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Preparation and properties of an ordered, uniform 0.9 nm Ag array assembled in a nanoporous VSB-1 by a simple soft chemical method

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An ordered, homogeneously distributed and uniform 0.9 nm Ag array, which exhibits an unusual UV–vis surface plasmon resonance absorption peak at 355 nm with the largest blue-shift position and controllable intensity, has been successfully prepared by a simple soft chemical approach using the nanoporous VSB-1 as the template.

The miniaturization of materials is being driven by the development of microelectronics, which has spurred worldwide interest in nano-research.[1] Cluster science plays an important role in understanding the changes in fundamental properties of materials as a function of size from isolated atoms or small molecules to the bulk phase.[2] Structures of small size, high aspect ratio and ordered morphologies may exhibit unusual quantum effects and enhanced physical and chemical properties, which will have potential applications in nanoconnectors and nanodevices.[3–5] Silver nanostructures with well-defined dimensions are particularly interesting to study and synthesize owing to their potential applications in interconnectors and active components of nanoscale electronic devices. Silver nanostructures have been prepared using mesoporous silica,[6–8] film,[9–11] mordenite,[12,13] and in solution.[14,15] These nanostructures have a particle size of about 5 nm, with a large size distribution due to part of the particles being outside the pores, and/or a complicated experimental procedure being required. The as-synthesized nanoporous VSB-1 crystal[16,17] has a smaller one dimensional channel or pore size and a more ordered structure compared with that of mesoporous silica, which may be applicable for making ordered, small sized and highly dispersed nanostructures for future quantum devices.

Nanoporous VSB-1 was synthesized in accordance with published procedures[16,17] using nickel(II) chloride hexahydrate (4.62 g), phosphoric acid (2.24 mL, 85 wt%), ethylenediamine (1.18 mL), hydrofluoric acid (0.97 mL, 40 wt%), and H_2O (14 mL). The mixture was stirred for 0.5 h and then heated at 170 °C for 5 d in a Teflon-lined autoclave. The solid products were filtered and dried at room temperature. Powder XRD pattern analyses recorded on a Rigaku Rotaflex Diffractometer with Cu Kα radiation (Fig. 1) show that they are pure VSB-1 samples.[16] High resolution transmission electron microscopy (HRTEM) (Fig. 2(a)) and selected area electron diffraction (SAED) (Fig. 2(a) inset) indicate that the nanoporous structures consist of well-ordered packed channels with a diameter of about 0.9 nm, which is in accordance with the results from crystal XRD analyses.[16]

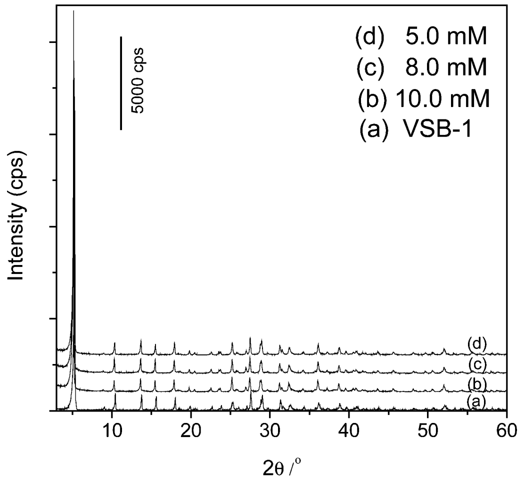

Fig. 1 XRD patterns of VSB-1 (a) and Ag–VSB-1 samples prepared from $AgNO_3$ solutions with concentrations of 10.0 (b), 8.0 (c), and 5.0 mM (d), respectively.

To prepare the nanomaterials inside the channels of the nanoporous VSB-1, 0.5 g as-synthesized VSB-1 powder was put in solutions with different $AgNO_3$ concentrations of 5.0, 8.0 and 10.0 mM, respectively. The mixture was stirred for 2 d and sheltered from light to avoid the reduction of Ag^+ ions. Ion-exchange occurred between the Ag^+ ion and the H^+ ion of the P–OH on the channel surface of VSB-1, determined by the decrease of pH along with the increase of the ion-exchange time.

The green Ag^+ containing solid (called Ag^+–VSB-1) was acquired with the Ag^+ ions on the outside of the surface which were removed after carrying out several centrifugal processes. After heating under a gas-flow mixture of hydrogen and nitrogen (3% H_2, volume ratio) at 200 °C for 2 h, the dark grey Ag array assembled in the channels of VSB-1 (Ag–VSB-1) was obtained.

UV–vis reflectance spectra of the samples were measured on a Shimadzu UV-3101 instrument equipped with an integrating sphere using $BaSO_4$ as the reference. As shown in Fig. 3, one unusually prominent UV–vis absorption peak at 355 nm is present, which can be attributed to the characteristic dipole-like oscillation surface plasmon resonance of metallic Ag nanoparticles.[18,19] The significant blue shift of the plasmon peak is up to 155 nm compared with that of 510 nm for the 100 nm Ag particles.[18] To the best of our knowledge, this Ag plasmon resonance peak with the largest blue shift originated from the quantum size effects of the smaller Ag particle inside the channels of VSB-1; this is consistent with the size dependence of plasmon resonance energy of 1–6 nm Ag particles.[20] The plasmon resonance peak shifts to higher energy with a decrease in particle size when the particle size is below 6 nm. The plasmon peak was distinguished from the d–d electron transition of Ni^{2+} in the framework of VSB-1 using Gaussian distribution analyses as shown in the inset of Fig. 3. The narrowly separated peaks with a full width at half-maximum (FWHM) of about 34 nm and the unchangeable plasmon peak positions of the Ag–VSB-1 samples prepared with different concentrations of $AgNO_3$ in the solution indicate that the Ag particles have a focused size distribution and are limited by the channels of VSB-1, which means that the diameters of most of the Ag particles are equal to or very close to that of the channel of VSB-1, *e.g.* 0.9 nm. The

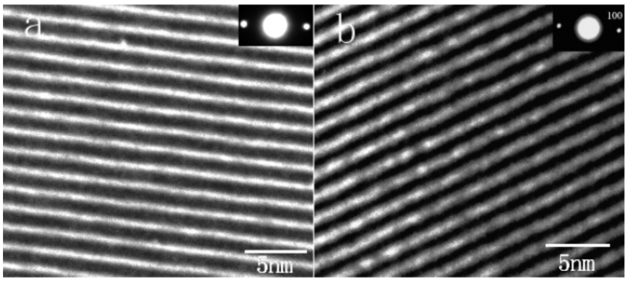

Fig. 2 HRTEM images of the as-synthesized pure VSB-1 (a) and Ag–VSB-1 (b) prepared in a 10.0 mM $AgNO_3$ solution recorded along a [100] zone axis. The inset pictures, enlarged twice, are the SAED patterns for both.

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intensity of the plasmon peak at 355 nm increased along with the increase of Ag^+ ion concentrations in the solution, using the electron transition peak of Ni^{2+} (at 417 nm) in the framework of VSB-1 as the standard. This may be due to the increased length (volume) along the channels of VSB-1 for the precipitated Ag particles.[20] When the Ag^+ concentration was higher than 0.1 M, the growth of Ag particles outside the channels occurred even if the Ag^+–VSB-1 samples had been washed by a centrifugal process several times in our experiment. The 355 nm plasmon peak was unchanged for 6 months at room temperature, which shows that the nanosized Ag is quite stable in the channels of VSB-1.

More evidence that Ag particles have been assembled inside the channels of VSB-1 is provided by direct observation using high resolution transmission electron microscopy (HRTEM) operated on a JEM 2010 electron microscope at 200 kV. The Ag particles in the channels or pores are observed directly in Fig. 2(b). The small obscurity in the morphology of the Ag particles may be due to the fact that the contrast between the nickel phosphate framework of VSB-1 and Ag is low. However, one can obviously see the dark grey array of Ag containing samples compared with that of pure VSB-1 in Fig. 2(a). The Ag–Ni molar ratio of the as-synthesized Ag–VSB-1 prepared in the 10.0 mM $AgNO_3$ solution is 2.15%, higher than the 0.03% ratio of the sample prepared in 5.0 mM $AgNO_3$ solution, based on EDX analyses conducted on an OXFORD Links ISIS EDX attached to the HRTEM. VSB-1 and Ag–VSB-1 were also studied by SAED. As shown in the inset of Figs. 2(a) and 2(b), both the pure VSB-1 and Ag–VSB-1 are crystalline and confirm that the Ag containing samples have a well preserved structure of VSB-1 in good agreement with the results from HRTEM and XRD. The *d*-spacing of Ag–VSB-1 acquired from the SAED analyses is 1.6 nm, which agrees well with the result of XRD analyses at 1.69 nm. The channel or pore size, which is believed to be related to the diameter of Ag particles in the array, is about 0.9 nm observed from the HRTEM images corresponding to those of reported crystal XRD analyses.[16]

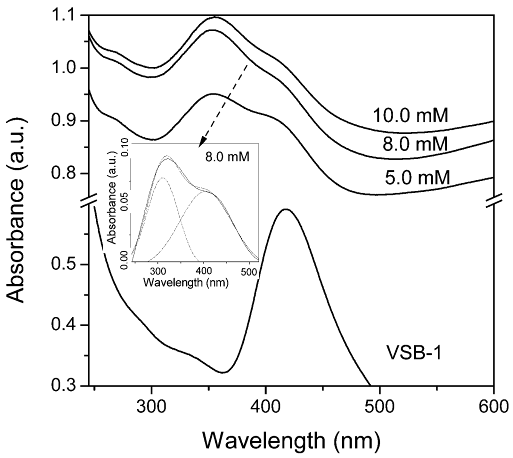

Fig. 3 UV–vis absorption spectra of pure VSB-1 and Ag–VSB-1 samples prepared from $AgNO_3$ solutions with concentrations of 5.0, 8.0, and 10.0 mM, respectively. The plasmon peak of Ag was distinguished from the d–d electron transition of Ni^{2+} in the framework of VSB-1 using Gaussian distribution analyses as shown in the inset figure.

The effect of concentration of $AgNO_3$ solution can be observed clearly on the HRTEM images causing different morphologies of Ag particles. More obvious images with the longer dark grey Ag particles in the channels of VSB-1 are observed for the Ag–VSB-1 sample prepared in a 10.0 mM $AgNO_3$ solution compared with that prepared in a 5.0 mM $AgNO_3$ solution. The channels of Ag–VSB-1, with a diameter of 0.9 nm for both, are well resolved. These results further prove the fact that the increase of quantity (volume) and high aspect ratio of Ag nanoparticles with a particle diameter of 0.9 nm formed in the channels of VSB-1 for the Ag array prepared in 10.0 mM $AgNO_3$ solution, is consistent with the EDX and UV–vis analytical results.

To summarize, an ordered and uniform 0.9 nm Ag array has been successfully assembled in the channels of VSB-1 presenting potential applications in the theoretical research and in the fabrication of future quantum devices.

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