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Au, Cu, Ag, Ni, and Pd Particles Grown in Solution at Different Electrode Potentials

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The multiply twinned particles (MTPs) of Cu, Ni, Ag, and Pd formed on an electrode in solution at low electrode potentials were systematically studied by means of transmission electron microscopy (TEM). At low electrode potentials the icosahedral and dedahedral particles were observed for gold, silver, and palladium, but only the decahedral particles were observed for copper and nickel. The icosahedral particles of copper and nickel are less stable compared to the decahedral particles. The decahedral Ag particles were oxidized during the observation by TEM and changed into Ag_2O having fcc structure. The stability of these transition metal MTPs formed in solution is in the sequence Au > Ag > Cu and Pt > Pd > Ni. The differences of d−s hybridization or s,p−d hybridization among 3d, 4d, and 5d transition metals will increase the surface electron density, which results in the contraction of the lattice in the lateral direction. The decahedral and icosahedral particles of Au were formed on an SnO_2 electrode, which indicates that the MTPs of Au are grown not only on carbon film but on SnO_2 film depending on the electrode potential.

Introduction

Since decahedron and icosahedron of fine gold particles evaporated in ultrahigh vacuum (UHV) were first observed by Mihama[1] and were analyzed by Ino[2,3] who designated these particles as "multiply twinned particles" (MTPs), several groups investigated other fcc metal particles, e.g., Ag,[6,7,10] Ni,[4,5,8] Al,[4] and Pd,[4,5,9] made by evaporation in UHV and found that these particles have MTPs. MTPs were also observed while the preparation of fine particles of these metals was carried out in an inert gas, that is, in argon,[11−13] helium,[14] or xenon[15] gases. In this paper we report the formation of MTPs of Cu, Ag, Ni, and Pd by electrochemical deposition on amorphous carbon electrode in a neutral electrolyte or in acid solution. The MTPs of gold were also grown on SnO_2 film. On the basis of our previous reports on the particles of gold[16−18] and platinum,[19] we could say that the MTPs of fcc transition metals can be prepared not only in UHV and inert gases but also in solution under certain electrode potentials.

Experimental Section

The experimental procedure was described in detail in previous reports.[16−18] The working electrode was a Au mesh for transmission electron microscopy (TEM). The mesh was covered with a collodion film on which an amorphous carbon film was evaporated. SnO_2 film for the electrodeposition of Au was made by evaporating Sn on a collodion film prepared on a Au mesh, and then the Au mesh with Sn film was heated and kept at 500 K for 2 h in air. Before the deposition of Au, the mesh with SnO_2 film was investigated by TEM. It was observed from the diffraction pattern that the previous Sn film was completely oxidized to SnO_2 film. The TEM observation indicated that this SnO_2 film was a polycrystalline film showing clear lattice structures.

Electrode potentials were measured and quoted in this paper against the saturated calomel electrode (SCE). The electrolyte was prepared with $HClO_4$ (Wako), $HAuCl_4$ (Kanto), $CsClO_4$, $AgClO_4$, $CuClO_4$, $NiSO_4$, $PdSO_4$ (Aldrich), and triply distilled water. All experiments were performed in a classic three-electrode cell at room temperature. The particles were grown on the carbon electrode or SnO_2 electrode and observed by means of a Hitachi 9000 high-resolution TEM.

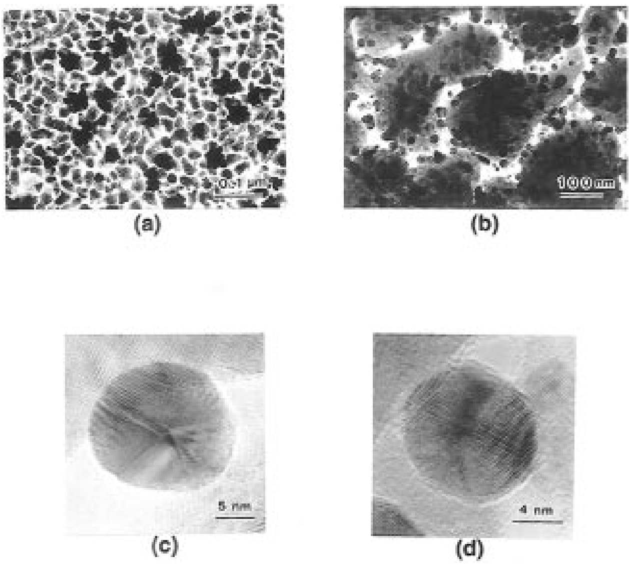

Figure 1. TEM images of gold particles formed in 50 mM $CsClO_4$ + 1 mM $HAuCl_4$ solution on SnO_2 electrode at (a) 0.3 V for 300 s and (b) −0.3 V for 60 s. In (a) the gray particles are SnO_2, the black particles are Au deposited on the SnO_2 particles. In (b) the small black Au particles formed on the large gray particles of SnO_2. Note the scales in (a) and (b). A typical decahedral Au particle and an icosahedral Au particle formed at −0.3 V are shown in (c) and (d), respectively.

Results

Gold. Gold particles grown on a SnO_2 electrode in 0.05 M $CsClO_4$ + 1 mM $HAuCl_4$ solution at different electrode potentials are shown in Figure 1. The gold particles formed at 0.3 V are polycrystalline (Figure 1a). However, most of the gold particles formed at −0.3 V are MTPs, that is, decahedral and icosahedral particles (parts b−d of Figure 1). This phenomenon is similar to the growth of gold particles on a carbon electrode on which the octahedral fcc single-crystalline

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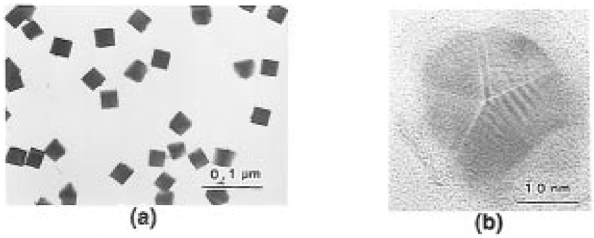

Figure 2. (a) Image of Cu_2O particles formed in 50 mM $CsClO_4$ + 1 mM $CuSO_4$ solution on carbon electrode at −0.1 V for 600 s. (b) Image of a decahedral Cu particle grown at −0.6 V for 60 s.

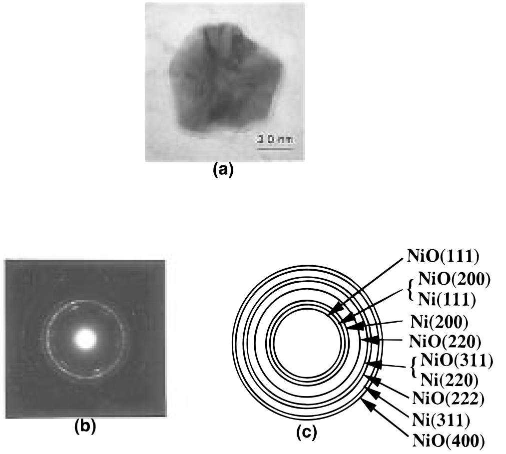

Figure 3. (a) Image of a decahedral Ni particle formed in 50 mM $CsClO_4$ + 1 mM $NiSO_4$ solution on carbon electrode at −0.9 V for 300 s. However, NiO and Ni particles grew simultaneously at −0.9 V. (b) Image of electron diffraction pattern of NiO and Ni particles formed at −0.9 V. (c) Illustration of (b).

gold particles are formed at 0.3 V and the decahedral and icosahedral gold particles are formed at −0.3 V.[16,17] It is clear that the SnO_2 electrode has no effect on the growing of gold MTPs at lower potentials; even the islands of SnO_2 film are not amorphous but a polycrystalline film because it takes lattice structures (see the background of parts c and d of Figure 1).

Copper. The particles of copper formed at different electrode potentials in 0.05 M $CsClO_4$ + 1 mM $Cu(ClO_4)_2$ solution are shown in Figure 2. At −0.1 V the grown particles are Cu_2O (Figure 2a), which was discussed in detail in our previous paper.[20] The decahedral copper particles were observed at −0.6 V (Figure 2b). However, the decahedral copper particles were not stable; they changed to polycrystalline particles quickly during observations by TEM. There was no icosahedral copper particle to be found in this experiment.

Nickel. Figure 3a shows a typical decahedral particle of nickel formed in 0.05 M $CsClO_4$ + 1 mM $NiSO_4$ solution at −0.9 V. As in the case of decahedral copper particles, the decahedral particles of nickel were not stable for TEM. The icosahedral particle of nickel was not observed. Takahashi et al.[8] also observed only the decahedral particle of nickel evaporated in vacuum. It is supposed that the icosahedral particles of nickel and copper cannot be formed in the present case, which will be discussed in detail in discussion. We found that NiO grew simultaneously with nickel particles at −0.9 V (Figure 3b). According to the thermodynamic chart given by Pourbaix,[21] when the pH of the electrolyte is 7, the deposited particle should be only nickel below −0.6 V vs SCE. Therefore, it can be considered that the formation of NiO at −0.9 V is controlled by kinetics, that is, the reaction of nickel cation with H_2O to form NiO is faster than the formation of nickel particle.

Silver. The phenomenon of silver particles formed at different electrode potentials is about the same with that of gold particles,[16] that is, the fcc single-crystalline particles form at higher potentials and the decahedral and icosahedral particles grow at lower potentials. Figure 4 shows the particles of silver formed at 0.2 V in 0.05 M $CsClO_4$ + 1 mM $AgClO_4$ solution. From the diffraction patterns of the particles (parts b and e of Figure 4) and their dark field images (parts d and g of Figure 4), there is no doubt that these silver particles are fcc single crystalline ones; even the shape of these particles seems to be polycrystalline.

Parts a and b of Figure 5 show a TEM image and a corresponding dark field image of a decahedral particle of silver formed at 0 V, which is a little lower than the initial occurrence potential (0.05 V) of decahedral particles of gold. It should be pointed out that the MTPs of silver are not stable for TEM, especially icosahedral particles, which changed very quickly during observations with TEM. If the observation time for one decahedral particle of silver is longer, that particle will be oxidized to Ag_2O which has a cubic structure, and the shape of the particle will vary (see Figure 6).

No silver particles were observed as the electrodeposition was carried out at 0.3 V. At this potential the grown particles had a hexagonal diffraction pattern (Figure 7b) and the diffraction

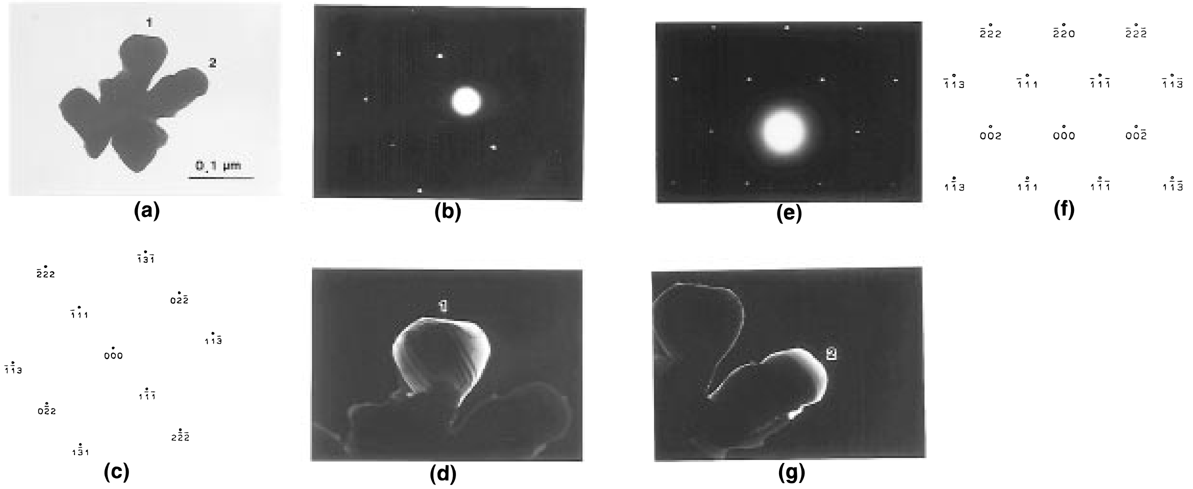

Figure 4. (a) Image of Ag particles formed in 50 mM $CsClO_4$ + 1 mM $AgClO_4$ solution on carbon electrode at 0.2 V for 300 s. The particles that are marked by 1 and 2 were investigated in detail. (b) Diffraction pattern of particle 1 taken along the [211] direction. (c) Illustration of (b). (d) Dark field image of particle 1 using a (111) spot. (e) Diffraction pattern of particle 2 taken along the [110] direction. (f) Illustration of (e). (g) Dark field image of particle 2 using a (111) spot. It is clear that the gathered Ag particles are fcc single-crystal particles.

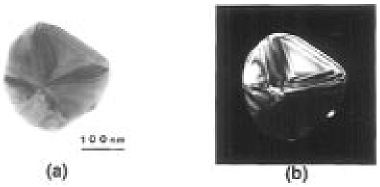

Figure 5. Decahedral Ag particle (a) formed in 50 mM $CsClO_4$ + 1 mM $AgClO_4$ solution at 0 V for 60 s and its dark field image (b).

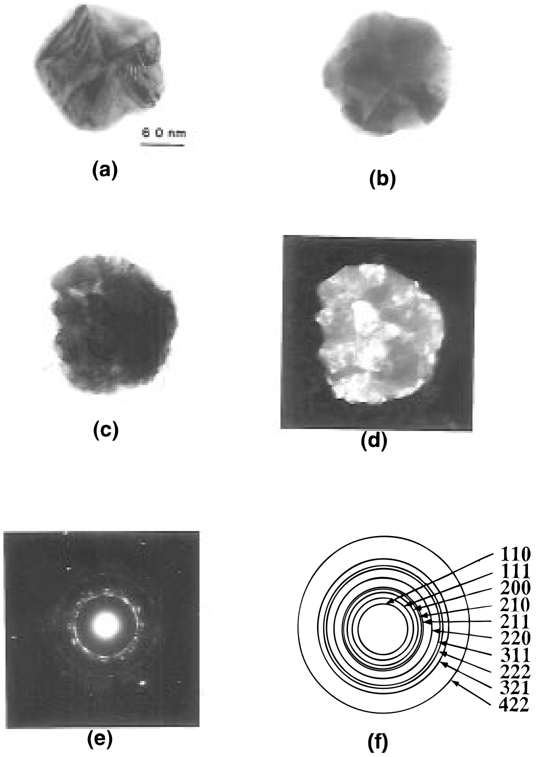

Figure 6. (a) Decahedral Ag particle formed in 50 mM $CsClO_4$ + 1 mM $AgClO_4$ solution at 0 V for 60 s. (b) After 35 min observation by TEM the twins of this particle disappeared. (c) After 50 min observation the particle was oxidized to Ag_2O and its shape changed. (d) Dark field image of (c). (e) Diffraction patter of this oxidized particle. (f) Illustration of (e). The lattice structure of this Ag_2O particle is fcc.

patterns of these particles were identical, that is, all the particles had the same crystalline orientation—[001]. The element analysis of these particles by SEM (Figure 7e) suggests that these particles contain silver. By the calculation of the diffraction pattern and the comparison with the calculation results and the powder diffraction data, these particles are assigned as Ag_2O. It is interest that the structure of these Ag_2O particles is hexagonal, which is different from the cubic structure of Ag_2O particles oxidized from the decahedral particles of silver during the TEM observation as mentioned above. From the thermodynamic chart given by Pourbaix[22] Ag_2O should exist above 0.5 V vs SCE under pH 7. It is supposed that this case is the same as that of Cu_2O, that is, the formation of Ag_2O is controlled by the kinetics.

Palladium. Palladium particles grown in 1 M $HClO_4$ + 1 mM $PdSO_4$ solution at higher electrode potentials are different with the particles of copper, nickel, or silver, that is, there was neither single-crystal particle nor oxide to be formed; only the polycrystalline palladium particles were formed (Figure 8a). However, the MTPs were formed at lower electrode potentials (Figure 8b). Parts c and d of Figure 8 show typical decahedral and icosahedral particles of palladium, respectively. It should be noticed that the MTPs of palladium are more stable than those of silver. The platelike palladium particle with (111) face was observed at −0.3 V (Figure 8c). It indicates that at lower potentials not only the MTPs are formed but also the growth of platelike particles with (111) orientation are preferred because of the morphology with lower surface free energy.

Discussion

The decahedron and icosahedron of particles are surrounded by 10 and 20 close-packed faces, respectively. In our previous paper[16] it was pointed out that Au atoms on the low-index clean Au surfaces are compressed in the lateral direction on the surfaces at lower potentials, which is responsible for the potential-induced reconstruction. The gold particles grown in this potential range prefer to take a hexagonal stacking at the outermost layer, which results in the growth of decahedral and icosahedral particles. Platinum was known to have the reconstruction only on the (100) and (110) surfaces, but recently, it has been shown that the reconstruction can occur on Pt(111) surface at 1330 K[23,24] or at 400 K in the presence of supersaturated platinum vapor.[25,26] We also observed the decahedron and icosahedron of platinum particles grown in salt solution at lower electrode potentials, and fcc single-crystal platinum particles formed at higher electrode potentials.[19] It seems that if the close-packed stacking could occur on all the low-index planes, the decahedral and icosahedral particles of metals can be formed in solution as well as in UHV. To confirm this postulate, we studied the electrochemical deposition of Cu−Au alloy particles.[27] We found formation of decahedral and icosahedral Cu−Au alloy at the electrode potentials at which Au particles give no decahedron or icosahedron but only fcc single-crystal ones. Taking account of the reconstruction of Au single-crystal surfaces induced by alkali metal adsorption,[28,29] it was inferred that the underpotential deposited copper takes Cu^+ on the Au layer of the alloy particles, which may increase the electron density of the gold layer at the surface. As a result, the interatomic distance of the Au outermost layer is compressed as in the case at lower electrode potentials, and the decahedral and icosahedral alloy particles are formed. From the above results if the surface of a metal can be compressed by some means, the decahedral and/or icosahedral particles of the metal will be produced in solution.

As a reminder, no reconstruction occurs on the clean low-index surfaces of copper, silver, nickel, and palladium in UHV. Theoretical calculations[30−32] suggest that the reconstructions of Au and Pt are favored and that Pd and Ag have about the same energy for the reconstruction and the unreconstruction. In contrast, the unreconstruction is energetically preferred for Ni and Cu. However, when alkali metal is deposited on the surfaces of these metals in UHV, the reconstruction is induced (Cu,[33,34] Ag,[35,36] Ni,[37] Pd[38,39]). This phenomenon is interpreted by the charge transfer from alkali adatom to substrate surface, and then the s−p electron density is increased at the surface and reconstruction is induced.

From our experimental results it can be concluded that the stability of MTPs of these metals formed in solution is as follows:

$$\mathrm{Au} > \mathrm{Ag} > \mathrm{Cu} \quad \text{and} \quad \mathrm{Pt} > \mathrm{Pd} > \mathrm{Ni}$$

These sequences are in quite good agreement with the theoretical prediction for reconstruction. Therefore, it is possible that the sequence of stability of these metal MTPs relates to the electron density in s−p and/or s,p−d orbitals. For a certain metal, e.g., Au, at low electrode potentials a negative charge induced at the surface leads to a strengthened in-plane s−p bonding.[40] Increase of the electron density at the surface favors a more densely packed surface to lower the surface energy.[41] Therefore,

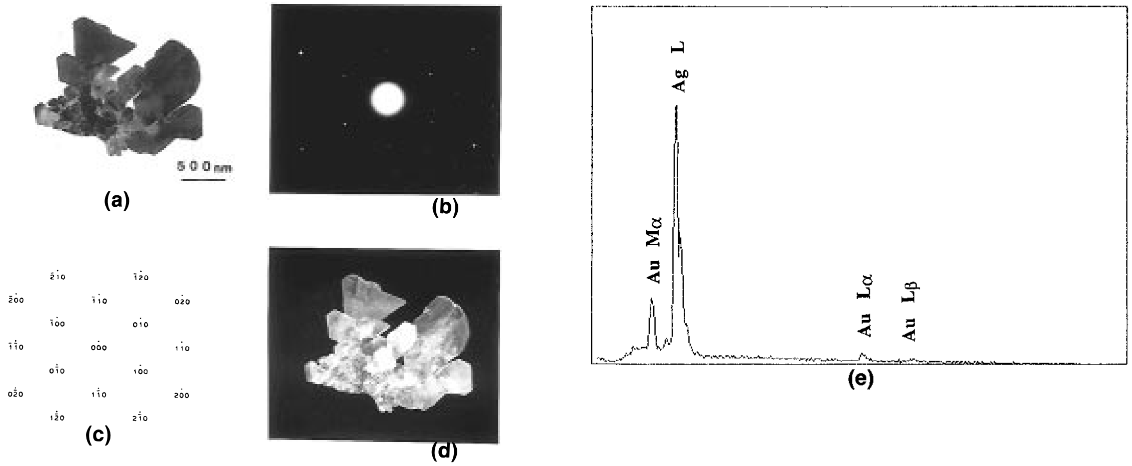

Figure 7. (a) Ag_2O particles formed in 50 mM $CsClO_4$ + 1 mM $AgClO_4$ solution at 0.3 V for 300 s. (b) Diffraction pattern of (a) taken along the [001] direction. It should be noted that the diffraction patterns of these particles are identical. (c) Illustration of (b). The lattice structure of these Ag_2O particles is hexagonal. (d) Dark field image of (a) using a (100) spot. (e) Element analysis of these particles by SEM. The peaks of Au came from the Au mesh.

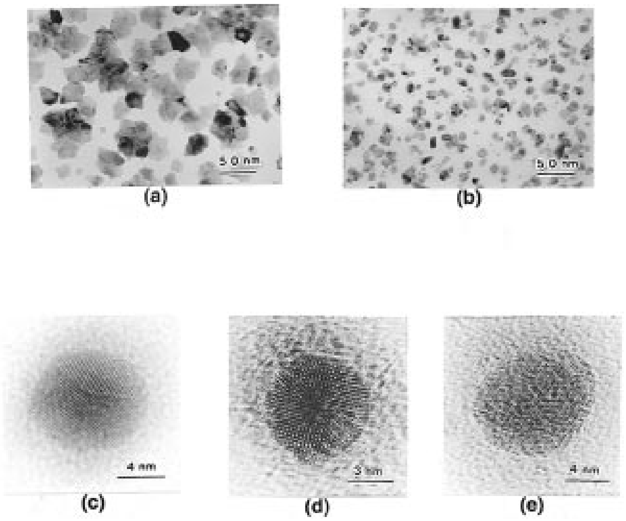

Figure 8. Images of Pd particles formed in 1 M $HClO_4$ + 1 mM $PdSO_4$ solution on carbon electrode at 0 V for 180 s (a) and −0.2 V for 120 s (b). (c) Decahedral Pd particle formed at −0.2 V. (d) and (e) are an icosahedral Pd particle and a plate of Pd particle formed at −0.3 V, respectively.

the MTPs, which have a more dense structure than fcc, of IB and IIB transition metals can be formed at lower electrode potentials. However, one should consider the contribution of the d electrons when the stability of MTPs of IB or IIB metals is compared. Ho et al.[31,32] pointed out that the d electrons play an important role in determining the difference between Au and Ag. For transition metals with a nearly full d band, a substantial part of the bonding forces between atoms comes from the d−s hybridization or s,p−d hybridization, which increases the density of delocalized electrons between the atoms and leads to a stronger bonding. The larger the s−p compression, the bigger the contraction of the lattice as observed on the reconstruction of clean gold surfaces. This kind of hybridization is weaker in the 4d transition metals than in the 5d transition metals. On the basis of our experimental results, it could be proposed that the d−s hybridization or s,p−d hybridization of the 3d transition metals is much weaker than that of the 4d transition metals so that the bonding is weaker and the contraction of the lattice is smaller in the sequence of 5d, 4d, and 3d transition metals. In another way this can be understood from the oxidizability of 3d, 4d, and 5d transition metals. Because 3d transition metals, e.g., Cu and Ni, are easier to be oxidized than 4d and 5d transition metals, there is a stronger tendency to decrease the surface charge density in the sequence 3d > 4d > 5d. Therefore, the surface structure of MTPs of 3d transition metals formed in solution at lower electrode potentials is less compressed than that of 4d and 5d transition metals. The icosahedron, which has a more compressed structure than that of decahedron, of Cu and Ni are not formed, and the MTPs of these metals are easier to change into a fcc polycrystalline.

Conclusion

We presented the results of MTPs of Cu, Ni, Ag, and Pd grown in solution at low electrode potentials. This phenomenon is similar to that of Au and Pt. However, at higher electrode potentials the formed particles are Pd polycrystalline ones for Pd but Cu_2O for Cu and Ag_2O for Ag. NiO particles and Ni decahedral particles grow simultaneously at −0.9 V. The icosahedron and decahedron of Au formed on the SnO_2 electrode below −0.3 V, which indicates that the surface structure of SnO_2 film has no effect on the growing of the MTPs of Au.

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