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Tuning the architectures of lead deposits on metal substrates by electrodeposition

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1. Introduction

The preparation of micro/nanostructural materials has been a research hotspot in recent years due to their inimitable properties and potential applications in building blocks [1-4]. The properties of nanomaterials, which strongly depend on size, size distribution, shape, and chemical composition, vary widely [5-11]. In addition, the various nanostructures can offer fundamental scientific opportunities for investigating the influence of size and dimensionality with respect to their collective magnetic, optical, and electronic properties and would provide possibilities to investigate the novel properties and applications. Metallic nanoparticles exhibit peculiar characteristics in quantized excitation coulomb blockade, single-electron tunneling and metal-insulator transition, due to a combination of the large proportion of high-energy surface atoms compared with the bulk solid and the nanometerscale mean free path of an electron [12-15]. However, four critical challenges in the development of nanoscale science and technology still exist: materials synthesis with controlled structures and precision at the atomic/molecular scale, property characterization of the structurally well understood components, nanodevice fabrication, and system manipulation and integration [3]. Hereinto,

ABSTRACT

Different morphologies of lead (Pb) deposited on different metal substrates have been prepared via electrochemical deposition in aqueous solution. The morphologies of as-deposited lead were determined by scanning electron microscope (SEM). It is found that the various morphologies of the products are dependent on the electrodeposition conditions, including the deposition current densities, concentration of additives, substrates and deposition time. X-ray diffraction (XRD) and transmission electron microscope (TEM) results reveal that all these lead deposits with different morphologies can be assigned to the space group *Fm*-3*m* (225).

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the systematical synthesis of various nanomaterials remains an important research focus in the modern material chemistry [16]. Although different methods, such as template synthesis including hard templates [17,18] or soft directing agents [19–25], chemical vapor deposition, and colloidal synthesis, have been proved to be successful in preparing diversified nanomaterials, self-organized micro/nanostructures of metals at solid surfaces are attracting much attention because it is possible to prepare stripes, dot arrays, spiral patterns, etc. [26]. The solution phase approaches of metal deposition have become a promising technique in the field of nanostructure fabrication [27]. Among them, electrodeposition is very attractive, for that the easy control of its parameters such as deposition potential, time, and solution composition can be used to adjust the growth rate, particle size and number density, with precision and relatively low cost.

Lead is an especially attractive element, due to its extremely high reactivity and superconductivity [28]. The underpotential deposition of Pb on some noble metal surfaces has been extensively examined because monolayers and submonolayers of Pb can enhance catalytic activity of the noble metal in a variety of electroreduction processes, such as the reduction of H_2O_2 to H_2O , the reduction of O_2 to H_2O in aqueous fuel cells, etc. [29,30]. Dubois et al. [31,32] reported that lead nanowires grown in the nanopores of porous track-etched polymer membranes via normal electrodeposition possess the characteristics of superconductivity. Single crystal or polycrystalline Pb nanowires with diameter of about





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50 nm can be prepared by pulse electrodeposition in nanoporous membrane [33]. However, these methods have a common disad-vantage of removing the unwanted materials because the removal of the template or directing agent from the surface of the nanomaterials requires harsh conditions or multiple washing procedures. Moreover, the presence of residue may influence the properties and increase the difficulty of analysis [15,34–36].

Electrodeposition without templates can provide versatility in tailoring the architectures of nanostructures. In this paper, octahedra, zigzag nanowires and nanoclusters on copper (Cu), hollow cubic columns on aluminum (Al) and flowerlike architectures on titanium (Ti) were synthesized by electrodeposition through systematically adjusting the parameters, such as the current density, the concentration of boric acid, deposition time and the substrates. The X-ray diffraction (XRD) and electron diffraction (ED) patterns illustrate that face-centered cubic structure of lead is apt to be formed.

2. Experimental

Cyclic voltammetry (CV) and constant–current chronopotentiometric (E–t) were employed to study Pb electrocrystallization onto Cu, Al and Ti substrates, respectively. All of the electrochemical experiments were carried out in a conventional three-electrode cell system. Cu, Al and Ti wires were used as the working electrodes. A graphite electrode was used as a counter electrode (spectral grade). A saturated calomel electrode (SCE) was used as the reference electrode that was connected to the cell with a double salt bridge system. All potential values determined in this study were the values versus SCE.

Galvanostatic electrolysis was utilized in all electrochemical depositions under different current densities from 0.25 to 1.0 mA cm⁻². The architecture of the deposits is strongly dependent on the electrolyte concentration. The best concentration range for growing lead mesostructures with controlled architectures is from 0.001 to 0.01 mol L⁻¹ and most experiments were carried out with a concentration of 0.005 mol L^{-1} [38]. H₃BO₃ is usually used as the additive and buffer agent. In our experiment, the electrochemical deposition of Pb was carried out in aqueous solution containing the following composition: $0.005 \text{ mol } L^{-1} Pb(CH_3CO_2)_2$, $0.2 \text{ mol } L^{-1} \text{ CH}_3 \text{CO}_2 \text{NH}_4$, and $0.5 \text{ mol } L^{-1} \text{ H}_3 \text{BO}_3$ with pH of about 4-5. An IM6e electrochemical workstation (Zahner, Elektrik) was used for the electrochemical measurements. The electrodeposition experiments were carried out by galvanostatic electrolysis at room temperature. The deposits were analyzed by X-ray diffraction (PIGAKU, D/MAX 2200 VPC) to determine the film structures. The surface morphologies of the as-deposited films were observed by field emission scanning electron microscope (FE-SEM, JSM-6330F), thermal field emission environment scanning electron microscope (TFE-SEM, FEI, Quanta 400), and transmission electron microscope (TEM, JEM-2010HR).

3. Results and discussion

3.1. Electrochemical measurements

Fig. 1(a) shows the CV of a Cu electrode in the solution of $0.2 \text{ mol } \text{L}^{-1}$ CH₃CO₂NH₄ and $0.5 \text{ mol } \text{L}^{-1}$ H₃BO₃ as a blank CV. Fig. 1(b) shows the CV of Cu electrode in the solution of $0.005 \text{ mol } \text{L}^{-1}$ Pb(CH₃CO₂)₂, $0.2 \text{ mol } \text{L}^{-1}$ CH₃CO₂NH₄ and $0.5 \text{ mol } \text{L}^{-1}$ H₃BO₃ at different scan rates. A cathodic peak potential (E_{pc}) at around -0.52 V and an anodic peak (E_{pa}) at around -0.39 V can be seen at a scan rate of 0.020 V s⁻¹, corresponding to the reduction of Pb²⁺ to Pb, and anodic stripping of the electrode, respectively.



Fig. 1. (a) CV of Cu electrode in the solution of 0.2 mol L⁻¹ CH₃CO₂NH₄ and 0.5 mol L⁻¹ H₃BO₃ at a scan rate of 0.080 V s⁻¹; (b) CV of Cu electrode in the solution of 0.005 mol L⁻¹ Pb(CH₃CO₂)₂, 0.2 mol L⁻¹ CH₃CO₂NH₄ and 0.5 mol L⁻¹ H₃BO₃ at different scan rates (V s⁻¹): (a) 0.080, (b) 0.060, (c) 0.040 and (d) 0.020; (c) plot of E_p versus ln v; (d) plot of j_p versus $v^{1/2}$.

The cathodic peak potential shifted negatively with the increase of the sweep rate, the separation of the cathodic and anodic peak potentials is large. The relation between the cathodic peak current density (j_p) and the square root of sweep rate $v^{1/2}$ is linear. It indicates that the reaction of Pb²⁺ + 2e = Pb is irreversible. For an irreversible charge-transfer electrodic process, the peak potential and the peak current density change can be explained by the following equation [37]:

$$E_{\rm p} = K - \frac{RT}{2\alpha F} \ln \frac{\alpha F v}{RT} \tag{1}$$

$$j_{\rm p} = (2.99 \times 10^5) \alpha^{1/2} n^{3/2} C_0 D_0^{1/2} v^{1/2}$$
⁽²⁾

where E_p , K, α , v, j_p , C_0 and D_0 stand for peak potential (for cathodic peak), constant, electron-transfer coefficient, scan rate, peak current density, ion concentration and diffusion coefficient. The E_{pc} moves to more negative potential linearly along with the natural logarithm of v, and the j_{pc} versus $v^{1/2}$ exhibits a linear increase by degrees when the scan rate augments as shown in Fig. 1(c) and (d). This also indicates that the reduction of Pb²⁺ is an irreversible electrodic process. According to Eq. (1), $\alpha = 0.632$ was calculated from the slope of the plot of E_{pc} versus $\ln v$. The relationship between j_p and the potential sweep rate (v) is given by Eq. (2) at 298 K. $D_0 = 1.75 \times 10^{-9}$ m² s⁻¹ can be calculated from the plot of j_p versus $v^{1/2}$ for the reduction peak shown in Fig. 1(d).

Fig. 2 shows E-t curves of the Cu electrode in the solution of 0.005 mol L⁻¹ Pb(CH₃CO₂)₂, 0.2 mol L⁻¹ CH₃CO₂NH₄ and 0.5 mol L⁻¹ H₃BO₃ at different current densities. Along with the time, the potentials become relatively stable under applied current densities. Under the lowest applied current density of 0.25 mA cm⁻², there is a long transition time reaching about 12 s (Fig. 2(1)). Then the electrode potential reduces to -0.48 V and holds at this potential. This current density meets the growth of Pb nuclei which are sufficiently small and well separated. This behav-



Fig. 2. Constant–current chronopotentiometric curves of Cu electrode in 0.005 mol L⁻¹ Pb(CH₃CO₂)₂, 0.2 mol L⁻¹ CH₃CO₂NH₄ and 0.5 mol L⁻¹ H₃BO₃ aqueous solution with different current densities: (1) 0.25 mA cm⁻²; (2) 0.5 mA cm⁻²; (3) 0.75 mA cm⁻²; (4) 0.85 mA cm⁻²; (5) 1.0 mA cm⁻²; (6) 1.5 mA cm⁻².

ior is similar to that at 0.5 mA cm^{-2} , although the transition time rapidly reduced to 2.5 s, and the electrode potential is steady at -0.51 V (Fig. 2(2)). As can be seen in Fig. 2(3), the transition time is 16 s under current density of 0.75 mA cm^{-2} which is longer than the value of 0.25 mA cm^{-2} , and the electrode potential is -0.68 Vthat is more negative than the cathodic potential of -0.52 V shown in Fig. 1(b). Under this condition, a small amount of bubbles were observed on the surface of the Cu electrode, which may be due to the hydrogen evolution. The *E*-*t* curves at higher current densities, such as 0.85, 1.0 and 1.5 mA cm}{-2}, show that the transition time becomes shorter and the electrode potential more negative.

The CV curves on Al and Ti electrodes in the solution of $0.005\,mol\,L^{-1}$ $Pb(CH_3CO_2)_2,~0.2\,mol\,L^{-1}$ $CH_3CO_2NH_4$ and



Fig. 3. (a) CV curve of Al electrode at 0.080 V s^{-1} ; (b) constant-current chronopotentiometric curves of Al electrode with different current densities: (i) 0.75 mA cm⁻², (ii) 0.5 mA cm⁻²; (c) CV curve of Ti electrode at 0.080 V s^{-1} ; and (d) constant-current chronopotentiometric curves of Ti electrode with different current densities: (i) 0.75 mA cm⁻², (ii) 0.5 mA cm⁻²; (c) CV curve of Ti electrode at 0.080 V s^{-1} ; and (d) constant-current chronopotentiometric curves of Ti electrode with different current densities: (i) 0.75 mA cm⁻², (ii) 0.5 mA cm⁻² and (iii) 0.25 mA cm⁻² in the solution of $0.005 \text{ mol } L^{-1} \text{ Pb}(CH_3 CO_2)_2$, $0.2 \text{ mol } L^{-1} CH_3 CO_2 NH_4$ and $0.5 \text{ mol } L^{-1} H_3 BO_3$.

 $0.5 \text{ mol } L^{-1} H_3 BO_3$ at a scan rate of 0.020 V s^{-1} are shown in Fig. 3(a) and (c). The cathodic peaks appear at around -0.65 V and the anodic peaks at about -0.35 V. Fig. 3(b) and (d) shows the *E*-*t* curves of Al and Ti electrodes at different current densities. Under a current density of 0.25 mA $\rm cm^{-2}$, the transition times are about 12 and 15 s, and the electrode potentials hold at -0.67 and -0.58 V on Al and Ti electrodes, respectively. With the current density increasing, the transition times become longer and the electrode potentials shift more negatively.

3.2. Synthesis, characterization, and formation mechanism of multiform Pb architectures

Fig. 4 shows the different shapes of lead deposits, such as octahedra, nonregular crystals, zigzag nanowires and nanoclusters, which grow on Cu electrodes under different current densities in the range of (a) $0.25 \,\mathrm{mA \, cm^{-2}}$, (b) $0.5 \,\mathrm{mA \, cm^{-2}}$, (c) 0.75 mA cm^{-2} , (d) 0.85 mA cm^{-2} , and (e) 1.0 mA cm^{-2} . When deposited at 0.25 mA cm⁻², the average edge length of the octahedra is about 400 nm. The smallest one is about 100 nm and the biggest one is about 1 µm. The obtained lead octahedra are regular without any disfigurement on the edges and the angles, and the size distribution is wide. Moreover, there exist joined octahedra in our experiment (inset in Fig. 4(a)). This may be explained as follows. The reduction rate of Pb²⁺ is relatively slow under low current density and the decrease of the Pb²⁺ concentration at the Cu electrode interface can be sufficiently supplemented from the bulk solution (away from the electrode) by the transport of the Pb²⁺ ions. The abundant Pb²⁺ ions meet the feasibility of forming stable Pb octahedra that can reduce the surface energy as small as possible [34].

When the applied current density increases to $0.5 \,\mathrm{mA}\,\mathrm{cm}^{-2}$, dense and spherical crystals were obtained, which greatly contributed to the reduction of the surface energy (Fig. 4(b)). Rod-like lead deposits were obtained with the applied current density increasing to 0.75 mA cm^{-2} . Most of these nanorods are 5 μ m long, and the typical diameters are $1 \mu m$ as shown in Fig. 4(c). The lead zigzag nanowires and nanoclusters were obtained, when the current density increased to 0.85 and 1.0 mA cm⁻², as shown in Fig. 4(d) and (e).

The octahedral and spherical shapes of lead mesostructures obtained at relatively low current densities can be explained through the model based on a modified Wulff construction for shape formation [36,38]. According to this model, the polyhedra



(e)

onto stationary Cu substrates with different current densities: (a) 0.25 mA cm⁻²; (b) 0.5 mA cm⁻²; (c) 0.75 mA cm⁻²; (d) 0.85 mA cm⁻²; (e) 1.0 mA cm⁻². The insets in (a) and (d) are the high-resolution (HR) images of octahedrons and nanowires, respectively.



Fig. 5. SEM images of Pb deposits prepared in solutions of (a) 0.005 mol L^{-1} Pb(CH₃COO)₂, 0.2 mol L^{-1} CH₃CO₂NH₄ and 0.10 mol L^{-1} H₃BO₃ and (b) 0.005 mol L^{-1} Pb(CH₃COO)₂ and 0.2 mol L^{-1} CH₃CO₂NH₄ with current density of 0.25 mA cm⁻².



Fig. 6. SEM images of Pb deposits prepared in 0.005 mol L^{-1} Pb(CH₃CO₂)₂, 0.2 mol L^{-1} CH₃CO₂NH₄, 0.5 mol L^{-1} H₃BO₃ aqueous solution by electrochemical deposition onto stationary Cu substrates with current density of 0.25 mA cm⁻² for different time: (a) 30 min; (b) 60 min; (c) 90 min.

can be described as a collection of single-crystal tetrahedra that are twin-related at their adjoining faces. In our experiment, four tetrahedra arranged symmetrically can form an octahedron and sufficient tetrahedra in a three-dimensional configuration assembled at a common vertex produce a spherical crystal. The formation mechanisms for nanowires and nanoclusters are still under investigation.

The electrodeposition of Pb was carried out with $0.1 \text{ mol } \text{L}^{-1}$ boric acid and without boric acid. As shown in Fig. 5, the perfect octahedral structures of Pb were not obtained compared with Fig. 2(a). This clearly shows boric acid plays a crucial role in the formation of the octahedral lead structures. The effect of boric acid on the growth of Pb octahedral structures possibly may be attributed to specific interactions between Pb nuclei and boric acid. In the synthesis of materials, it is well known that some capping molecules can block the crystal growth of certain directions and enhance that of other directions [39,40]. The capping effect of boric acid may play a key role for the growth of Pb octahedral structures.

In addition, we investigated the different time intervals for a better understanding of the lead octahedra growth under the current density of 0.25 mA cm⁻² on Cu substrate and the SEM images are shown in Fig. 6. On the surface of the octahedral lead crystals, a large number of particles with the size of much less than 100 nm can be observed along with the increase of the deposition time. And the sizes of lead octahedral crystals become larger and larger from nanoscale to microscale at the same time. The two results confirm that the farther nucleation and growth of Pb is inclined to reduce the surface energy of the crystals [34]. Moreover, nanoparticles with regular shape are difficult to be prepared compared with multi-particle aggregates. These newly generated nanocrystals are distributed on the whole surfaces of the bulk octahedral Pb crystals. The possible mechanism is proposed as follows. At the beginning of the growth of lead crystal, forming octahedral crystals may be in favor of reducing the surface energy of the crystals. Moreover, the surface energy is inclined to be the minimum value. Thus the new nucleation of lead will be



Fig. 7. SEM images of Pb deposits prepared in 0.005 mol L⁻¹ Pb(CH₃CO₂)₂, 0.2 mol L⁻¹ CH₃CO₂NH₄ and 0.5 mol L⁻¹ H₃BO₃ aqueous solution for 30 min with current density of 0.25 mA cm⁻² on substrates of (a) Al and (b) Ti substrate.



Fig. 8. (a) XRD patterns of lead deposits prepared in 0.005 mol L⁻¹ Pb(CH₃CO₂)₂, 0.2 mol L⁻¹ CH₃CO₂NH₄ and 0.5 mol L⁻¹ H₃BO₃ aqueous solution by electrochemical deposition onto stationary Cu substrates at room temperature with different current densities: (i) 0.25 mA cm⁻² for 80 min and (ii) 0.85 mA cm⁻² for 20 min at a scan rate of 5°/min. (b) TEM image of an individual lead octahedron. The inset gives an ED pattern obtained by the electron beam on the octahedron. (c) TEM image of single lead zigzag nanowire. The inset gives an ED pattern recorded by focusing the electron beam on the whole wire and high-resolution TEM image taken from the tip of lead nanowire. The fringe spacing along the [1 1 $\overline{1}$] axis is indicated.

first absorbed on the edge and corner due to its higher surface energy.

Also, the substrates exert an obvious influence on the morphologies of the Pb deposits. The pattern of Pb deposited onto Al substrate (Fig. 7(a)) shows that the hollow cubic columns are shaped at 0.25 mA cm⁻². The thickness and width of the walls of the column are about 100 nm and 1 μ m, respectively. The center of the column is filled with stacking square platform which is in-tangent with the walls of the column. When Ti is used as electrodes, a high-resolution SEM examination shows that the morphologies of lead deposits are flowerlike architecture, which is composed of interlaced nanopetals (Fig. 7(b)).

3.3. Structural analysis of lead octahedra and zigzag nanowires

Fig. 8(a) represents the XRD patterns of lead octahedra and nanowires electrodeposited under 0.25 and 0.85 mA cm⁻², respectively, at room temperature. It is observed that as-deposited Pb patterns of octahedra and nanowires are in excellent accordance with a cubic structure that can be assigned to the space group *Fm*-3*m* (225). The lattice parameters of the nanowires were a = b = c = 4.951 Å. The shifts of the nanowires were Δ (2 θ) = -0.144°, -0.131°, -0.127° and -0.140° for the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) peaks, respectively, and the Δ (2 θ) shifts of the octahedra -0.021°, -0.029°, -0.004° and 0.032°. This can be explained as follows. It is



Fig. 9. XRD patterns of lead deposits prepared in $0.005 \text{ mol } L^{-1} \text{ Pb}(CH_3CO_2)_2$, 0.2 mol $L^{-1} CH_3CO_2NH_4$ and 0.5 mol $L^{-1} H_3BO_3$ aqueous solution with current density of 0.25 mA cm⁻² onto substrates of (a) Al and (b) Ti at room temperature.

well known that a nanowire form with a high aspect ratio experiences more tensile stress along the *c*-axis direction on the surface than the other forms, which leads to an increase in the *c* value [41]. In accord with this, *c*-axis-related peak shifts to lower angles of Pb nanowires compared with the octahedra.

Fig. 8(b) shows the TEM image and the inset displays the typical ED pattern of the selected octahedron. The ED pattern demonstrates the whole lead octahedron is single crystal and the diffraction spots can be indexed to the face-centered cubic phase of lead. The TEM image of single zigzag lead nanowire is shown in Fig. 8(c). The ED pattern was obtained when the beam direction was parallel to the $[11\bar{1}]$ axis. ED study also indicates a growth direction along the [110] axis. The high-resolution TEM image displayed in Fig. 8(c) was taken from the tip of the nanowire. The lattice spacing of the Pb nanowire is 0.29 nm. This result is in accordance with the XRD result, which could also be indexed to that of face-centered cubic lead.

The XRD patterns of the cubic columns on Al and flowerlike architectures on Ti were also studied. As shown in Fig. 9(a) and (b), the patterns of the as-deposited Pb on the two substrates are face-centered cubic structure, as well as on the Cu substrate. All the homologous XRD patterns on different substrates illustrate that the cubic structure of Pb is inclined to be shaped and independent of the substrates and the morphologies during electrochemical preparation.

4. Conclusions

In summary, different morphologies of lead (Pb), such as octahedra, zigzag nanowires and nanoclusters on copper (Cu), hollow cubic columns on aluminum (Al) and flowerlike architectures on titanium (Ti) have been prepared via electrochemical deposition in aqueous solution. The cubic structure of Pb is inclined to be shaped on different substrates. The various morphologies of as-deposited lead can be controlled by changing the conditions of electrodeposition which is proved to be a simple and efficient path. It offers an attractive way to seek for novel structures of other elements and to study their new properties.

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