Extended Abstracts of the 2015 International Conference on Solid State Devices and Materials, Sapporo, 2015, pp916-917

Organic-Assisted Oriented Attachment of Silver Nanosheets

Sanong Ekgasit and Parinton Jangtawee

Sensor Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University
254 Phayathai Road, Patumwan, Bangkok, 10330, Thailand

Abstract

A simple and rapid method was developed for large-scale production of silver nanosheets with high density of SERS hotspot. The nanometer-thin sheets with micrometer lateral size were fabricated under a oriented attachment of small nanosheets in aqueous media with hydrogen peroxide as a reducing agent. Small organic molecules such as ethyl acetate and butyl acetate were deliberately put into the reaction medium as surface modifying agents that facilitate the oriented attachment process. The obtained nanosheets could be transferred to an aqueous/organic interface for ease separation by an addition of organic solvent.

1. Introduction

A rapid and green one-pot synthetic protocol for silver microsheets/nanosheets under an ambient condition was developed. A surface passivation by acetate ion enables a selective formation of microsheets or nanosheets. The nano-rough and nano-groove silver sheets contain high density of hot spots for efficient surface-enhanced Raman scattering (SERS).

2. Experimental

Silver sheets with an average lateral size of 2-5 µm were synthesized by hydrogen peroxide (HP) reduction of silver acetate (AgOAc). Briefly, an aliquot of HP solution (9.794 M, 15µL) was injected into a saturated solution of AgOAc (10 mL) under a vigorous stir. The transparent solution turned turbid within 30 s indicating the formation of the silver metal. The precipitated silver metal was separated from the aqueous solution by an addition of ethyl acetate (EtOAc). The silver metal assembled into a thin metallic film at the interface between organic phase and aqueous phase. The silver metal was separated from the aqueous phase by a separation funnel. When de-ionized (DI) water was employed as the solvent, 100-200 nm thick silver microsheets were obtained. Interestingly, when EtOAc-saturated water was employed as the solvent, 40-50 nm thick silver nanosheets were obtained. The nanosheets and microsheets showed unique dendritic growth pattern with an oriented attachment assemble of primary nanoplates originated from the centers, Figure 1. The dissolved organic solvent as well as adsorbed acetate ions played a significant role on the crystal growth as the deposition of silver atoms on the basal planes was severely restricted while induced a formation of nanosheets instead of microsheets.

3. Results and discussion

The silver microstructures were synthesized by a wet chemical reduction of silver acetate by hydrogen peroxide under a slightly acidic condition (pH 6-7). The redox reaction is given by:

$$2CH_3COOAg + H_2O_2 \rightarrow 2Ag + 2CH_3COOH + O_2$$

The synthesized nanosheets can be easily separated from the reacting medium by an addition of sparingly water soluble organic solvent such as ethyl acetate and toluene. The separated micro/nanostructures from our synthetic protocol will form into a thin metallic silver film at the aqueous/organic interface.

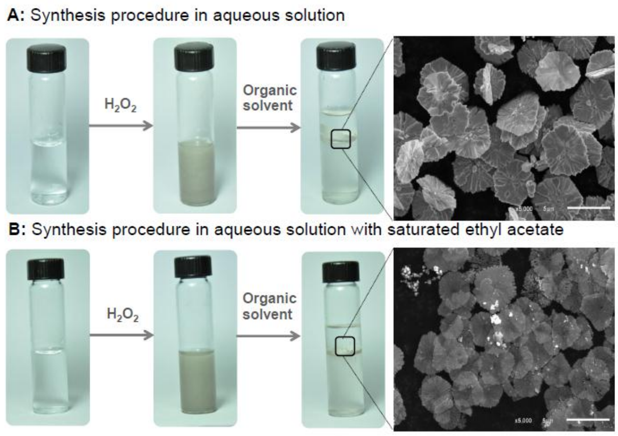

Fig. 1 Synthetic procedures for silver micro/nanosheets by hydrogen peroxide reduction of silver acetate.

The rough surface and high density of nano-groove on silver surface (Fig. 2) could be employed as an efficient SERS hot spot. A Raman spectrum of bare silver microsheets having strong molecular signature of acetate suggested the high SERS activity even at a monolayer of organic species (Fig. 3A). The highly SERS activity of silver microsheets was confirmed by a low detection limit of 0.1 nM R6G without any surface functionalization (Fig. 3B).

Conclusions

We have demonstrated that silver microsheets and nanosheets with rough surface and high density of nano-groove prepared by the chemical reaction between silver acetate and hydrogen peroxide can be functioned as efficient SERS substrate. The selective fabrication of silver microsheets or silver nanosheets could be achieved by an addition of organic solvent in the reaction media. The acetate ion plays an important role on structural selectivity as well as hydrophobicity/hydrophilicity as it is strongly bound onto the basal plan of the microsheets/nanosheets.

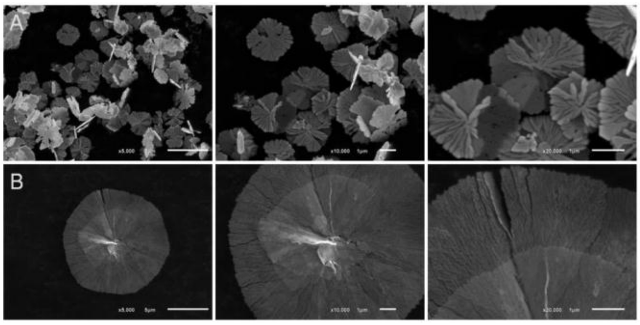

Fig. 2 Silver nanostructures prepared by HP reduction of AgOAc: (A) silver microsheets prepared with DI water and (B) silver nanosheets prepared with EtOAc-saturated water. Both microsheets and nanosheets show unique dendritic growth pattern of assembled silver nanoplates

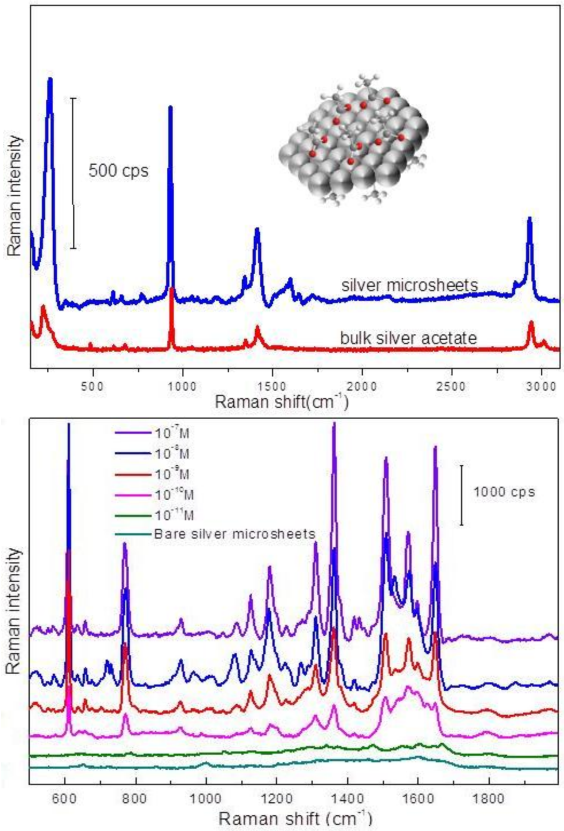

Fig. 3 (A) Raman spectra of bulk silver acetate and purified silver microsheets and (B) SERS spectra of R6G (10^{-7} - 10^{-11} M) with silver microsheets as the substrates.

Acknowledgements

This research has been supported by the National Research University Project, the Office of Higher Education Commission (CU-033-AM-57).

References

[1] J. M. Delgado, A. Rodes, J.M. Orts, *J. Phys. Chem. C.*, 2007, **111,** 14476-14483.

[2] J. Delgado, J. Orts, *Langmuir*, 2005, **21**, 8809–8816.

[3] P. Hildebrandt, M. Stockburger, *J. Phys. Chem.*, 1984, **88**, 5935-5944.