

Temperature and pH influences on the structural and the emission properties of electrodeposited CdSe nanowires

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Abstract Cadmium selenite (CdSe) nanowires have been electrodeposited by potentiostatic method using polycarbonate membranes as template. For the same potential value, the pH modification of the solution or the temperature variation of the substrate leads to drastic differences of the CdSe composition. A meticulous study of the influence of both temperature and pH value on the stoichiometry of electrodeposited CdSe nanowires has been done and several combinations of temperature/pH leading to the 50–50 CdSe composition have been found. The as-electrodeposited CdSe nanowires under these specific conditions reveal a good crystallinity with a $\langle 111 \rangle$ preferred growth orientation exhibiting a luminescence band in the visible range corresponding to the CdSe gap.

Keywords Nanowires · Electrodeposition · CdSe · pH · Temperature · Photoluminescence

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Introduction

For several years, many research groups have focused on semiconductor materials in the nanoscale range to develop new electronic, optical, and biological devices [1–3]. To realize such devices, the cadmium selenite (CdSe), an important II–VI semiconducting compound with a direct band gap of around 1.7 eV, seems to be a very interesting candidate. Effectively, recent studies demonstrate high-efficiency carrier multiplication in CdSe nanostructures which give numerous potential applications ranging from nonlinear optics and lasing to photovoltaic and photochemistry [4, 5]. The possibility of using CdSe nanostructures for laser diodes, nanosensing, and biomedical imaging has already been demonstrated successfully [6–10]. It shows the important role that the CdSe plays in photoelectronics [11, 12] due extensively to its highly tunable luminescence properties related to the quantum confinement for nanometric sizes.

Among the nanostructures, semiconductor nanowires (NWs), as one-dimensional nanostructures, are of both fundamental and technological importance. Due to their large aspect ratio and easily textured growth direction, nanowires can exhibit unique optical and electrical properties. Moreover, the excellent flexibility of nanowires permits their use in the assembly of nanoscale electronic devices.

Conventionally, the widest used technique to elaborate the CdSe nanostructures is the vapor liquid solid process [13, 14]. However, despite of the good quality of the produced materials, this technique needs high vacuum, high temperature, and is expensive. As an alternative method,

electrodeposition is a simple and low price approach which offers the possibility of growing many materials and in particular CdSe [15]. Moreover, using a patterning substrate such as nanoporous-insulating membrane, well-organized networks of nanowires can be electrodeposited with a reliable quality [15–18].

The conventional potentiostatic process is certainly the simplest method to grow CdSe compound and the theoretical study of Kröger [19] confirms the possibility of obtaining stoichiometric CdSe using this process. However, many studies reveal that the deposition of CdSe is in fact a codeposition of Cd and Se, with the presence of selenium excess inside the deposit [20–24]. To overcome this issue, in 1991, Kressin et al. [20] have adopted a cyclic voltammetry deposition technique in order to ensure the good “50–50” stoichiometry. Such technique gives a macroscopic good stoichiometry of CdSe, but locally reveals numerous non-homogeneous regions [21, 22].

Since then, many papers deal with the electrodeposition of CdSe via potentiostatic process, focusing on the impact of several parameters on the stoichiometry and the crystallinity. Most of the research groups demonstrate that either the pH or the temperature drastically affects the intrinsic crystalline properties of CdSe in the case of thin films.

An important issue is that CdSe thin films with non-homogeneous regions have poor emission properties and this problem of non-homogeneity becomes even more important at the nanometer scale. A bad stoichiometry and the possible presence of nanoscale grains with many defects such as dislocations and grain boundary will severely affect the optical properties of CdSe nanowires [25, 26]. For these reasons, most as-electrodeposited CdSe nanowires do not show any luminescence signal without surface treatments (ZnS or CdS capping for instance) or annealing [23]. This is of course a drawback which needs to be overcome if the electrodeposition process is used for growing CdSe nanoscale materials with good physical properties. This paper focuses on a meticulous study of CdSe nanowires electro-

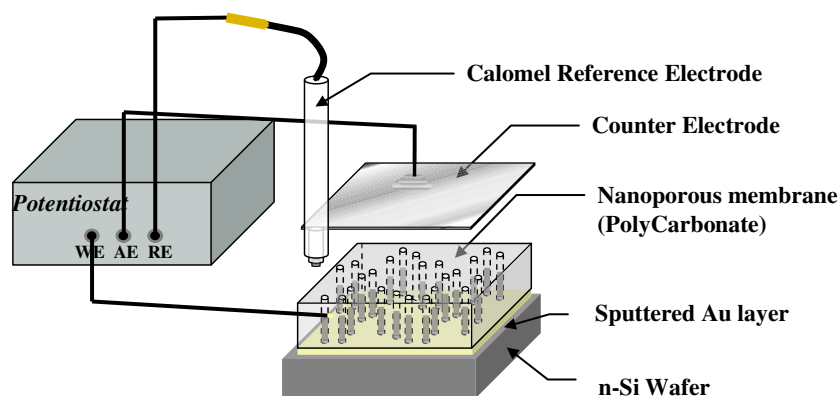
deposition and more precisely on the influences of both pH and temperature to improve CdSe nanowires electrodeposition via potentiostatic process. Moreover, the perspective of realizing devices with CdSe nanowires can require different nanoporous templates. However, an unfortunate combination of temperature and pH of the electrolyte used to deposit the CdSe could damage the template during the electrodeposition of the nanowires.

The following study demonstrates that several temperature/pH values can give stoichiometric CdSe nanowires and that these NWs exhibit in their as-deposited form good optical properties an excitonic emission band corresponding to the bandgap of CdSe confirming the good crystallinity and stoichiometry of the NWs.

Experimental

The nanowire electrodeposition process (previously described in details in ref. [15] concerning our preliminary results on CdSe electrodeposition) is described below. Figure 1 is a sketch of the used electrodeposition setup. Deposition was carried out in a conventional three-electrode (Fig. 1) cell with a platinum counter electrode and a saturated calomel reference electrode (SCE). A polycarbonate nanoporous template (IT4IP S.A., Belgium) with nanopores of 110 nm in diameter was used as working electrode and a thin layer of gold (180 nm) was sputtered on one side of the membrane before deposition. All the deposits were plated using the potentiostatic method (-750 mV vs. SCE) during 60 min. The temperature of the substrate was controlled with a thermoelectric Peltier device (from 25 to 70 °C). The electrolyte contains $(\text{CdSO}_4)_3 \cdot 8\text{H}_2\text{O}$ and H_2SeO_3 , both chemicals were reagent grade (VWR International SAS and Fluka, respectively). The pH value of the solution was adjusted from 1.9 to 2.7 with diluted NaOH and/or H_2SO_4 . The electrolytic bath for CdSe film plating was a solution containing typically 0.1 M $\text{CdSO}_4 + 0.005$ M H_2SeO_3 .

Fig. 1 Experimental sketch of CdSe electrodeposition device



The CdSe nanowires were characterized by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer with CuK α 1 line radiation, $\lambda=1.5406\text{ \AA}$ and by scanning electron microscope (SEM) (JEOL JSM-6460LA) with energy dispersive X-ray analysis (EDX).

Continuous wave photoluminescence (PL) experiments were performed in the range 500–1,600 nm. The samples were excited by a 30-mW He-Cd laser using the 325-nm line. The PL signal was analyzed by a monochromator equipped with a 600 grooves/mm grating and by a photomultiplier tube cooled at 190 K. A cryostat was used to perform the PL experiments at 77 K. To avoid a possible parasitic signal coming from the membrane or the gold (Au) layer, the PL experiments were performed using CdSe nanowires collected onto a monocrystalline (100) silicon substrate. The Au layer was dissolved in KI/I₂ solution and the nanowires were released by dissolving the membrane in distilled CH₂Cl₂. The suspension was then centrifuged and the wires were washed several times with distilled water, acetone, and ethanol to remove impurities. Small drops of the solution were deposited on the substrate and dried in air at room temperature.

Results and discussion

Electrochemical study

Figure 2 displays a voltammogram realized at a sweep rate of 2 mV/s under the following conditions: pH 2.7, $T=25^\circ\text{C}$ inside a polycarbonate membrane with nanopores of 110 nm in diameter. To understand the role played by the pH and the temperature on the electrochemical process of cadmium–selenium nanowires deposition, three different zones had to be identified. One can notice that the purpose of this study is not to precisely identify the reactions taking place during the CdSe nanowires electrodeposition, but to

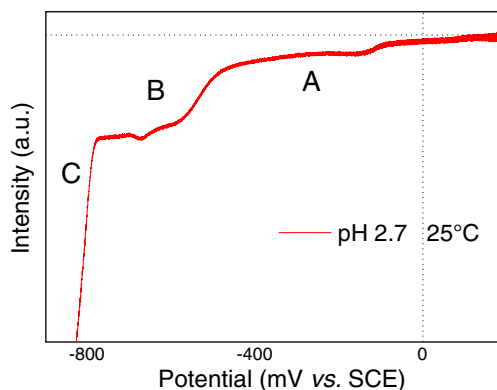
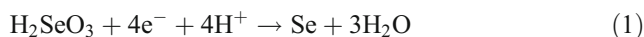


Fig. 2 Voltammograms done at a sweep rate of 2 mV/s. The pH values and the temperature of the electrolyte are the following: pH 2.7 and $T=25^\circ\text{C}$

understand how both pH and temperature influence the electrodeposition.

In the literature [20, 23, 24, 27, 28], various reactions have been proposed to be involved in the electrodeposition of CdSe. Most of them are summarized below:



According to these reactions, the following considerations can be made:

Se deposition occurs via reaction 1 or both reactions 2 and 3.

Skyllas Kazacos et al. [24] and Pawar et al. [29] suggest that CdSe is obtained via reaction 4 after a first step in which H₂SeO₃ gives H₂Se via reaction 2. However, an excess of metallic Se can be present in the deposit because of the sequences 2 and 3. It had to be pointed out that high Se (IV) concentration makes the chemical reaction 3 so quick that the overall process appears to be identical to reaction 1 resulting in the formation of metallic selenium. Consequently, CdSe is obtained with a percentage of Se which depends on the ratio between the concentration of Se (IV) and Cd²⁺ inside the solution.

For Kressin et al. [20], the presence of CdSe is directly occurring via reaction 5 involving a six electron reaction. But according to the polarization, an excess of metallic cadmium could be obtained via reaction 6.

Finally, according to Bouroushian et al. [27], CdSe could be electrodeposited via reaction 7, thanks to the reduction of Cd²⁺ [reaction (6)] which occurs by UPD because of the presence of selenium.

In conclusion, considering the voltammogram displayed in Fig. 2, the zone A can be attributed to the reduction of Se (IV) in Se (0) via reaction path 1 or 2 and 3. Effectively, in this zone, the performed deposits are only composed by Se. The zone B corresponds to the CdSe deposition either by

reactions 4 or 5. Here, the Cd reduction occurs by UPD potential because of the presence of selenium species. Finally, the zone C is attributed to the reduction of Cd via reaction 7 and to the reduction of hydrogen coming from the solvent via reaction.

Under the conditions corresponding to Fig. 2 (pH 2.7, $T=25\text{ }^{\circ}\text{C}$), CdSe deposits performed at -750 mV vs. SCE give perfect 50–50 stoichiometry. Nevertheless, for the same polarization, the change of pH and/or temperature leads to drastic modification of the composition. A plot of the evolution of the Cd proportion inside the CdSe nanowires (measured by EDX analysis) vs. the pH value of different temperatures has been drawn on Fig. 3. It clearly appears that temperature and pH have a strong influence on the CdSe deposition. Following the trends of each line, 50–50 stoichiometric CdSe is reachable at all temperatures except at $70\text{ }^{\circ}\text{C}$. For temperatures between 25 and $60\text{ }^{\circ}\text{C}$, the CdSe compound is reachable for different pH values which depend on the temperature. To get equi-atomic CdSe, the pH value of the electrolyte has to be decreased when the electrodeposition temperature increases. For instance, at $60\text{ }^{\circ}\text{C}$, the range to obtain CdSe is between pH 1.9 and 2.1, whereas at $25\text{ }^{\circ}\text{C}$, the pH has to be adjusted beyond 2.7 (this is in good agreement with the work of Pawar et al. [29]). Finally, Fig. 3 shows that at a given temperature, the Cd atomic concentration in the deposit vs. pH increases until 50 at.% and then decreases.

Achieving a 50–50 CdSe stoichiometry requires to apply potentials into the range defined by the limiting diffusion current of the B zone. However, this zone is characterized by a small potential domain which is shifted upon temperature and/or pH change as explained below.

Effect of temperature With an enhancement of the temperature, the kinetics becomes faster, giving a steeper slope in the voltammogram. As a consequence, the diffusion regime should begin at a smaller overpotential. Nevertheless, the augmentation of the limiting current shifts the potential where

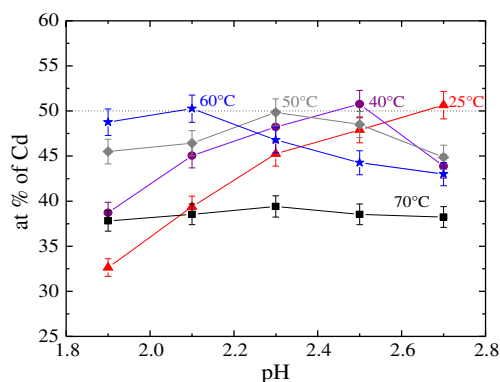


Fig. 3 Atomic percent of Cd in the deposited CdSe nanowires (-750 mV vs. SCE) vs. pH

the limiting current appears towards higher overpotential. This effect is intensified by an increase of the ohmic drop in the solution due to the higher currents at higher temperature. These considerations are responsible of a shift of the limiting current and then, at high temperature the applied potential (-750 mV/SCE) could not fit with the limiting diffusion current of the B zone and the 50–50 stoichiometry disappears.

Effect of pH Considering for instance the Eq. 1, Se (IV) is represented by both H_2SeO_3 and HSeO_3^- due to its $\text{p}K_a$ value of 2.5. Using this $\text{p}K_a$ value and the concentration of H_2SeO_3 introduced in the solution, real concentrations between the species H_2SeO_3 and HSeO_3^- can be calculated. With pH 1.9, the calculation gives $4 \times 10^{-3}\text{ mol L}^{-1}$ for H_2SeO_3 and $10^{-3}\text{ mol L}^{-1}$ for HSeO_3^- . With pH 2.7, the concentrations become $2 \times 10^{-3}\text{ mol L}^{-1}$ for H_2SeO_3 and $3 \times 10^{-3}\text{ mol L}^{-1}$ for HSeO_3^- . The Nernst potentials obtained for Eq. 1 are then 0.59 V for pH 1.9 and 0.54 V for pH 2.7, respectively. That corresponds to a 50-mV shift of the reaction potential between the two extreme pH values. The same shift is obtained for reaction 2. Consequently, the diffusion plateau of the zone B can be significantly shifted affecting the stoichiometry of CdSe during the electrodeposition process.

At last, if the pH is too acidic, according to Pawar et al. [29], reaction 4 is not sufficiently reactive and a competition between 3 and 4 appears, leading to an increase of the Se inside the deposit.

As a first conclusion, this electrochemical study shows how both pH and temperature can influence the electrodeposition of CdSe nanowires. At a given applied potential, it is possible to obtain a pure CdSe compound only if a good compromise between pH and temperature is found, otherwise an excess of Se is present in the deposit. However, if the pH or temperature is really too high, it may become impossible to find such a combination (cf. Fig. 3 for $70\text{ }^{\circ}\text{C}$).

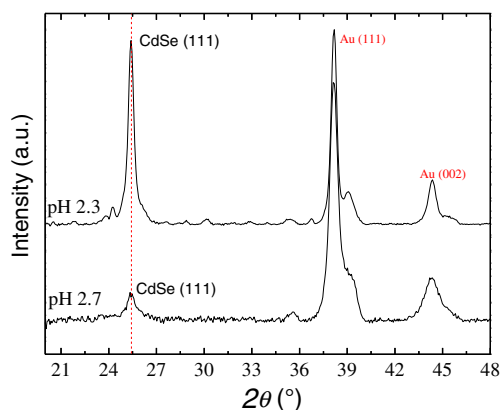
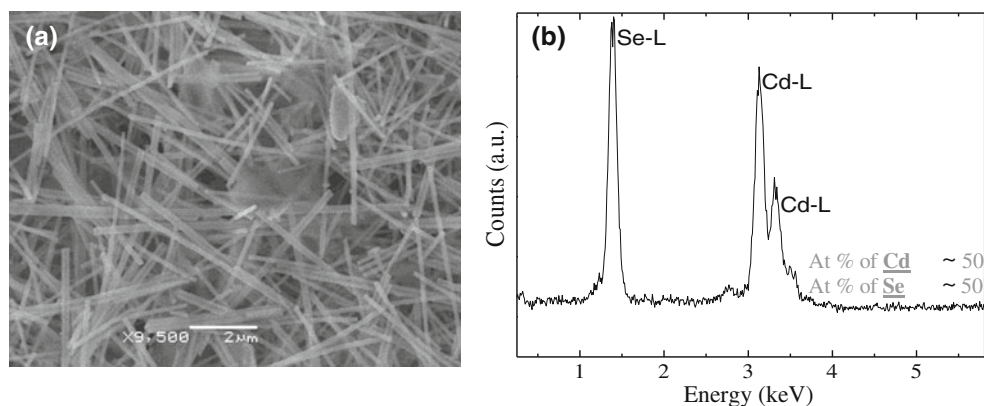


Fig. 4 Diffractograms of CdSe nanowires electrodeposited at pH 2.3 and 2.7. Deposition conditions: $T=50\text{ }^{\circ}\text{C}$, applied potential of -750 mV/SCE

Fig. 5 SEM image (a) and EDAX analysis (b) of CdSe nanowires electrodeposited obtained at pH 1.9, potential = -750 mV vs. SCE and $T = 60\text{ }^{\circ}\text{C}$



Finally at a given temperature (Fig. 3), the Cd atomic concentration in the deposit increases until 50 at.% and then decreases as the pH increases. This behavior could be explained first by the shift of the diffusion plateau of zone B, and in a second time, the competition between reactions 3 and 4.

Morphological and structural analysis of CdSe nanowires

Figure 4 shows two typical XRD patterns of bunches of CdSe nanowires electrodeposited at a temperature of $50\text{ }^{\circ}\text{C}$. For all other samples, depending on the stoichiometry, the XRD spectra are similar to those presented for the samples prepared at $50\text{ }^{\circ}\text{C}$. Samples have been fabricated at a potential of -750 mV vs. SCE during 60 min using a solution with a pH value of 2.3 for the first sample and to 2.7 for the second. Only the (111) diffraction peak of the cubic CdSe is visible and that is the only peak corresponding to the CdSe compound that exists in almost all deposits. The other peaks come from the Au substrate. The presence of the (111) peak demonstrates the possibility of synthesizing cubic CdSe for pH values between 1.9 and 2.7 for different temperatures. It clearly shows a $\langle 111 \rangle$ preferential growth orientation for CdSe nanowires. For all the samples, the quantity of elaborated nanowires, in term of material volume, is the same (within $\pm 5\text{ at.}\%$ error). However, if the electrochemical conditions are not optimized, only a certain percentage of the deposit is made of CdSe compound; the rest consists of Se or Cd deposition. As a consequence, the big difference between the area of the (111) peak of the two samples (cf. Fig. 4) does not only come from the difference of the amount of CdSe between the two samples. As shown in Fig. 3, the sample made at pH 2.7 and $50\text{ }^{\circ}\text{C}$ is composed of a mixture of CdSe and Se, whereas for pH 2.3 and $50\text{ }^{\circ}\text{C}$, it is composed of pure CdSe. As a consequence, a high amount of cubic CdSe compound is expected for nanowires elaborated at pH 2.3 and $50\text{ }^{\circ}\text{C}$. The results displayed in Fig. 4 are in total agreement with the results displayed in Fig. 3 which show

that at $50\text{ }^{\circ}\text{C}$, the 50–50 stoichiometric composition is reached for pH values between 2.1 and 2.3.

It can also be noticed that compared to the other preparation methods in which the CdSe nanoobjects are most of the time hexagonal (wurtzite) in structure, which is the stable phase of CdSe, as-electrodeposited NWs are cubic (zinc blende) and stable with time. The preparation of stable cubic CdSe is of interest because it could be easily alloyed with other cubic structure, such as ZnSe for example to form ZnCdSe compound with applications in optoelectronic [30].

The typical morphology of stoichiometric CdSe nanowires (pH 1.9, potential = -750 mV vs. SCE and $T = 60\text{ }^{\circ}\text{C}$) is shown in Fig. 5. The SEM observation shows an average diameter of $110 \pm 15\text{ nm}$ for CdSe nanowires with a length between 2 and $5\text{ }\mu\text{m}$. One can see that the NW diameters are very uniform and well correspond to the pore diameters. After entire dissolution of the membrane, the prepared NWs exhibit a cylindrical shape with very regular and smooth edges. The analysis of images coming from different samples shows that all the observed NW diameters are very homogeneous. Despite all the cleaning process, only a few NWs are smaller due to a possible breaking and most

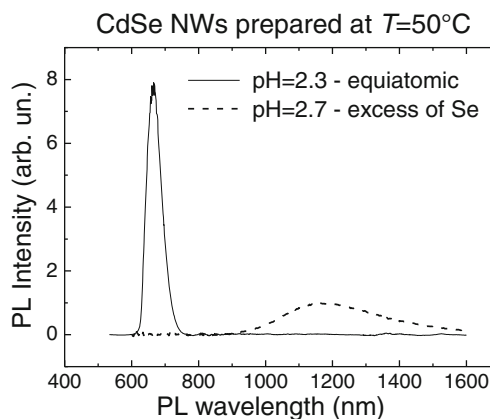


Fig. 6 Emission spectra at 77 K of CdSe nanowires electrodeposited at pH 2.3 and 2.7. Deposition conditions, $T = 50\text{ }^{\circ}\text{C}$, applied potential of -750 mV/SCE

of them keep their integrity which clearly shows the robust character of our NWs. For the NW size control, our preparation method is very interesting because it only depends on the membrane characteristics (pore diameters and membrane thickness).

To confirm the good quality of our stoichiometric NWs and to compare their optical properties with the non-stoichiometric NWs, PL experiments were performed at low temperature (77 K) as it is known that in its as-deposited form, CdSe has a huge amount of dangling bonds which hinder an efficient emission at room temperature. In Fig. 6, the two emission spectra corresponding to the CdSe NWs electrodeposited at 50 °C and at pH 2.3 and 2.7, i.e., a sample with a 50/50 Cd/Se ratio and one with an excess of Selenium are shown. The stoichiometric sample exhibits a sharp peak around 680 nm while the non-stoichiometric NWs have a broad emission band located around 1,180 nm. The peak around 680 nm is obtained for all the stoichiometric samples with only a variation of its intensity while the broad emission band at high wavelength is characteristic of the samples with an excess of Se. For the stoichiometric NWs, the peak position and the narrow shape are coherent with the experimental and calculated bandgap of cubic CdSe films slightly superior to the bandgap of hexagonal CdSe [31–33] and the PL band could be assigned to excitonic emission. Let us remark that due to the large NW diameters (around 100 nm), no confinement effect can occur. No other peak at higher wavelength is detected, which is an indication that no radiative defects exist in those NWs. For the non-stoichiometric NWs with an excess of Se, this peak assigned to the band-to-band recombination of carriers has disappeared, surely because of the presence of numerous radiative defects located within the gap of the CdSe. The broad band located around 1,180 nm has already been observed in CdSe films or nanostructures and has been attributed to deep-level emission centers and defects [34, 35]. Even if the exact nature of defect responsible of this band has not been clearly identified, a cadmium vacancy (V_{Cd} or V_{Cd}^-) or a divacancy-associated defect is often cited, which is coherent with our structural results showing an excess of Se in our NWs.

Conclusions

CdSe nanowires have been electrodeposited using an aqueous solution containing $CdSO_4$ and H_2SeO_3 at an applied potential of -750 mV vs. SCE. Our study demonstrates that both pH values and deposition temperature need to be controlled to obtain 50–50 stoichiometric CdSe nanowires. Several combinations of pH and temperature lead to the perfect stoichiometry of CdSe nanowires.

XRD analysis shows that pure CdSe nanowires are obtained with a good crystallinity and a $\langle 111 \rangle$ preferred growth orientation. Photoluminescence measurements of as-deposited stoichiometric CdSe nanowires show a visible emission band corresponding to the cubic CdSe bandgap. Finally, this study demonstrates the possible fabrication of as-deposited good quality and single-phase CdSe NWs using potentiostatic deposition method.

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