ChemComm
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Synthesis of silver nanoparticles *via* electrochemical reduction on compact zeolite film modified electrodes†

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Received (in Cambridge, UK) 22nd August 2002, Accepted 14th October 2002
First published as an Advance Article on the web 25th October 2002

Monodisperse silver nanoparticles with different sizes were synthesized by electrochemical reduction inside or outside zeolite crystals according to the silver exchange degree of compact zeolite film modified electrodes.

Nanoscale metal particles are becoming increasingly important due to their remarkable catalytic properties[1] and potential applications in microelectronical, optical and magnetic devices.[2] Up to now, numerous chemical methods have been developed for their preparation,[3] including chemical reduction,[4] photoreduction,[5] thermal decomposition[6] and electrochemical reduction.[7] The most important key in these methods is to avoid the agglomeration of metal nanoparticles during and after syntheses. Usually special organic compounds, such as stabilizing ligands, polymers or surfactants,[8] are used as protecting agents so allowing isolated nanoparticles to be produced. Zeolites are stable aluminosilicate materials with ordered micropores or/and nanosized cages, and such ordered inorganic nanostructures provide a good barrier to avoid the agglomeration of metal nanoparticles. Recently there has been progress in the reliable preparation of monodisperse metal nanoparticles which are of continued interest for fabrication of composite materials on the nanoscale including selectively operating catalysts. Tiny transition metal clusters, including silver clusters, with extrodinary catalytic performance have been synthesized in the microcages and pores of zeolites by autoreduction by calcination or reduction with chemical reagents or γ-/X-ray irradiation.[9] Furthermore, miscellaneous silver particles also have been observed by electrochemical reduction in silver-exchanged zeolite modified electrodes (ZMEs) during research of ZMEs.[10] However, due to the incompact structure of zeolite films in the conventional ZMEs, it seems difficult to obtain monodisperse silver nanoparticles.

In this paper, a new strategy, using compact ultrathin faujasite zeolite film modified electrodes (CZFMEs-FAU) as a substrate, is reported to prepare silver nanoparticles with monodisperse size by electrochemical reduction. The continuous ultrathin zeolite film attaching compactly to the surface of Pt electrode prevents the agglomeration of silver nanoparticles during and after the reduction. Moreover, we can finely control the size and the sites (inside or outside of the zeolites) of silver nanoparticles by changing the ion exchange degree of CZFMEs. Such a feature is very useful because silver nanoparticles with different sizes and surroundings will exhibit different performances in catalysis and other fields.[11] By analyzing the experimental results of the samples with different silver exchange degrees, the reduction mechanisms of silver ions in ZMEs are also discussed.

The CZFMEs-FAU were prepared using a previously reported seeding technique.[12] The surface of a Pt electrode was first seeded with pre-prepared FAU nanoparticles[13] through electrostatic adsorption with the aid of polyelectrolytes.[14] Then, a compact ultrathin zeolite film on a Pt electrode was formed *via* secondary growth in a solution with the molar ratio of 14 $Na_2O:Al_2O_3:10\ SiO_2:798\ H_2O:3\ Na_2SO_4$ at 80 °C for 3 h. Fig. 1 clearly displays the surface morphology of the as-prepared CZFMEs-FAU. The Pt electrode is well covered by a dense ultrathin zeolite film of about 400 nm in thickness as shown in the scanning electron microscopy (SEM) image of Fig. 1(a), and the transmission electron microscopy (TEM) image in Fig. 1(b) indicates that the FAU zeolite in the film is well-crystallized after the second growth process.

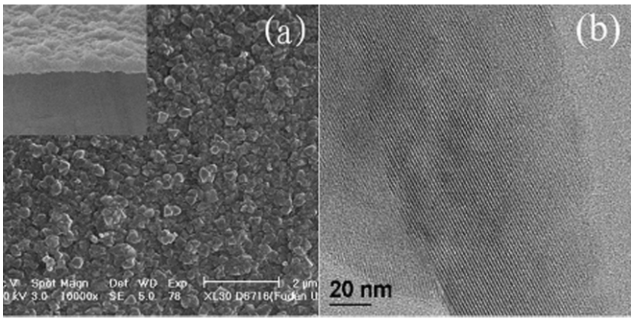

Fig. 1 Micrographs of CZFMEs-FAU: (a) SEM images of CZFMEs-FAU; (b) TEM image of CZFMEs-FAU.

The prepared CZFMEs-FAU was ion exchanged to desired Ag contents in $AgNO_3$ solutions of various concentrations for 15–30 min, and then reduced electrochemically in a CHI660A Electrochemical Workstation by linear sweep voltammetry from + 0.3 to -0.1 V at a scan rate of 50 mV s^{-1} in a 0.05 M $NaNO_3$ solution. Table 1 shows typical samples tested in our experiments. The Ag/Al and Na/Al ratios in the Table indicate the molar ratio of silver and sodium to aluminium in the samples before reduction, respectively, and roughly indicate their degree of silver exchange. Fig. 2 shows the morphologies and the size distributions of the silver nanoparticles after electrochemical reduction. It is clear that the ion exchange degree strongly influences the resulting silver particles. When the CZFMEs-FAUs were silver ion exchanged to a low degree as in sample 1, after electrochemical reduction, an abundance of nanoparticles with good monodispersity and diameter of about 18 nm appeared on the surface of the zeolite film [Fig. 2(a, b)]. When the CZFMEs-FAU was highly silver exchanged as in sample 3

Table 1 Relation between degree of silver exchange and sizes of silver nanoparticles

Sample	Concentration of $AgNO_3$/ mol L^{-1}	Ion exchange time/min	Ag/Al[a]	Na/Al[a]	Diameter[b]/ nm
1	0.001	15	0.3	0.5	18
2	0.001	30	0.4	0.4	5
3	0.1	30	0.8	< 0.1	1–2

[a] Determined by electron dispersive spectroscopy. [b] Diameters of silver nanoparticles after reduction as estimated by TEM images.

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† Electronic supplementary information (ESI) available: Fig. S1: TEM images of silver nanoparticles prepared from CZFMEs-FAU with different silver exchange degree. Fig. S2: Electron dispersive spectrum analyses of CZFMEs-FAU with different silver exchange degree and electron diffraction analysis of silver nanoparticles with an intermediate size. See http://www.rsc.org/suppdata/cc/b2/b208222e/

DOI: 10.1039/b208222e

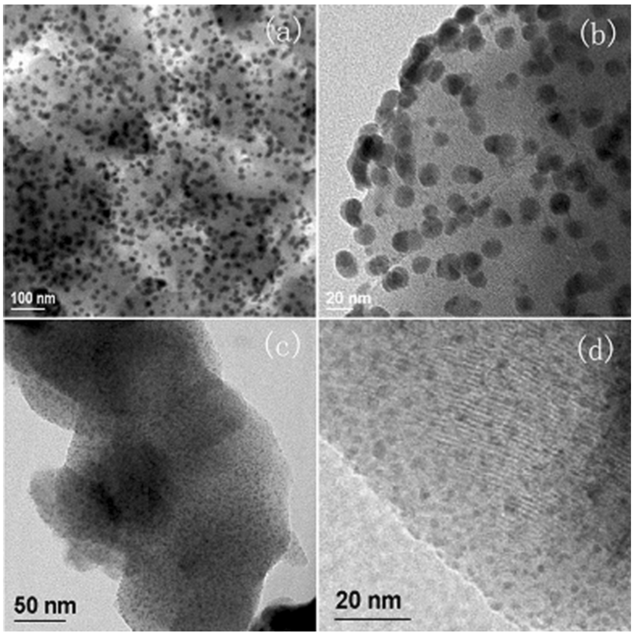

Fig. 2 TEM micrographs of sample 1 (a, b) and sample 3 (c, d) at low (a, c) and high (b, d) magnification.

in which almost all Na^+ ions were exchanged by Ag^+ ions, the diameter of the silver nanoparticles decreased to only about 1–2 nm [Fig. 2(c, d)]. When the CZFMEs-FAU was intermediately exchanged as shown in sample 2, silver nanoparticles with an intermediate size (about 5 nm) were obtained (ESI†). An electron dispersive spectrum and electron diffraction analyses show that these nanoparticles are silver polycrystals (ESI†). More interestingly, such silver nanoparticles dispersed by zeolites appear to have a high stability, the sizes of which are well retained after several weeks.

The diameter change of silver nanoparticles with the increase of silver exchange degree can be roughly ascribed to two different reduction mechanisms, termed as intra- and extra-zeolitic reduction.[15] The former requires electron transfer to occur in the zeolites, which will result in the formation of metal clusters inside the zeolite crystals. The latter infers electron transfer to occur at the electrode–solution interphase, which causes the deposition of metal either on the electrode surface or onto the external surface of the zeolite. Our results show that these two mechanisms work cooperatively and each of them predominates at different conditions. When the silver-exchange degree is high, *e.g.* in sample 3, the conductivity of the zeolite film is high, so that most of the Ag^+ ions appear to be reduced in the zeolite crystals *via* an intrazeolitic mechanism. As the result, silver clusters with diameter close to that of the supercage [Fig. 2(d)] would be formed inside the FAU supercages (d = 1.3 nm), and cannot migrate out through the narrow pores (d = 0.74 nm) of FAU. When the silver-exchange degree is low, the conductivity of the zeolite film is not high enough for the Ag^+ ions to be reduced *in situ* in the zeolite crystals. The silver ions are thus exchanged by cations from the electrolyte and migrate to the interface of the zeolite film and the Pt electrode under the drive of the electric field. Accordingly, the silver ions are inclined to be reduced *via* an extrazeolitic mechanism, and larger silver nanoparticles are formed due to the absence of the limitation of the zeolite cages. However, probably because the limitation effect of the compact contact between the dense zeolite film and Pt electrode retards the further random growth of silver particles, in contrast to previous results in conventional ZMEs, the formed nano-silver particles still possess a good monodispersivity.

In summary, monodisperse silver nanoparticles with different diameters are synthesized inside or outside zeolites on CZFMEs-FAU *via* electrochemical reduction. The presence of supercages and the dense zeolite film adhering compactly to the Pt electrode are two key factors for the formation of monodisperse silver nanoparticles with different sizes. The sizes and sites of the silver nonaparticles can be well controlled through changing the silver exchange degree in CZFMEs-FAU, and these phenomena can be attributed to intra- and extra-zeolite reduction mechanisms of ZMEs. In principle, this method can also be applied to the preparation of other metal nanoparticles with FAU and other zeolites.

The authors thank Professor D. Y. Zhao and Prof. Z. Y. Jiang of Fudan University for their help and discussion. This work is supported by the NSFC (20273016, 20233030), the SNPC (0144nm067) and the Doctoral fund of Ministry of Education.

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