Machinable Long PVP-Stabilized Silver Nanowires

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Abstract: PVP-capped silver nanowires with a diameter range from 150 to 200 nm and a length range from 50 to 100 μm have been synthesized in large quantity by using a soft-template liquid-phase method. The so-obtained longer and thicker metallic nanowires exhibit fivefold-twinned structures bound by five {100} wall-planes and two spearlike ends around five {111} facets. X-ray photoelectron spectroscopy (XPS) investigations show that a strong interaction exists between the carboxyl oxygen atom (C=O) of PVP and the Ag core interface. The PVP-capped Ag nanowires can either self-assemble into ordered raft structures or form a complicated network, depending on the dispersive solvent employed. In addition, the Ag nanowires can also be specifically bent into various angles, demonstrating their excellent mechanical stability.

Keywords: mechanical stability · nanostructures · silver · template synthesis

Introduction

Rapidly shrinking micro-integration of electronic units requires the ability to manufacture and manipulate of nanometer-scaled materials.[1,2] Wiring techniques might be one of the most difficult steps down to nanometer regime. The process first requires the excellent conductivity of used material, and then machinability in the nanometer range. Although some alternatives in existing microelectronic systems are still being considered, few would hesitate to agree that there are tough obstacles completely along this route.[3,4] In contrast, some new strategies, that is, nano- or atomic-scaled manipulation techniques, based on scanning probe microscopy,[5] and self-assembly methods, based on nanometer-scaled basic building blocks,[6] are becoming the main focus of research for solving the conundrum. In particular, self-assembly approaches are attracting increasing attention due to recent successful arrangement of semiconductor nanowires and carbon nanotubes.[7–9] However, as far as nanowiring is concerned, the assembly of metallic nanowires is still at the edge of success, partly because of the difficulty of synthesizing them with high aspect ratios in large numbers and shaping them. Although carbon nanotubes with diameters of several nanometers exhibit good electrical conductive properties, their machinability is still a problem. Thus, it becomes more and more urgent to find a method to make metallic nanowires with high aspect ratios and further to explore their machinable properties.

Bulk silver exhibits the highest electrical and thermal conductivity in all metals. From the view of this point, Ag nanowires may be one of the most suitable nanowiring materials. Up to now, many techniques, for example, electrochemical deposition[10] and chemical reduction in an inorganic or polymeric matrix,[11–13] have been successfully developed for the synthesis of Ag nanowires. Various one-dimensional templates, for example, microchannels in alumina or polymer membranes, mesoporous materials, carbon nanotubes, and so forth, play important roles in these approaches. The physical templates can limit the growth of Ag only in the micropores, thus providing a good morphology and length control. However, an intrinsic number of the microchannels confines the quantity of obtained product. Recently, a soft-template method was suggested for the preparation of PVP-capped Ag nanowires, in which the Ag nanowires were produced by reducing silver nitrate (AgNO$_3$) in ethylene glycol (EG) with the addition of poly(vinyl pyrrolidone) (PVP).[14] The so-synthesized Ag nanowires are usually capped by

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PVP molecules. They have two spearlike ends and exhibit fivefold-twinned crystal structures with pentagonal-shaped cross sections.[15,16] The solution-phase approach was extensively applied to the synthesis of Ag nanoparticles, with EG serving as both reducing agent and solvent. An advantage of the technique is that Ag nanowires with a high aspect ratio can be obtained on a large scale.

In this work, we describe the synthesis of PVP-capped metallic Ag nanowires, with the length range from 50 to 100 μm and the diameter range from 150 to 200 nm, in large quantity. Characterization techniques such as X-ray diffraction (XRD) and scanning electron microscopy (SEM) were employed to elucidate the structure of the Ag nanowires. The surface chemical state of the Ag nanowires was also investigated by X-ray photoelectron spectroscopy (XPS). Two-dimensional self-assembly and complex crossed arrangements of Ag nanowires have been realized by selecting different Ag nanowire suspensions. Furthermore, the mechanical properties of the Ag nanowires have been explored.

Results and Discussion

The PVP molecules can serve as protective molecules, based on their structure character. As shown in Scheme 1, the
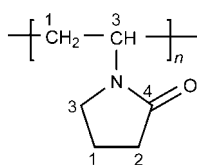
Scheme 1. Formula of PVP repeated unit, with carbon atom numbering.

polymer has a polyvinyl skeleton with polar groups. The lone pair of electrons from the nitrogen and oxygen atoms in the polar groups of the PVP repeated unit may be donated into sp hybrid orbitals of Ag$^+$ ions to construct complex

Abstract in Chinese:
摘 要：

一种液相软模板方法已经被用于大量地合成由聚乙烯吡咯烷酮稳定的金属银纳米线。这种银纳米线的粗细范围在150-200纳米，长度范围在50-100微米。 它的结构为五重孪晶结构。侧向为五个{100}面所包裹，两端为矛状结构，每个顶部由五个{111}面构成。X-射线光电子能谱研究表明：聚乙烯吡咯烷酮分子链中的羰基氧与金属银核之间有着较为强烈的相互作用，显示了聚乙烯吡咯烷酮分子对裸的金属银核的稳定作用。使用该种方法合成的聚乙烯吡咯烷酮分子包裹的银纳米线能自组装成有序的排筏结构，也能被排列成各种复杂的交叉结构，取决于所使用的溶剂。此外，这种银纳米线还能被人为地弯曲成各种形状，显示了精彩的机械稳定性。
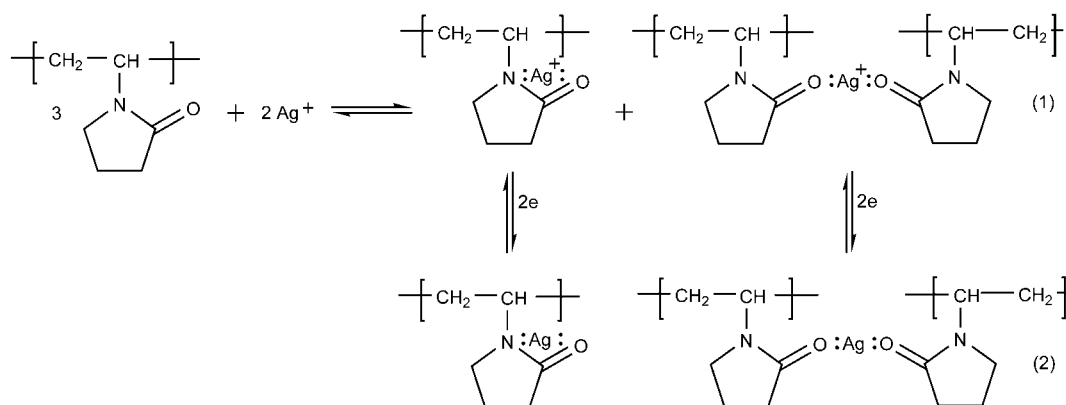
compounds; an sp hybrid usually forms a linear coordinative bond. Thus, the two possible bonding styles, that is, PVP molecule intra- and interchain interactions, may occur when Ag$^+$ ions interact with PVP molecules [see Eq. (1) in Scheme 2, showing how a repeated unit of PVP molecules bonds with an Ag$^+$ ion]. The two kind of coordinative types can effectively decrease chemical potential and further enable the PVP-bound Ag$^+$ ions to be reduced more easily [see Eq. (2) in Scheme 2] by EG. During the preparation process of the Ag nanowires, it was found that the color of the EG solution changed gradually from pale yellow, to dark red, to gray-white with the decreasing concentration of the reactant in EG; this implies the PVP-assisted evolution process from the formation of Ag nuclei to their growth. Noting that PVP-capped Ag particles always exist in final product under whatever conditions, probably because different coordination modes between the Ag$^+$ ions and the PVP molecules induces different nucleation. The Ag particles usually exhibit cubic, trianglular, or hexagonal morphology and can be separated from the Ag nanowires by a step precipitation technique. Figure 1a illustrates a typical SEM image of as-separated Ag nanowires with the diameter range from 150 to 200 nm in high quantity. The longest Ag nanowires can reach about 100 μm, as shown in Figure 1b. The longer Ag nanowires normally exhibit a slightly curved character, while the shorter are very straight with two sharp spearlike ends (see Figure 1c). The crystallite phase and purity of as-synthesized Ag nanowires can be measured by using X-ray diffraction (XRD) methods. Figure 1d shows the XRD pattern of the Ag nanowires deposited on a glass substrate. All diffraction peaks can be indexed as the face-centered cubic phase of Ag. No peaks attributed to Ag oxide were found. In our previous work,[16] we found that Ag nanowires with narrower diameters have a fivefold-twinned structure bounded by five {100} wall planes with a ⟨110⟩ growth direction. We believe that the formation process of the Ag nanowires was initiated from fivefold-twinned Ag nanoparticle nuclei, and then preferential adsorption of PVP molecules to {100} facets of the Ag nuclei might lead to their anisotropic growth from both ends, resulting in occurrence of the Ag nanowires. Both ends of the Ag nanowires exhibit a sharp spear shape around five {111} facets. In the present investigation, the Ag nanowires with larger diameters were synthesized under different reaction conditions. Figure 2 shows a typical SEM image of the sections of as-obtained Ag nanowires, from which the pentagonal shape can be clearly seen. It appears that the Ag nanowires retain the same fivefold-twinned structure. The lateral increase of the Ag nanowires implies that the growth of the Ag nanowires is not solely limited to the ⟨100⟩ direction.

To gain more information on oxidation state of the obtained Ag nanowires, X-ray photoelectron spectroscopy (XPS) techniques were employed to detect the composition of the Ag nanowires. The top left panel in Figure 3 shows a typical XPS spectrum of the Ag nanowires. The occurrence of oxygen, nitrogen, and carbon signals confirm the presence of PVP and possibly of EG molecules on the surface of the Ag nanowires. Various Ag binding energy peaks were also found. The other panels in Figure 3 show high-resolution

Scheme 2. Possible coordination and reaction process for PVP and Ag⁺ ions.
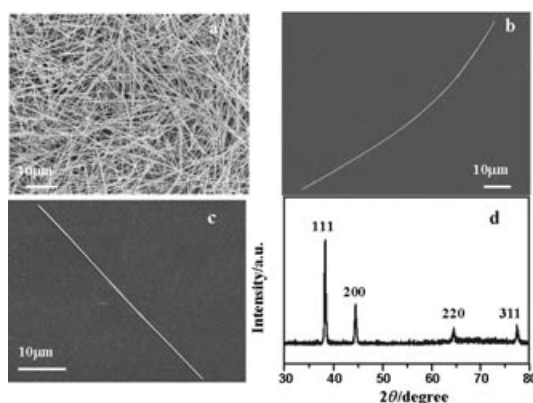

Figure 1. a) A typical SEM image of the PVP-capped Ag nanowires in large quantity. b) A slightly curved PVP-capped Ag nanowire with the length of approximately 100 μm and diameter of about 150 nm on Cu slice substrate. c) A representative straight PVP-capped Ag nanowire with the length of approximately 50 μm and diameter of about 150 nm on an Si substrate. d) X-ray diffraction (XRD) pattern of the PVP-capped Ag nanowires, showing the diffraction peaks indexed as face-centered cubic phase of Ag. No peaks attributed to Ag oxide were found.
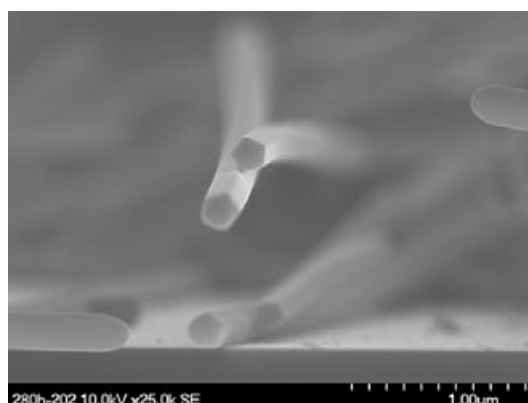

Figure 2. A representative SEM image of the sections of thus-obtained Ag nanowires, from which the pentagonal shape can be clearly observed.

tively. Relative to pure PVP, the O 1s peak from the carboxyl (C=O) oxygen atom shifts to higher binding energy, implying the decrease of electron density, probably due to both interaction between PVP and the Ag nanowire core and hydrogen-bond formation between PVP and an EG molecule. The N 1s peak (399.6 eV) seems not to be influenced by the Ag nanowire core. The Ag regions of the XPS
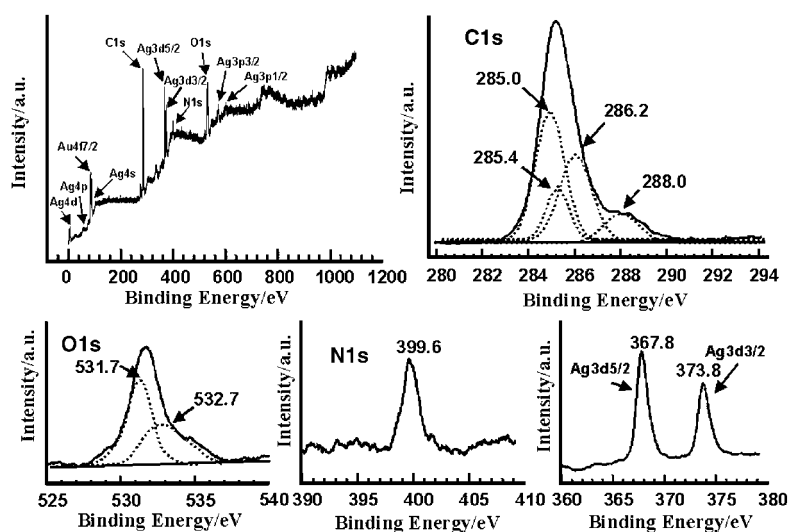
XPS regions of various elements for the Ag nanowires. For clarity, XPS spectra of C 1s and O 1s have been fitted by multiple Gaussians. Through curve fitting it can be seen that the C 1s spectrum is composed of four peaks. The binding energies of the peaks are determined to be at 285.0, 285.4, 286.2 and 288.0 eV; these can be attributed to carbon atoms C1 to C4 for PVP molecule (see Scheme 1), respectively, depending on different chemical environments. The peak at 286.2 eV can also be assigned to C 1s in the EG molecule. Curve fitting in the O 1s region led to two peaks at 531.7 eV and 532.5 eV, originating from carboxyl (C=O) and hydroxyl (C−OH) oxygen atoms, respec-

Figure 3. XPS spectra of the PVP-capped Ag nanowires (top left) and C 1s, O 1s, N 1s, and Ag 3d regions.

spectra of the Ag nanowires are very sensitive to the chemical environment around the Ag nanowire core, particularly to the electron-donating ability of the polymeric ligand and to the strength of the interaction between Ag and the polymeric ligand. The bottom right panel in Figure 3 shows two peaks at 367.8 and 373.8 eV, resulting from Ag 3d5/2 and Ag 3d3/2, respectively. The peaks positions are between those for metal Ag (368.2 eV for Ag 3d5/2, 374.2 eV for Ag 3d3/2) and for Ag_2O (367.5 eV for Ag 3d5/2, 373.5 eV for Ag 3d3/2), indicating a strong interaction between the carboxyl (C=O) oxygen atom of PVP and the Ag core.

Understanding the structure and surface chemical state of the Ag nanowires would be helpful for the investigation of their other properties, for example, self-assembly, and electric and machinable properties. The following question we want to address is the influence of the used suspension to manipulate the Ag nanowires. We have found that the PVP-capped Ag nanowires can self-assemble into an ordered raft structure (see Figure 4a) when solutions of them in EG are
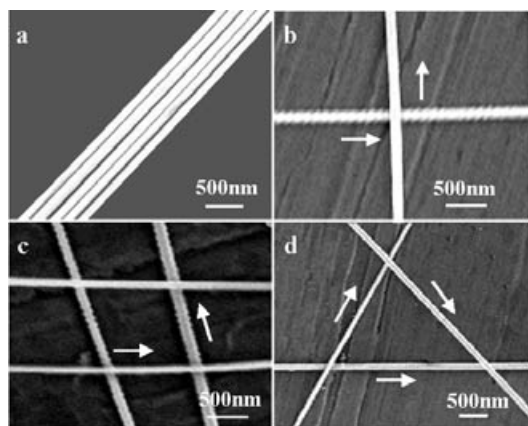

Figure 4. SEM images of a raft array and various networks constructed by the PVP-capped Ag nanowires on a Cu grid substrate attached to conductive double-sided tape. a) The raft array formed by employing ethylene glycol as a solvent. b), c), and d): Three kinds of networks constructed by using ethanol as a solvent and by controlling the flow direction of evaporating solvent, arrows indicate the directions of the solvent flow.

dropped onto various substrates (Si,[14] Cu grids, etc.). The exact reasons for this still need clarification; however, two factors need to be considered at least. One is the PVP layer that covers the Ag nanowire cores; this provides possible interaction among the neighboring Ag nanowires. Another is the nonvolatility and higher viscosity of EG. The raft can not be obtained when using ethanol as dispersion solvent; highly dispersed Ag nanowires are observed instead, due to high volatility and rapid diffusion of ethanol molecules. These phenomena indicate the EG molecules play a very important role in attracting the Ag nanowires together through hydrogen bonding, while ethanol molecules tend to separate them from aggregation. Based on this fact, we can expect to use the Ag-nanowire/ethanol suspension to explore the mechanical stability of the Ag nanowires. In addition, complex nets can even be constructed by careful selection of the suspension conditions. As shown in Figure 4b–d, various crossed complex net structures of Ag nanowires can

be built, by employing the technique of controlling the flow directions of evaporating ethanol solvent in the suspension. The result clearly demonstrates that the PVP-capped Ag nanowires can be separately dispersed in ethanol.

In order to further evaluate the mechanical stability of the Ag nanowires, a drop of a dilute solution of Ag nanowires in ethanol was placed on Cu grid substrate attached to conductive double-sided adhesive tape. Under an optical microscope, we could see that the Ag nanowires rapidly diffused along the direction of the solvent flow. By inclining the substrate to force the evaporating solvent to flow downwards, the Ag nanowires were found to be bent into different shapes after the solvent evaporated completely. Some of them were attached to the tape, others were positioned on the edge of the Cu grid. Figure 5a–c show the typical scan-
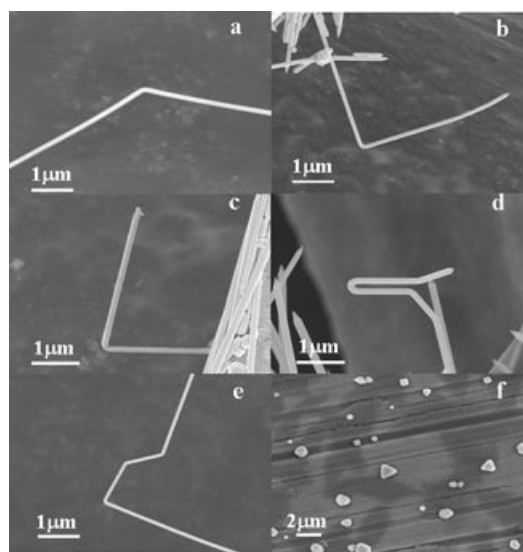

Figure 5. SEM images of various bent PVP-capped Ag nanowires and Ag particles on a Cu substrate. Nanowires with a) an obtuse angle, b) a right angle, c) an acute angle, d) and e) complicated shapes, and f) some Ag particles with special morphologies.

ning electron microscope (SEM) images of the bent Ag nanowires with three kinds of angles from acute to obtuse. Figure 5d and e give much more complicated shapes of the bent Ag nanowires. One can see that the nanowires can even be bent back on itself, as shown in Figure 5d. It is worth noting that we did not find bent Ag nanowires in normal synthesis product. The heavily bent Ag nanowires were formed very probably by extruding laterally hindered Ag nanowires against obstacles in the transfer process with the flowing solvent. Further insight into the bent angles of the Ag nanowires demonstrates that they are very close to 60°, 90°, and 120°. The real reason why the Ag nanowires can be bent into the special angles still remains unclear. However, in our experiments, some Ag particles with special morphologies, that is, cube, triangle, or hexagonal prisms, were also observed in addition to the long Ag nanowires (see Figure 5f). These Ag particles might serve as the obstacles. A possible example is shown in Figure 6. In addition, a rough Cu substrate may also play the role of the obstacles.
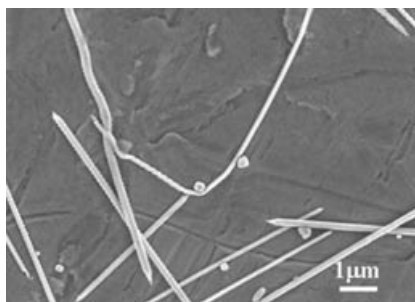
Figure 6. An SEM image of the status of the PVP-capped Ag nanowires flowing down along inclined Cu grid attached to conductive double-sided tape, in which single Ag nanowire is bent into nearly a right angle around a cubic Ag particle.

Anyway, the above results evidently demonstrate that the long Ag nanowires exhibit good mechanical stability at room temperature and can be shaped into various possible structures, which might act as interconnects towards to fabricating future nanoelectronic devices. Sun et. al[17] reported a method to prepare Ag nanobelts with the diameter of 10 nm. They found that the Ag nanobelts broke easily into fragments due to thermal fluctuation, demonstrating weak mechanical stability of the Ag nanobelts. In our case, the PVP-capped Ag nanowires present excellent mechanical stability. It is unclear what causes the flexibility of the Ag nanowires, but three elements need to be considered. The first is the diameter of the Ag nanowires, because nanowires tend to break when their lateral dimensions are decreased down to certain critical value; the second might be the PVP capping, which provides a protect sheath; and the third is the structure of the Ag nanowires. In order to shed light on the flexibility of the Ag nanowires in detail, further investigation is in progress.

Conclusion

In summary, PVP-capped Ag nanowires with high aspect ratios have been synthesized by soft-template solution-phase methods under optimal experiment conditions. The as-produced Ag nanowires have a diameter range from 150 to 200 nm and a length range from 50 to 100 μm. They usually exhibit a fivefold-twinned structure bounded by five $\{100\}$ wall planes and two spearlike ends around five $\{111\}$ facets. XPS investigations show that carboxyl (C=O) oxygen atom in PVP strongly coordinates to Ag core surface. More excitingly, the nanowires not only can self-assemble themselves into ordered raft structures, but also can be intentionally constructed into various complex networks, depending on the solvent used. In addition, they can also be intentionally bent into various angles and shapes, demonstrating excellent mechanical stability at room temperature. All these characteristics indicate the preferential potential value of the Ag nanowires in future nanoelectronic devices.

Experimental Section

The longer Ag nanowires with high aspect ratios were synthesized by means of a soft-template liquid-phase method. In the synthesis process, EG (10 mL) was firstly refluxed in a three-necked round-bottom flask at 160 °C for 2 h, and then solution of 0.1 M AgNO$_3$ (99.8 %, Chameleon Reagent) in EG (5 mL) and solution of 0.2 M poly(vinyl pyrrolidone) (PVP, M_w = 55000, Aldrich) in EG (5 mL) were simultaneously injected into the refluxing solvent, by using two syringes, drop by drop, at a rate of 0.2 mL min^{-1}. Once solutions of AgNO$_3$ and PVP in EG were added, the whole refluxing solution immediately turned pale yellow. With further injection of the reactants, the solution gradually became gray-white, implying the appearance of Ag nanowires. By controlling the dropping rate under optimal reaction conditions, the diameter and length of the PVP-capped Ag nanowires can be adjusted. The reaction continued at 160 °C for 60 min. When the reaction was finished, the supernatant was poured away and the gray precipitate remained. The as-obtained gray-white residual material was then diluted with acetone (100 mL) and placed in a refrigerator at 0 °C for effective precipitation of the Ag nanowires. Part of the precipitate was collected during a certain time period. The method can effectively separate the Ag nanowires from Ag particles. The obtained Ag nanowire aggregate was used for the other characterization experiments. The samples for scanning electron microscope (SEM) measurement were prepared on p-Si(100) or copper substrates. The SEM images were obtained by using a field emmison SEM (JEOL, JSM-6300F) operated at an accaleration voltage of 15 kV. The X-ray diffraction (XRD) pattern was recorded on a Rigaku X-ray diffractometer with Cu$_{K\alpha}$ radiation (λ = 0.15405 nm). Scanning range was from 30° to 80° at a scanning rate of 0.02° s^{-1}. XPS analysis was performed on AXIS Shimadzu-Kartos spectrometer. The Mg$_{K\alpha}$ (1253.6 eV) X-ray source was operated at 12 kV and 10 mA current emission and at an electron take-off angle of 90° relative to the surface substrate. All the binding energies were calculated by reference to Au 4f$_{7/2}$ peak at 84.0 eV.

Acknowledgement

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