusters thus formed and their hierarchical structures. In the present paper, we demonstrated this simple, but very effective, approach to various novel hierarchical structures of silver nanoclusters by carrying out the silver mirror reaction on copper foils of controllable surface features. A possible formation mechanism for the newly observed silver nanoclusters and their hierarchical structures are also discussed.

Experimental Section

Materials. $AgNO_3$, $Ag(NH_3)_2^+$, glucose, and tartaric acid were purchased from Sigma-Aldrich and used as received. Copper foils were purchased from EMS US, while sandpapers (both 180-C and 600-B) were obtained from GatorGrit, Finland. The CatorGrit 180-C sandpaper is rougher than its 600-B counterpart. HCl used was analytical grade from Fluka. The silver mirror solution[3] contains a freshly prepared silver complex of $Ag(NH_3)_2^+$ (6.375×10^{-3} M), glucose (3.405×10^{-2} M), and tartaric acid (4.005×10^{-3} M). In a typical experiment, silver microstructures were produced by immersing a Cu foil into the silver mirror solution for a certain time at room temperature, followed by rinsing with a large amount of distilled water.

Characterization. Scanning electron microscopic (SEM) and energy-dispersive X-ray analysis (EDX, or EDS: energy dispersive spectroscopy) were carried out by using a Philips XL30 FEG scanning electron microscope equipped with an energy-dispersive X-ray detector. UV-vis spectra were recorded on a Lambda 900 UV/VIS/NIR Spectrometer (PerkinElmer). X-ray diffraction (XRD) measurements were performed on a Rigaku X-ray generator at 50 kV and 150 mA using a monochromatic Cu Kα X-ray beam.

Results and Discussion

To start with, we carried out the control experiment by immersing a smooth glass plate (Figure 1a) into a freshly prepared aqueous silver mirror solution[3] containing $Ag(NH_3)_2^+$ (6.375×10^{-3} M), glucose (3.405×10^{-2} M), and tartaric acid (4.005×10^{-3} M) for several hours. As expected, the classical silver mirror reaction led to the coating of silver nanoparticles on the surface of the glass plate with regular size and shape (Figure 1b,c).

When the above silver mirror reaction was performed on a commercially available copper foil (Figure 2a) under the same conditions, however, large scale leaf-like microstructures of a fractal geometry were formed (Figure 2b,c). SEM images taken

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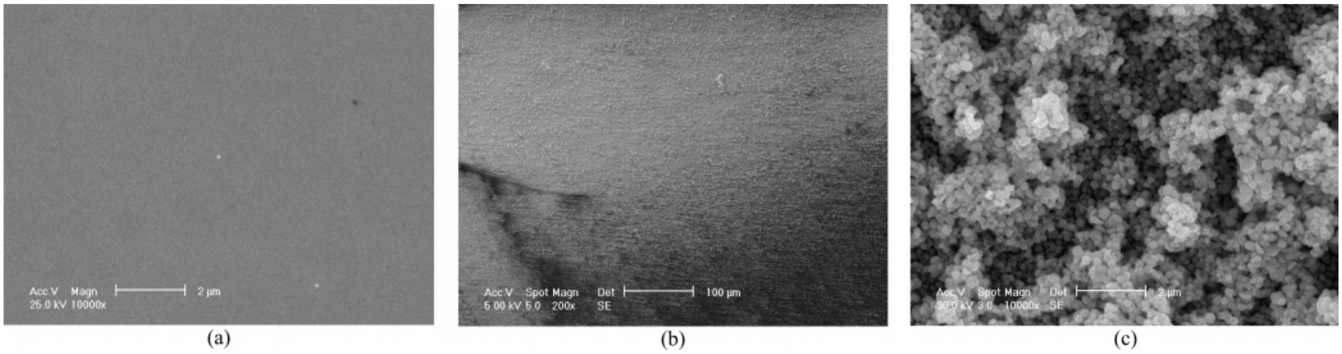
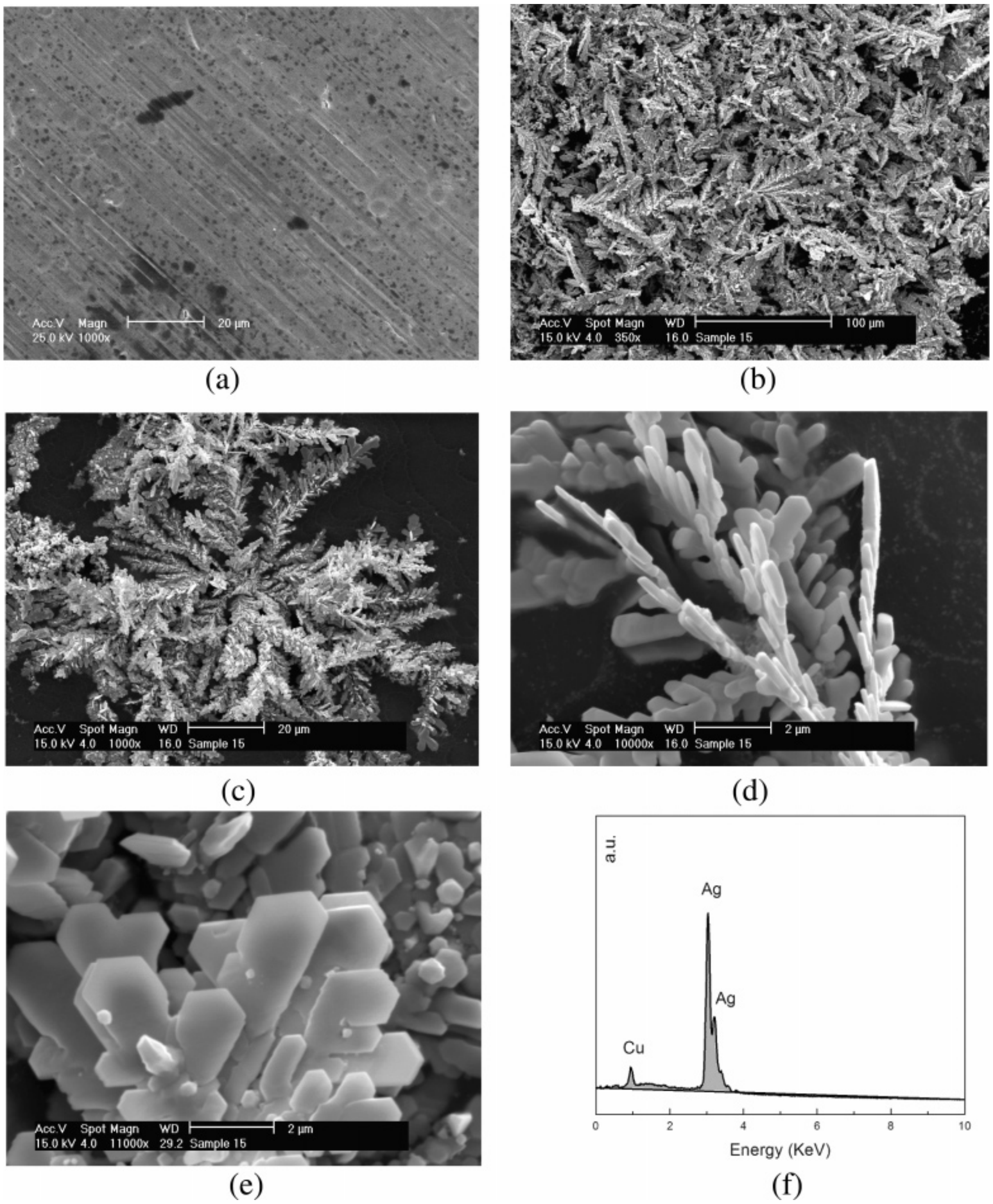


(a) (b) (c)

Figure 1. SEM images of (a) smooth glass plate, (b) silver nanostructures deposited on the glass surface, and (c) as for (b) under a higher magnification.

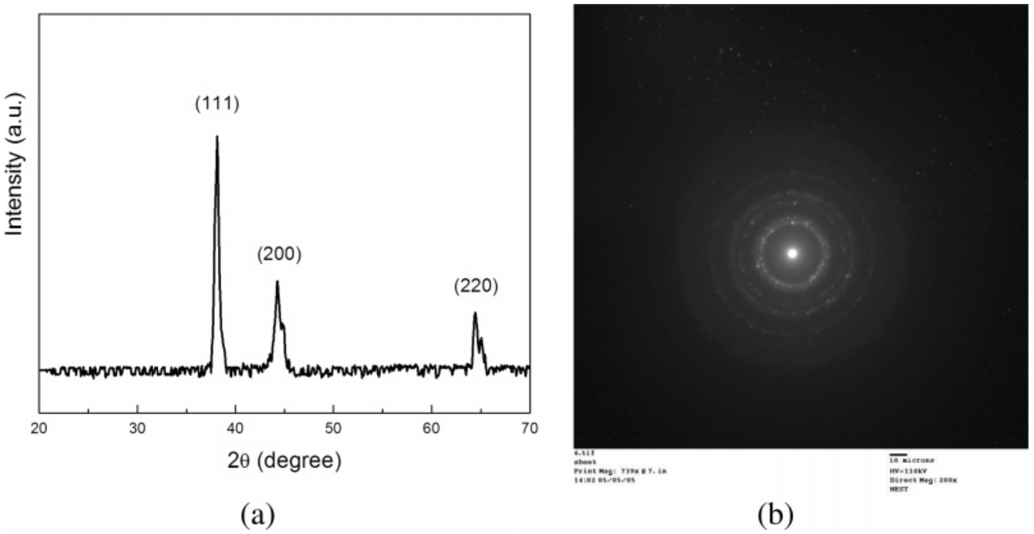


(a) (b) (c) (d) (e) (f)

Figure 2. SEM images of (a) surface of the Cu foil, (b,c) leaflike silver microstructures formed on the Cu surface, (d,e) as for (c) taken from different areas under a higher magnification, and (f) EDX spectrum of the silver nanoclusters.

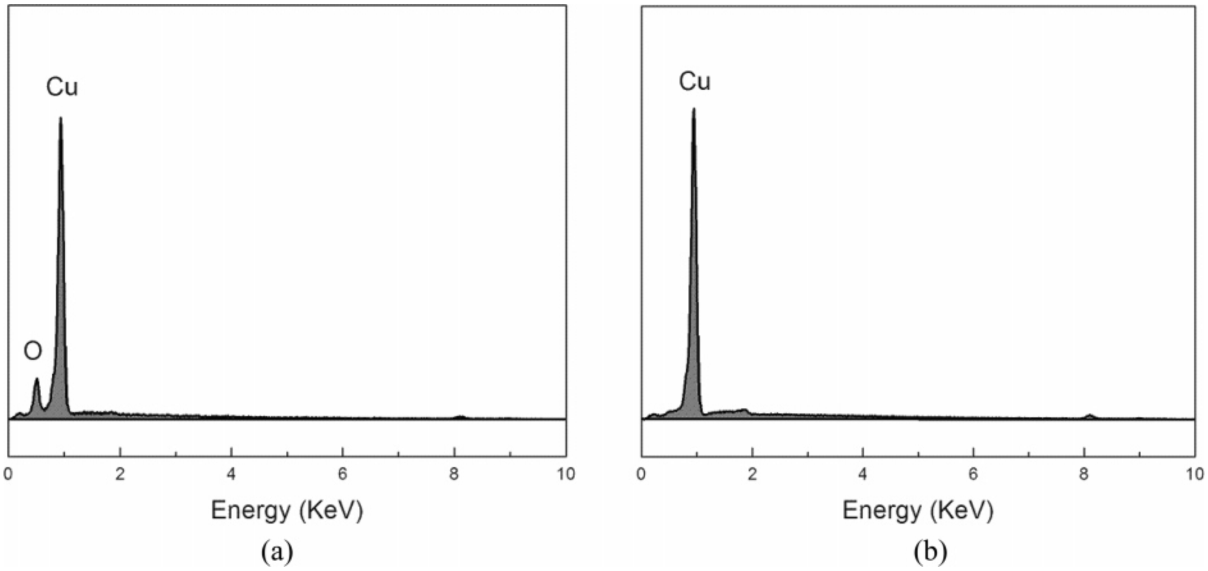
under a higher magnification (e.g., Figure 2d,e) clearly show that these “leaves” are composed of a large number of polygonal nanosheets with a thickness of about 200 nm self-assembled into a 3D hierarchical structure. The EDX analyses on the cluster “building blocks” (Figure 2f) clearly show a major peak of silver with a much weaker peak for Cu, arising from the copper substrate.

Figure 3a shows a typical XRD pattern for the as-prepared Ag nanoclusters. Consistent with previously reported XRD patterns for highly crystalline silver nanoclustes,[3,4] three diffraction peaks characteristic of a face-centered cubic (fcc) crystalline structure are clearly evident in Figure 3a. These diffraction peaks can be attributed to the (111), (200), and (220) planes (JCPDS, File No. 04-0783). The corresponding electron



(a) (b)

Figure 3. Typical (a) XRD and (b) ED patterns for the as-prepared Ag nanoclusters.



(a) (b)

Figure 4. EDX spectra of the (a) commercially available and (b) sandpaper-rubbed copper foils.

diffraction (ED) pattern of the silver nanoparticles (Figure 3b) also shows fringes related to the (111), (200), and (220) planes of pure fcc silver.[4]

The commercially available copper foils are often partially covered by copper oxides arising from air oxidation, as indicated by those scattered dark dots in Figure 2a and verified by the EDX analysis (Figure 4a). To perform the silver mirror reaction on pure copper surfaces, we used sandpapers to remove the oxide coating. The effectiveness of removal of the copper oxides by rubbing with sandpapers is confirmed by the absence of the oxygen peak in Figure 4b.

Having effectively removed the copper oxide layer, we used the freshly prepared pure copper surface as the substrate for the silver mirror reaction. In contrast to Figure 2, Figure 5 shows completely different silver nanostructures formed on the sandpaper-rubbed copper foil from the same silver mirror solution under the same reaction conditions. On the copper foil rubbed by a rough sandpaper (GatorGrit 180-C, Figure 5a), densely packed silver nanostructures with somewhat scattered spherical microclusters formed (Figure 5c). Close inspections of the nanostructured surface and spherical microcluster under higher magnifications show similar “building blocks” of perpendicularly aligned silver nanosheets in both areas (Figure 5e,g). The randomly interconnected silver nanosheets within the spherical microcluster stand out from the surface like a silver “flower”. These nanosheets are very thin with a thickness less than 100 nm. After rubbing the copper foil more extensively with a finer sandpaper (GatorGrit 600-B, Figure 5b), the same silver mirror reaction produced a more tightly packed nanostructured silver coating (Figure 5d,f,h) with an increased number of the silver “flowers” (Figure 5d) made from perpendicularly aligned silver sheets of about 200-nm thick (Figure 5f).

In view of the above observation and a recent report on the formation of silver nano-inukshuks on germanium via a galvanic displacement reaction,[5a] we anticipate that the following reaction occurs with copper atoms actively participating in the silver mirror reaction as the reductive reagent:

$$\mathrm{Cu(s)} + 2\mathrm{Ag}^{+}\mathrm{(aq)} \rightarrow \mathrm{Cu}^{2+}\mathrm{(aq)} + 2\mathrm{Ag(s)} \qquad (1)$$

The above process is not inconsistent with our SEM images shown in Figures 2 and 5. For the commercially available copper foil partially coated with spotlike oxide defects (Figure 2a), the above reaction could take place at the sites where pure Cu atoms are in direct contact with the silver mirror solution. Continuous reduction of Ag^{+} ions by Cu atoms requires electron-transfers

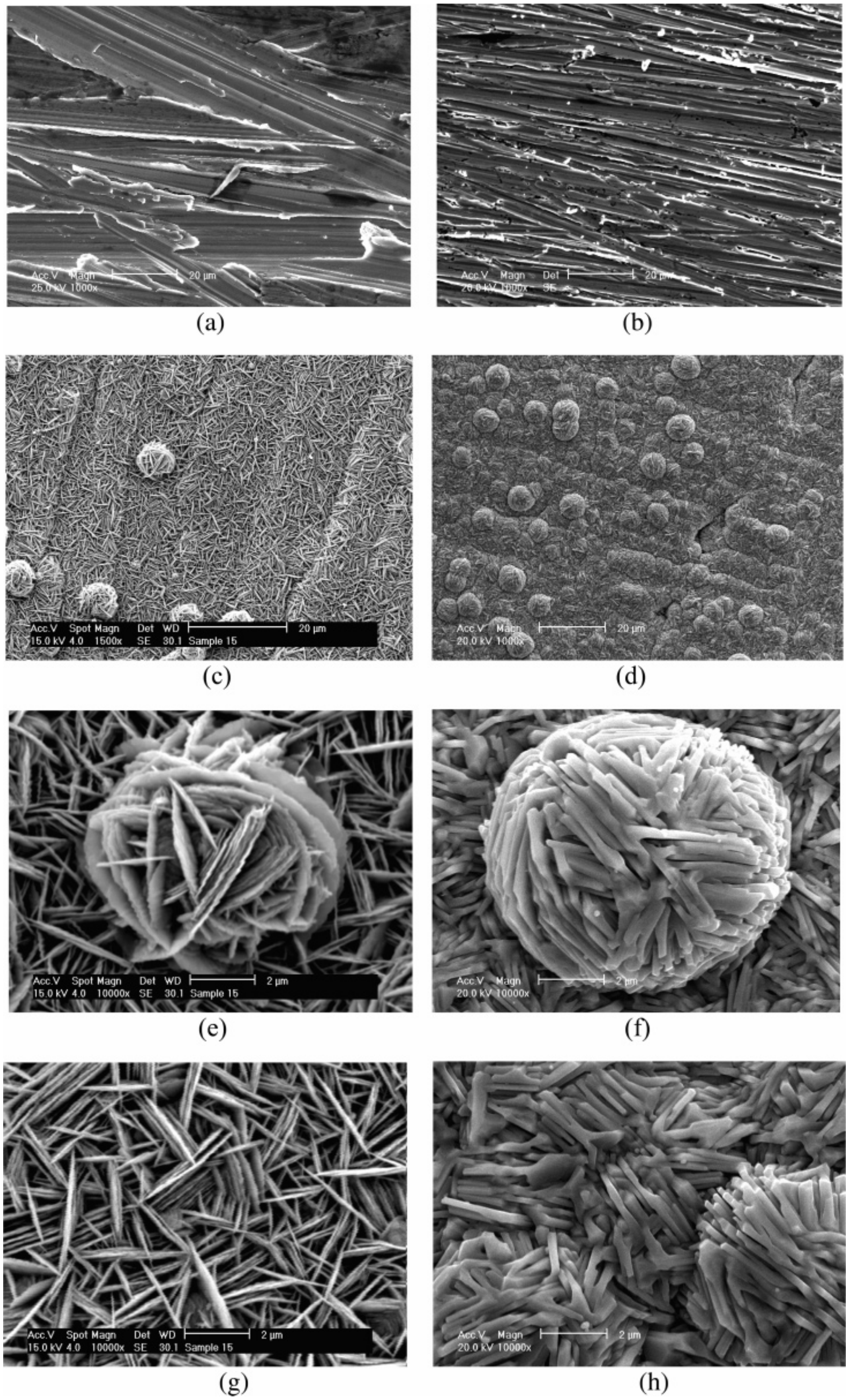
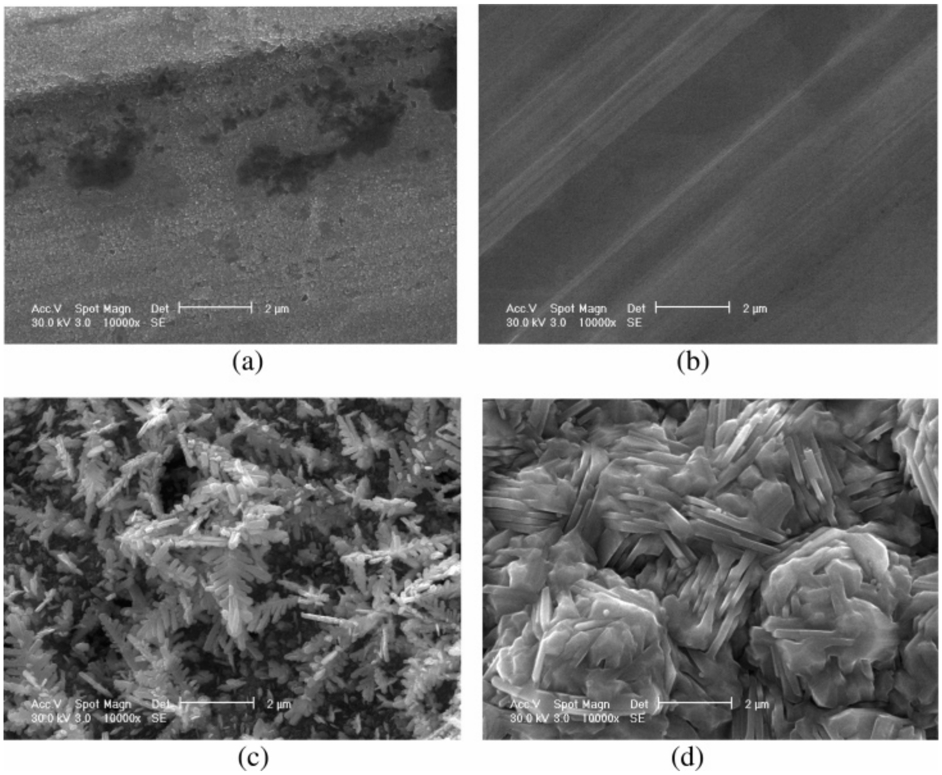


Figure 5. SEM images of Cu foils rubbed with the (a) 180-C and (b) 600-B sandpapers, and silver nanostructures from the silver mirror reaction on the corresponding Cu foils (c,e,g and d,f,h for the 180-C and 600-B sandpaper-rubbed Cu substrates, respectively) under different magnifications.

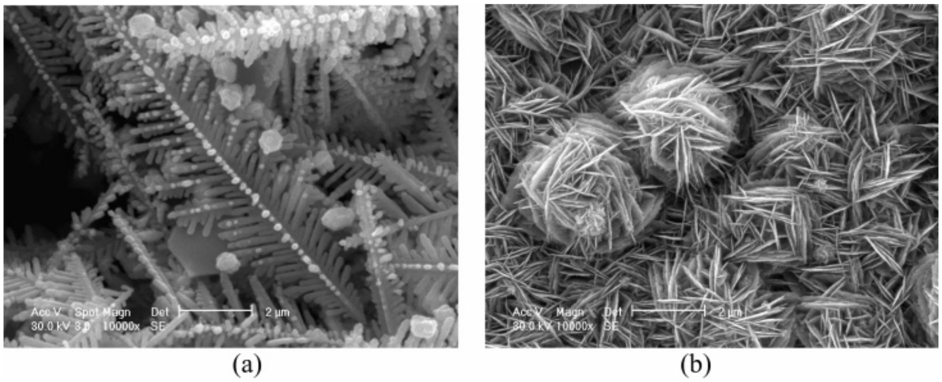
from the underlying Cu atoms, apart from the concomitant reduction of Ag^+ ions by the classical silver mirror reducing reagent (i.e., glucose and tartaric acid) in the solution. As the presence of the electron-rich copper oxide defects could set up a fractal potential gradient over the surface,[5,6] the fractal “leaflike” silver nanostructures parallel to the surface were formed in this particular case (Figure 2b−e). Once the insulating copper oxide layer was removed by rubbing with sandpapers, the underlying Cu atoms over the whole substrate surface actively participated in Reaction 1 to produce the densely packed silver nanostructures (Figure 5). As seen in Figure 5, the rubbing process created line-shaped structures of Cu atoms with a high packing density on the sandpaper-rubbed copper foil (Figure 5a,b), which allowed for a preferential growth of the silver nanosheets along the direction perpendicular to the substrate surface (Figure 5e−h). More silver species have been deposited along the protruding surface lines over the sandpaper-rubbed copper foils (Figure 5a,b), most probably due to the surface



(a) (b)

(c) (d)

Figure 6. SEM images of Cu foils treated with an aqueous solution of HCl (0.5 M) for (a) 5 min and (b) 60 min, and silver nanostructures from the silver mirror reaction on the corresponding Cu foils (c) for (a) and (d) for (b).



(a) (b)

Figure 7. SEM images of silver nanostructures formed by reacting (a) a commercially available Cu foil with an aqueous solution of $AgNO_3$ (6.375×10^{-3} M), and (b) a sandpaper (180-c)-rubbed Cu foil with an aqueous solution of $Ag(NH_3)_2^+$ (6.375×10^{-3} M).

potential gradient. Similarly, the point-type protruding surface sites in Figure 5a,b have led to a faster growth of the silver nanoclusters in a form of the standing-out silver "flowers" (Figure 5c−f). Comparing Figure 5b with Figure 5a, the copper foil rubbed with a finer sandpaper produced more point-type protruding surface sites (Figure 5b) for the formation of more flowerlike silver microclusters in Figure 5d than in Figure 5c.

As can be seen from Figures 2a and 5a,b, the rubbing with sandpapers caused severe surface alterations of the copper foils. A more controllable and less harsh chemical treatment has been investigated for removal of the surface copper oxide layers by immersing the commercially available copper foils in a dilute aqueous HCl solution (0.5 M) for a predetermined period of time. Depending on the acid concentration and acid-treatment time, surfaces of different roughness with (Figure 6a) and without (Figure 6b) the oxide defect sites can be prepared to support the growth of silver nanoclusters with a large variety of morphologies, ranging from the leaflike (Figure 6c) to flowerlike (Figure 6d) hierarchical structures.

An important check for Reaction 1 is provided by the silver mirror reaction to be carried out by immersing copper foils in an aqueous solution of $AgNO_3$ (6.375×10^{-3} M) or $Ag(NH_3)_2^+$ (6.375×10^{-3} M) in the absence of any other reductive reagent. Silver nanostructures similar to those observed earlier on the commercially available (Figure 2b,c) and sandpaper-rubbed (Figure 5c,e) copper foils are seen in Figure 7 (parts a and b, respectively). Clearly, therefore, Cu atoms indeed participated in Reaction 1 as an efficient reductive reagent. Furthermore, we have also found that other metals of a low work function (e.g., Al foil) also underwent a reduction process similar to that shown in Reaction 1, indicating that the methodology developed in this study for producing novel silver nanostructures could be regarded as a versatile approach.

It is appropriate here to mention that the silver nanosheets produced in the present study possess optoelectronic properties different from those of silver nanoparticles prepared by the more conventional silver mirror reaction. While an aqueous solution of nanoparticles from the conventional silver mirror reaction

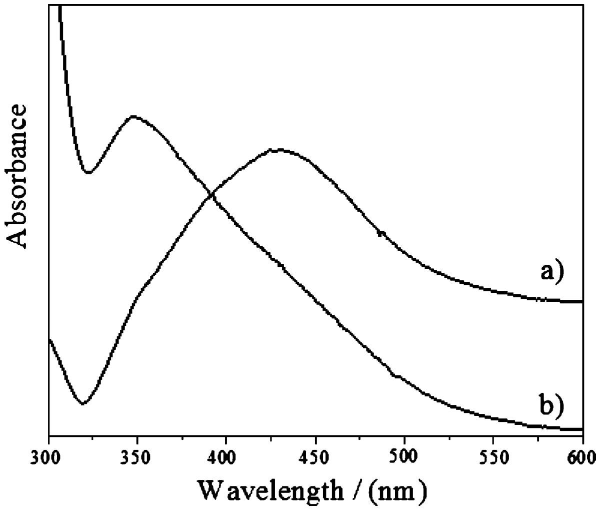


Figure 8. UV-vis spectra of (a) silver nanoparticles and (b) nanosheets dispersed in water by sonication.

(Figure 1b,c) shows a typical UV-vis spectrum with a strong surface plasmon absorption band around 430 nm (curve a, Figure 8) characteristic of silver nanoparticles,[4,7,8] the corresponding spectrum for the silver nanosheets prepared in the present study (curve b, Figure 8) reveals a light-scattering peak over 350 nm due to the relatively large particle size.[9] These observations clearly indicate that properties (e.g., optical absorption) of silver clusters are strongly dependent on their size and symmetry. Therefore, there is considerable room for tailoring the structure–property relationship of the silver clusters resulting from the silver mirror reaction by controlling the substrate nature and its surface features.

Conclusions

In summary, we have demonstrated that novel silver clusters could be reproducibly prepared by simply carrying out the silver mirror reaction on certain reactive substrates with specific surface features. While leaflike fractal silver microstructures were produced from the conventional silver mirror reaction on a commercially available copper foil with spotlike oxide defects, perpendicularly aligned silver nanosheets were prepared under the same reaction conditions on the copper foils after having been rubbed with sandpapers. Silver nanoclusters with various morphologies ranging from the leaflike to flowerlike hierarchical structures have been produced from the silver mirror reaction by removing the copper oxide layer from commercially available copper foils through relatively benign acid (e.g., dilute HCl) treatments under different conditions. Control experiments on reactions of $AgNO_3$ or $Ag(NH_3)_2^+$ with copper foils in the absence of any other reductive reagent indicated that Cu atoms actively participated in the silver mirror reaction as a reductive reagent. The surface morphology and chemical state of Cu foils play important roles in regulating the structure features, and hence properties, of the resulting silver clusters. While an aqueous solution of the silver nanoparticles formed on a glass plate from the conventional silver mirror reaction shows a broad surface plasmon absorption peak around 430 nm, the corresponding solution of the silver nanosheets prepared from the same silver mirror reaction on copper foils gives a light-scattering band over 350 nm. This work represents a general approach to the preparation of a large variety of new silver nanomaterials of potential applications in many areas, as other metals of a low work function (e.g., Al foil) have also been demonstrated to undergo similar galvanic displacement reactions.

Note Added in Proof. After the submission of our manuscript, we note that He et al. recently reported the preparation of silver nanosheets on an aluminum foil (He, Y.; Wu, X. F.; Lu, G. W.; Shi, G. Q. *Nanotechnology* **2005**, *16*, 791).

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