ORIGINAL PAPER

Da-ling Lu · Ken-ichi Tanaka

Crystal habit of fcc metal particles controlled by electrode potential in solution

Abstract The crystal habit of fcc metal particles formed on an amorphous carbon film electrode in solution at different electrode potentials is discussed. The fcc metal particles have different crystallographic habits depending on applied electrode potential; that is, icosahedral and/or decahedral particles are formed at lower potentials, and fcc single-crystalline or polycrystalline particles at higher potentials. It was found that decahedra and icosahedra of Cu-Au alloy particles are formed in the potential region of underpotential deposition (UPD) of Cu at which only fcc Au single-crystalline particles and Au polycrystalline particles appear. This is attributed to the charge transfer from the UPD Cu ions to the Au overlayer of Cu-Au alloy particles. The formation of decahedral and icosahedral Cu-Au alloy particles depends on the composition of the Cu-Au alloy. On the basis of these results it was deduced that the contraction of the surface lattice of the growing particles is responsible for the formation of icosahedral and decahedral particles.

Key words Crystal habit · fcc metal · Icosahedron · Decahedron · Multiply twinned particles · Electrode potential

Introduction

It has been known for many years that the surface structure of some metals and semiconductors is different from the truncated structure of the bulk material. Since reconstruction of the clean metal surface was discovered, it has been confirmed that Au, Pt, Ir, V, Cr, Mo and W undergo reconstruction in vacuo (see [1] and

references therein). On the other hand, Hamelin [2], Kolb and Schneider [3] and Schneider and Kolb [4] found that reconstruction also occurs on the surface of Au(100), Au(110) and Au(111) electrodes in solution at lower electrode potentials but not when the electrode potential is made more positive. Later, this kind of potential-induced reconstruction on Au electrodes was directly proved by Weaver et al. [5–7] and other groups [8–11] by means of electrochemical scanning tunneling microscopy (EC-STM). Surface reconstruction leads to a more close-packed arrangement of the surface atoms than the bulk. Therefore, potential-induced reconstruction of an Au electrode has been considered to be a contraction of the surface lattice induced by electrode potential [2–7] or surface charge [12]. Taking account of these facts, we thought that when metal particles grow on an electrode by electrodeposition in solution, the surface of the growing particles will be forced to take on a different surface atom density depending on the applied electrode potential. As a result, the particles may have different structures and/or habits. On the basis of this consideration, we investigated the formation of such fcc metal particles as Au [13–16], Ag [16], Cu [16, 17], Pt [18], Pd [16], Ni [16], Ir [19], Rh [19] and Cu-Au alloy [20, 21] in solutions. It was found that at lower electrode potentials all these metal particles have multiply twinned particles (MTPs), i.e., icosahedra and/or decahedra (Table 1).

Icosahedra and decahedra of gold particles were first observed in vacuo with an electron transmission microscope by Mihama and Yasuda [22] and then analyzed by Ino and Ogawa [23, 24], who named these particles multiply twinned particles (MTPs) and proposed a growth mechanism for these particles of coalescence of five or twenty tetrahedral nuclei for a decahedron or icosahedron, respectively. The structure and growth of MTPs were then investigated experimentally and have been theoretically explained by many groups [25–51]. It should be pointed out that so far the MTPs have only been prepared in vacuo or in inert gases. In this paper we show that the icosahedra or

D. Lu (✉) · K. Tanaka
The Institute for Solid State Physics, The University of Tokyo, 7-22-1, Roppongi, Minato-ku, Tokyo 106, Japan
Tel.: +81-3-34786811; Fax: +81-3-34015169

Table 1 List of particle habits of fcc metals formed in solution at different electrode potentials. Dc, decahedron; Ic, icosahedron; SC, fcc single crystal; Pl, fcc polycrystal

Element	Formation of particles		Electrolyte	References
	Lower potential	Higher potential		
Rh	Dc, Pl	Pl	$CsClO_4$	[9]
Ir	Dc, Pl	SC, Pl	HCl	[9]
Ni	Dc, Pl, NiO		$CsClO_4$	[10]
Pd	Dc, Ic, Pl	SC, Pl	$HClO_4$	[10]
Pt	Dc, Ic, Pl	SC, Pl	$CsClO_4$	[11]
Cu	Dc, Pl, Cu_2O	Cu_2O, Pl	$CsClO_4$	[10]
Ag	Dc, Ic, Pl	SC, Pl, Ag_2O	$CsClO_4$	[10]
Au	Dc, Ic	SC, Pl	$HClO_4$, H_2SO_4, HCl, $CsClO_4$, $KClO_4$	[12–14]
Cu–Au		Dc, Ic, Pl	$HClO_4$, H_2SO_4	[15, 16]

decahedra of fcc metal particles can also be formed in solution at lower electrode potentials, while the particles grown at more positive electrode potentials are fcc single-crystalline particles (Au, Pt, Ir, Ag and Pd) or polycrystalline particles (Rh) or oxide (Cu_2O and Ag_2O). From these results, it was deduced that the contraction of the surface lattice of the growing particles is responsible for the potential-dependent crystal habit.

Experimental

The experimental conditions, which have been described in detail in our previous papers [13–21], are mentioned simply here. The formation of metal particles was carried out in a conventional three-compartment electrochemical cell at room temperature. The working electrode was an Au mesh for transmission electron microscopy (TEM), which was covered with a collodion film and an amorphous carbon film. The collodion solution consists of nitrocellulose dissolved in isoamyl acetate. In our experiment, a 2% collodion solution was dripped into water contained in a glass dish, and a collodion film formed on the water. The collodion film was placed over an Au mesh, and the mesh was then transferred to a vacuum evaporator ($\sim10^{-5}$ Torr) for vapor deposition of an amorphous carbon film on the collodion film. The reference electrode was a saturated calomel electrode (SCE), and the counter electrode was a 0.5-mm diameter Pt wire. All electrode potentials in the experiment and in this paper were versus SCE.

Solutions were prepared with high purity chemicals and triply distilled water. The solution in the main compartment of the cell was deaerated with purified argon. The electrodeposited metal particles were observed by means of a Hitachi 9000 high-resolution TEM.

Au multiply twinned particles (MTPs) were formed at negative electrode potentials on the amorphous carbon film electrode [9] and on the SnO_2 film electrode [12], which has a crystalline structure. It is therefore clear that the formation of MTPs in solution occurs not only on an amorphous electrode but also on a crystalline electrode. These results show that it is possible that the formation of MTPs in solution has little relation to the nature of the working electrode.

Results and discussion

Icosahedra and decahedra of Au particles formed in vacuo have been studied in detail. Figure 1 shows the Au particles electrodeposited in perchloric acid solution on an amorphous carbon electrode. The same phenomenon was commonly observed in acidic solutions of sulfuric acid, hydrochloric acid [15] and salt solutions [14]. Icosahedra and decahedra of Au particles are formed at more negative potentials (Fig. 1a and b), but fcc octahedral single-crystal Au particles are formed at more positive potentials (Fig. 1c). These icosahedral and decahedral particles are completely identical to those MTPs formed in vacuum. However, an interesting phenomenon observed in solution is that when the electrode potential is made more positive, icosahedron and decahedron particles of Au cannot be formed but fcc single crystalline particles appear. It should be noted that icosahedra and decahedra of Au particles are formed in the electrode potential region where the reconstructed surface of the Au electrode is stable, while fcc single-crystal Au particles grow at potentials where
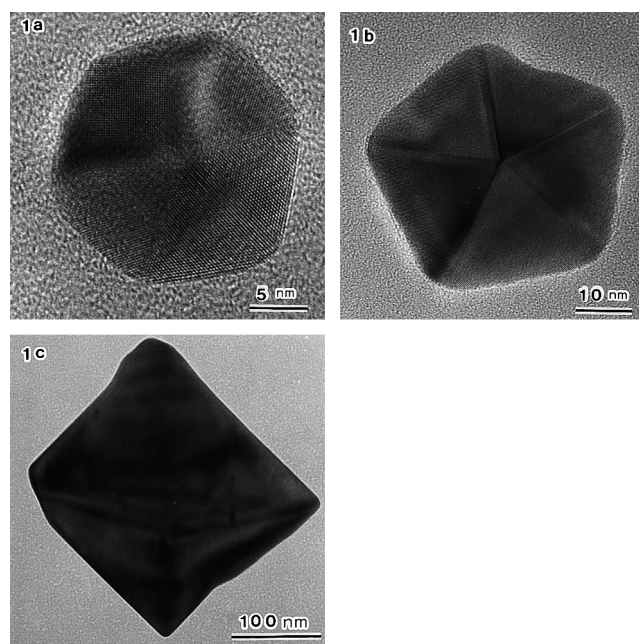
Fig. 1a–c TEM images of Au particles formed in 0.1 M $HClO_4$ + 10^{-3} M $HAuCl_4$ solution at different electrode potentials: **a** icosahedral particle at −0.3 V vs SCE, **b** decahedral particle at −0.3 V vs SCE, and **c** octahedral particle at 0.3 V vs SCE

the (1×1) structure of the Au electrode surface is stable (Fig. 2).

Icosahedra and decahedra of metal particles have twenty and ten {111} close-packed faces, respectively. The {111} face is the most close-packed face of the fcc metals. It is well known that the close-packed Au(111) surface has a $(23 \times \sqrt{3})$ reconstructed unit cell which is uniaxially contracted (4%) along the $\langle 110 \rangle$ direction in vacuo. This long-range reconstruction is made by packing more surface atoms than in the (1×1) structure on the Au(111) surface, where the regions of fcc (ABC) and hcp (ABA) stacking coexist [52, 53]. On the surface of the Au(111) electrode, an identical reconstruction to that observed in vacuo occurs at negative electrode potentials [5]. In the surface reconstruction, icosahedral and decahedral Au particles formed at negative electrode potentials are thought to take up a more close-packed structure than that of the bulk material in order to grow.

Reconstruction, lowering the surface free energy, may be related to the surface stress or surface tension. Ibach inferred that the surface stress is the driving force for surface reconstruction [54]. He also pointed out recently that surface stress plays a crucial role for the surface equilibrium structure of the electrode [55]. Variation of surface stress for a metal electrode is difficult to measure when the electrode potential is changed. However, recently Raiteri and Butt [56] and Ibach et al. [57] measured the potential-induced stress of an Au electrode by means of the atomic force microscope (AFM). They observed that the surface stress of an Au electrode increases as the electrode potential is changed from positive to negative; however, when the potential is subsequently lowered to more negative values the

surface stress decreases. The surface stress versus electrode potential displays an arc-like curve as the potential changes from positive to negative or vice versa. This phenomenon of subsequent decrease of the surface stress at more negative potential may accompany the potential-induced reconstruction. Weaver et al. deduced this phenomenon from the curves of surface tension versus electrode potential for both hexagonally reconstructed phase and (1x1) phase of Au(100) electrode in 0.01 M HClO$_4$ solution, which curves were obtained from their capacitance-potential (C_d-E) data (Fig. 9 of Ref. 58). Their curves showed that the hexagonally reconstructed phase exhibits lower surface tension at more negative potential and the (1×1) phase presents a lower surface tension at a more positive potential. When the electrode potential scans from positive to negative and crosses the intersection potential of the surface tension versus electrode potential curves of hexagonally reconstructed and (1×1) phases, the surface structure of the Au electrode changes from (1×1) to the hexagonally reconstructed phase. It indicates that the surface tension of the hexagonally reconstructed phase rises at positive potentials, where the surface prefers to take (1×1) phase; conversely, when the surface tension of the (1×1) phase increases at negative potentials, the hexagonal phase becomes the stable one. It can be expected that the surface tension or surface stress of an electrode is varied when the electrode potential is changed and the surface of the electrode prefers to take a structure with lower surface tension.

In vacuo, small Au particles spontaneously take a more close-packed surface structure to lower the total energy, which results in the growth of icosahedral and decahedral particles. Theoretical calculations also revealed that the closer the surface structure, the lower the total energy of growing particles in a limited size, that is, the total energy of MTPs is lower than that of fcc structure particles when the particles are smaller than a critical size [27, 28, 49, 50]. This kind of phenomenon is commonly observed for other fcc metals such as Pt [31], Ag [35, 37, 48], Pd [25, 43, 45, 48, 49] and Ni [25, 32, 42] in vacuo, Cu [26] in xenon gas and probably Rh [36]. In contrast to the size-dependent crystal habit of particles in vacuum, the crystal habit of the metal particles which are formed in solution by electrodeposition is controlled by the electrode potential because the surface energy is changed by the electrode potential. As shown in Table 1, we observed not only the MTPs of Au, Pt, Ag, Cu, Pd, Ni and Rh but also the MTPs of Ir and Cu-Au alloy, which have not been observed in vacuo but were first observed in electrochemical deposition at certain potentials. Because of the lower equilibrium Nernst potential or the stronger oxidizability of some metals, Ag$_2$O, Cu$_2$O and NiO particles are formed at potentials higher than a certain value, which has been discussed in other papers [16, 17]. From our results, it is deduced that the order of feasibility for the formation of MTPs in solution is in the sequence Au > Pt, Ir, Pd > Ag > Rh, Cu, Ni.
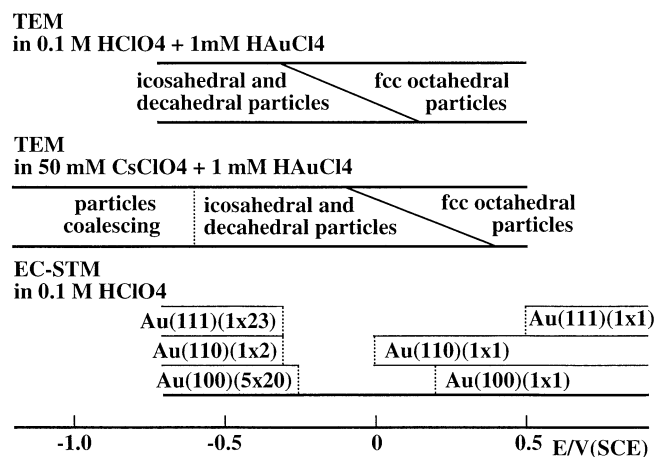
Fig. 2 Graph of the result of Au particles formed in 0.1 M HClO$_4$ + 10^{-3} M HAuCl$_4$ and 0.05 M CsClO$_4$ + 10^{-3} M HAuCl$_4$ solutions compared with the result of Au single-crystal surface structure changed by the electrode potential in 0.1 M HClO$_4$ solution observed by in situ EC-STM [5–7]. The oblique lines in the upper graph indicate an electrode potential region in which icosahedral and decahedral particles and fcc structure single-crystalline particles coexist

The 5d fcc metal particles of Au, Pt and Ir show a common phenomenon in solution, that is, the formation of icosahedra and decahedra at lower potentials and fcc single crystals at higher potentials. It had been known that the three low-index surfaces of Au, Pt and Ir apart from Pt(111) and Ir(111) undergo reconstruction in vacuo [1]. However, the reconstruction of a clean Pt(111) surface was observed recently above 1330 K [59, 60] or could be induced in the presence of supersaturated Pt vapor at 400 K [61, 62]. It should be pointed out that the reconstructed Au(100), Au(110) Au(111) and Pt(110) surfaces are stable in aqueous solution [5–7, 63] but the reconstructed Pt(100) surface is not [64]. In fact, Pt(111) does not undergo reconstruction in an electrolyte [65]. There are also no reports suggesting a surface reconstruction of an Ir electrode in solution. Ocko et al. pointed out [12] that the density of delocalized sp electrons are increased in the valleys between surface atoms, so that the in-plane sp bonding is strengthened, and a more densely packed reconstructed structure is formed in vacuo. At a negatively charged Au electrode surface in solution the excess electrons are accumulated in the valleys, which may be responsible for the reconstruction at lower electrode potentials. This deduction is consistent with experimental results, but the mechanism for the potential-induced reconstruction is difficult to rationalize at the present time. On the basis of the above statement it could be said that a certain amount of negative charge accumulated at the interface of the electrode induces a reconstruction which is formed by the contraction of the surface atom arrangement. Providing that icosahedral and decahedral particles have closer structures than that of fcc, formation of icosahedral and decahedral particles of Au, Pt and Ir in solution is accomplished by the stacking, on the surface of growing particles, of metal atoms with higher density than fcc crystal, which is attained when the negative charge on the surface of growing particles exceeds a critical value at lower electrode potentials. We discussed the formation of Au MTPs in detail in a previous paper [13] in which we proposed that due to the applied negative electrode potential the surface electron density or surface negative charge of growing Au particles is increased, and when the negative charge exceeds a critical value the atom density within the surface plane is increased. As a result, when Au particles are grown by retaining a more closed surface structure the MTPs are formed. This is the same mechanism for the potential-induced reconstruction at the Au electrode surface in solution. As mentioned above, Pt(111) and Ir(111) electrodes do not undergo surface reconstruction in solution. However, the formation of Pt MTPs (Fig. 3) and Ir MTPs (Fig. 4) at lower electrode potentials in solution suggests that the growing particles prefer to take higher atom density at more negative electrode potentials for both Pt and Ir particles than is the case for the growth of MTPs of Au.

Contrary to the negative charge theory, it has been accepted that when Au electrode surface takes a positive
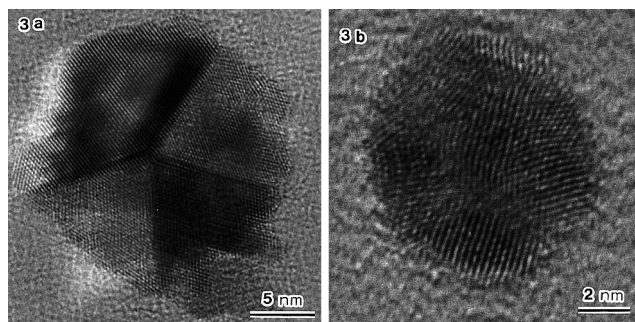
Fig. 3a, b TEM images of Pt MTPs formed in 0.05 M $CsClO_4$ + 10^{-3} M $PtCl_4$ solution: **a** decahedral particle at −0.9 V vs SCE and **b** icosahedral particle at −1.2 V vs SCE

charge, the reconstruction is lifted and (1 × 1) structure becomes stable [12]. In fact, the 5d metal particles grew by keeping the (1 × 1) structure at higher electrode potentials and the single crystalline particles with fcc structure were obtained.

These results indicate that the surface of the growing 5d metal particles in solution have a similar structure to that of the surface of 5d metal single crystal electrodes. It can be deduced that the crystal habit of growing particles is affected by the applied potential in way that resembles potential-induced reconstruction. From the viewpoint of potential-induced surface stress or surface tension, the surface negative charge may increase the surface stress of growing particles. The contraction of surface atoms of the particles then occurs, which makes the surface free energy lower because of the increase of surface atom density; therefore, icosahedral and decahedral particles form.

It was also pointed out by Ho et al. [66, 67] that the spd or sd hybridization in 5d metals more easily makes a close-packed surface than is the case to 3d and 4d metals. We deduced that the stability for the MTPs of Cu, Ni and Rh formed in solution is much less than that of Au, Pt and Ir, but the MTPs of Pd are as stable as those of Pt and Ir. That is, the MTPs of Pd are more stable than the MTPs of other 4d metals, Rh and Ag.
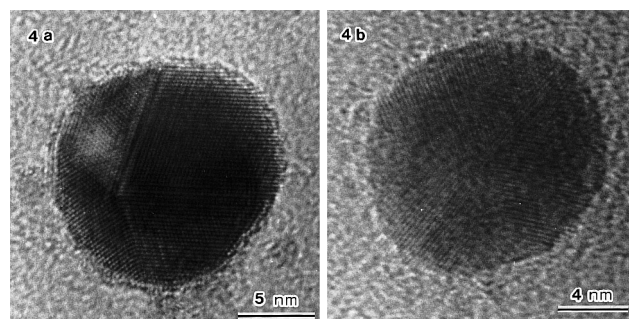
Fig. 4a, b TEM images of Ir MTPs formed in 3 M HCl + 10^{-3} M $IrCl_4$ solution at –0.35 V vs SCE: **a** decahedral particle and **b** icosahedral particle

Any low-index clean surface of Ag, Pd, Rh, Cu and Ni does not undergo reconstruction in vacuo. However, these surfaces can be reconstructed by the adsorption of alkali metals, where the negative charge may be induced by the ionized adsorbate on the substrate surface [68–71]. It is supposed that when electron density is increased at the surface by the adsorption, surface atoms would be arranged in higher density than the original one, as in the case of the surface reconstruction of the electrode induced by the negative potential. The extra charge in the s-p orbital increases the cohesive force of the surface atoms [70], which is manifested by the reconstruction of the Au electrode occurring at lower electrode potential. Our result shows that the MTPs of fcc $3d$, $4d$ and $5d$ metals can be grown in solution by applying negative potential, and it is supposed that the surface of the small particles might be contracted by applying the electrode potential. Even some surfaces of these large metal crystals cannot be reconstructed in vacuo.

It is interesting that decahedra and icosahedra of Cu-Au alloy particles are formed in the region of underpotential deposition (UPD) of Cu (Fig. 5) when the Cu content is lower than a certain value. It should be pointed out that the pure Au particles deposited in this potential region take only fcc single crystalline or polycrystalline forms. The UPD of the Cu^{2+} ion on the surfaces of Au electrodes has been investigated in detail [72–76], and it has been accepted that in the UPD potential region of the Cu^{2+} ion, the underpotential-deposited Cu^{2+} ion on Au surface is not completely discharged to Cu^0 but to the Cu^+ state [73, 75] and sequentially discharged to Cu^0 at potentials lower than the critical potential. If this is the case, the effect of Cu^+ ion on the Au layer of growing Cu-Au alloy particles is similar to that of alkali metal atoms deposited on an Au surface in vacuo, because the deposited alkali metal atoms are ionized on the Au surface and the surface reconstruction is then induced [77–79]. The growing Cu-Au particles are covered with the overpotential-deposited Au layer on which the deposited UPD Cu^{2+} ions
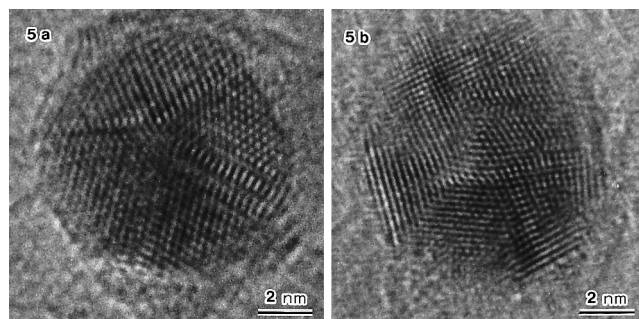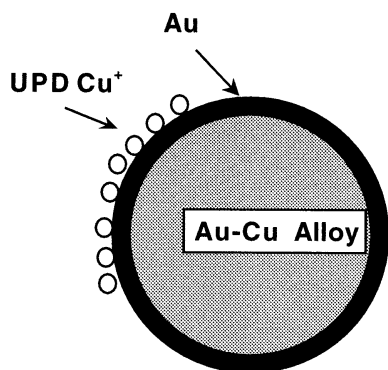
are reduced to Cu^+. The Cu^+ ions on the Au layer induce the negative charge increase of the Au layer, and the Au layer is contracted by the increased negative charge and prefers to take up a closer arrangement.

It has been accepted that the reconstruction of the Au(111)-surface is accompanied by about a 4% contraction of the lattice constant within the surface plane. When the composition of Cu in the surface plane of the Cu-Au alloy particles becomes ca. 30%, the surface lattice constant shortens by ca. 3% compared to that of Au. In this case the Au layer deposited on it cannot be effectively contracted to make a closer atomic arrangement by the adsorption of Cu^+ ion, and hence no MTPs are formed. This critical composition of Cu in the Cu-Au alloy particles suggests that the surface reconstruction will occur when the topmost layer can make a closer arrangement of atoms compared to that of the second layer. Therefore, we could say that the sufficient requirement for the formation of MTPs is not only the particle size but also the extent of the lattice contraction between the topmost layer and the second layer. This might be the reason why we have not found the icosahedra and decahedra of Cu-Au alloy particles to have more than 30%-Cu.

So far, two models have been proposed for the growth of MTPs. The first is that the MTPs are composed of tetrahedra in a twin relation with each other [24, 25]. The second is that the MTPs grow around five-fold symmetry axes, which structure has a lower total energy for smaller particles and is different from the fcc structure, i.e., it is orthorhombic for the decahedron or rhombic for the icosahedron [33, 34]. From the results on Cu-Au alloy particles we suppose that the MTPs grown in solution may be formed by the second model. If the MTPs were grown by the first model the UPD Cu^+ ions would have no influence on the growth of the MTPs. In other word, the MTPs of Cu-Au alloy particles should be formed at the same potentials as those for the formation of Au MTPs. However, this is not the case, i.e., the Cu-Au alloy MTPs are formed in the potential region of the UPD of the Cu^{2+} ion but no Au MTPs are formed in this potential region. When the concentration of Au ion in solution was sufficiently diluted, the Cu composition in the Cu-Au alloy particles became more than 30% and no Cu-Au alloy MTPs were formed [20]. As the UPD of Cu^{2+} will take place only on the Au layer, the Cu-Au alloy particles are formed by layer growth (Fig. 6) in the UPD region of the Cu^{2+} ion. When the UPD rate of Cu^{2+} is rapid enough compared to the OPD rate of Au, the UPD Cu necessarily makes one monolayer on the Au overlayer of the Cu-Au alloy particles, which produces the maximum copper content (50%) in the alloy particles because of a layer-by-layer deposition of Au and Cu. In fact, the alloy particles with 50% Cu were formed in a solution containing a low concentration of Au ion [20, 21].

Iijima and Ichihashi showed by means of TEM that the shape of gold particles changed continually through

Fig. 5a, b TEM images of Cu-Au alloy particles: **a** decahedral particle consisting of Au-71% formed in 0.1 M $HClO_4$ + 10^{-3} M $HAuCl_4$ + 0.05 M $Cu(ClO_4)_2$ solution at 0.1 V vs SCE and **b** icosahedral particle consisting of Au-80% formed in 0.1 M $HClO_4$ + 10^{-3} M $HAuCl_4$ + 10^{-3} M $Cu(ClO_4)_2$ solution at 0.1 V vs SCE

Fig. 6 Graph of supposed formation of Cu-Au alloy particle in the region of UPD of Cu

an internal transformation from a single crystal to a twinned crystal, and vice versa [38]. Taking account of above fact, the stability of Au MTPs prepared in solution was studied by elevating the electrode potential for the grown Au MTPs, but the habit and structure of these Au MTPs did not change. Accordingly, the change of shape and structure of Au MTPs revealed by TEM may be caused by the thermal oscillation of the bulk lattice induced by the incident electron beam. Similar thermal oscillation was also found for the change of shape and structure of decahedral Ag particles during the observations made with TEM [16]. Therefore, we could say that the applied electrode potential influences only the growth of icosahedral and decahedral particles.

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