Copper nanowires (Cu NWs), a new type of functional material, have high commercial value in the fields of electronics and catalysis owing to their excellent conductivity, good mechanical properties, high activity, and low cost. In recent years, various applications of Cu NWs have yielded many significant results, which are rapidly developing toward industrialization. This paper reviews the recent progress in the syntheses and applications of Cu NWs. Several wet chemical synthetic methods and the recent commercially promising applications of Cu NWs in flexible transparent electrodes, three-dimensional networks for lithium-ion batteries, and catalysts are described in detail. Additionally, the limitations of Cu NWs and available strategies for technical difficulties are introduced, which can be useful for researchers in related scientific fields. For each application, representative literature reports are overviewed and a brief objective evaluation is presented. Finally, the prospects of Cu NWs for future applications in various technologies are proposed.

Keywords: Copper nanowire, Flexible transparent electrode, Three-dimensional network, Catalysis, Synthesis

I. Introduction

Cu is one of earliest metals used by humans, and has significantly promoted the development of civilization. Since the second industrial revolution, extensive efforts have been directed toward the research and development of Cu because of its superior electrical, thermal, and mechanical properties [1-3]. In the current electronic technologies, Cu is still one of the most widely used metals for conductive materials. Although Pt, Au, Ag, and other precious metals also have similar properties, the high cost and insufficient resources are bottlenecks to their widespread application [4]. From the viewpoint of industrial production, Cu, as the third-largest annual produced metal in the world, fully compensates for the shortcomings of noble metals including variation in cost and resources [5]. Typically, the cost of Cu is approximately 1 % that of Ag, and Cu reserves in the earth’s crust are more than 700 times that of Ag. Therefore, compared with noble metals, Cu has been more widely used in various industrial fields including electronics and machinery [6,7].

Recently, with the increasing demand for various functional electrodes in futuristic technologies, metal nanowires (NWs) have attracted considerable attention [8,9]. NWs are defined as one-dimensional (1D) structures with a lateral size of less than 100 nm and an aspect ratio of above 1000. Metal NWs combine the 1D structures and metallic characteristics, exhibiting excellent physical and chemical properties that can be exploited for various potential applications in nanoelectronics and catalysis.

Among the metallic NWs, Cu NWs have been extensively explored in various fields such as advanced electronics and smart robotics as new functional materials, owing to their high electrical conductivity and excellent mechanical properties [4,10]. In the new electronic era in particular, the demand for new functional electrodes is gradually increasing. However, the inhomogeneity in morphology and size of Cu NWs, due to the rapid growth induced by the high activity of seeds during the synthetic process, still remains an issue [11]. Moreover, the high surface energy produced by the activated atoms of Cu NWs leads to oxidation and aggregation [12]. These phenomena result in the loss of useful characteristics of Cu NWs and limit the practical applications.

Till date, extensive research efforts have been directed toward the synthesis and applications of Cu NWs. This paper comprehensively overviews various wet chemical synthetic methods and recent commercial applications of Cu NWs in flexible transparent electrodes, three-dimensional (3D) networks for lithium-ion batteries (LIBs), and catalysts. The coating and welding processes for practical applications are illustrated and described in detail. Additionally, the limitations of Cu NWs and commonly available strategies for technical difficulties are introduced. Representative literature for each application has been discussed to provide an objective evaluation of the field.

II. Wet chemical syntheses of Cu NWs

Various synthetic methods for Cu NWs such as vapor-phase, template, electro-deposition, and wet chemical syntheses have been reported in the literature. Considering the advantages and limitations of each method, the most popular method for the preparation of Cu NWs in recent years has been wet chemical synthesis, owing to the mild synthetic conditions, facile size control, and low-cost production with high purity [2,13]. However, because of the use of surfactants and...
Cu NWs in the past two decades can be mainly divided into three substances significantly affect the morphology of Cu NWs. Based on the reducing agents and mechanisms, the wet chemical syntheses of Cu NWs in the past two decades can be mainly divided into three methods: polyol-, hydrazine-, and amine-based methods.

The polyol method is one of the most traditional synthetic methods for the preparation of nanomaterials [14,15]. This method uses polyols such as glycerol, glucose, ascorbic acid, or ethylene glycol as reduction agents because polyols typically exhibit strong reducing capabilities at specific temperatures. Jin et al. successfully synthesized Cu NWs by the polyol method in an aqueous solution with glucose as a reducing agent, CuCl2 as a precursor, and hexadecylamine and polyvinylpyrrolidone as surfactants [16]. The prepared Cu NWs had uniform diameters of 24 nm with lengths in the range of several tens to hundreds of micrometers. Based on the structural changes in Cu NWs during the synthetic process, the role of each reagent was explained in detail. Although solutions for various challenges encountered with the use of Cu NWs were not included, this study had important implications for the synthesis of Cu NWs and promoted the subsequent development of this field. In another important study, Yin et al. reported oxidation-resistant Cu NWs prepared using CuCl as a precursor and oleylamine and KBr as surfactants [17]. In contrast to prior research, this study used ethylene glycol as the reducing agent and solvent to synthesize Cu NWs to address challenges such as the oxidation and aggregation of Cu NWs. Under a reduction system with polyol molecules, the oxidation of Cu NWs during synthesis was minimized. Additionally, oxidation-resistant and highly dispersable Cu NWs with relatively stable sizes were obtained by the proportional control of surfactants, which effectively reduced their surface energy. A year later, Yin et al. modified the morphology of Cu NWs by the simultaneous co-reduction of two polyols, and successfully prepared Cu NWs with curved structures [Figs. 1(a) and 1(b)], which confirmed the role of the reducing agents [18]. The authors not only studied the structural changes and growth mechanism of Cu NWs, but also provided a feasible fabrication scheme for transparent electrodes.

The hydrazine method for Cu NW synthesis was first reported by Chang et al. in 2005, which involved the reduction of Cu(NO3)2 to pure Cu with hydrazine in an aqueous solution containing NaOH and ethylenediamine [Figs. 1(c)-(e)] [19]. However, the growth mechanism and practical applications of these Cu NWs were confirmed by Rathmell et al. in 2010 [20]. Through control of the experimental conditions, the growth mechanism of Cu NWs could be clearly observed and it was determined that Cu NWs grew from a spherical seed to branches in the [110] direction. In addition, the conductive ink was prepared using Cu NWs, and a flexible transparent electrode was successfully fabricated for the first time by Meyer rod coating. Although this method still needs improvement because hydrazine is toxic, it is suitable for mass production and therefore, is important in the development of science and industry.

The amine-based approach, in which a long-chain alkylamine is used as the reducing agent and solvent, is a nonaqueous synthetic method. Zhang et al. successfully synthesized ultra-long Cu NWs in hexadecylamine solution using copper acetylacetonate as a precursor and cetyltrimethyl ammonium bromide as a surfactant [21]. The NWs had an average diameter of 78 nm and lengths of tens to hundreds of micrometers with stable structures. The main advantage of the amine-based method is that the Cu NWs are relatively long and have high aspect ratios – features which are suitable for the fabrication of high-performance functional electrodes such as flexible transparent electrodes and 3D electrodes. However, compared with other methods, the amine-based method uses a higher amount of amine, which is a relatively expensive reagent and requires the use of an additional catalyst. Although the amine-based method is important in the control of the shape of Cu NWs, the price-performance ratio is not suitable for synthesizing low-cost Cu NWs.

III. Challenges and surface treatment

Typically, Cu NWs are dispersed and preserved in aqueous or organic solutions after synthesis to facilitate their use in the solution process [16,21]. However, these dispersed Cu NWs cannot avoid complete contact with oxygen in the solution. Even if these are preserved in a reducing solution, the dispersed Cu NWs are exposed to air during practical use [4]. Although Cu has a lower metal activity compared to hydrogen, the surface of a Cu NW is highly susceptible to oxidation due to the high activity and large surface area owing to its nanometer-sized width [12,22]. Furthermore, pure Cu NWs are particularly unstable at widths less than 100 nm, and aggregation is likely to occur. Therefore, many studies have focused on modifying the surfaces of Cu NWs, which not only prevents direct contact with oxygen, but also effectively reduces their surface energy [17,23]. Furthermore, the surfaces of Cu NWs are sometimes treated to improve their compatibility with other materials to increase the device performance.

In recent years, the most common method has involved the fabrication of an extra stable shell (other metals, metal oxides, and graphene) on the surfaces of Cu NWs [24]. Rathmell et al. synthesized oxidation-resistant cupronickel NWs composed of a Cu core and Ni shell to address the challenge of oxidation of pure Cu NWs [Figs. 2(a)-(c)] [24]. As a result, the transparent electrode consisting of cupronickel NWs exhibited oxidation resistance that was greater than...
IV. Film-making process (deposition)

The film-making process of Cu NWs is important for enhancing the performances of the functional electrodes. Each functional electrode is suitable for a different film-making method, and the best performance can be obtained by employing an appropriate method. Till date, various deposition methods have been investigated to ensure the uniformity of the Cu NW film, such as Meyer rod coating, filtration, and spraying. In addition to filtration, the other two methods are also accompanied by solvent evaporation.

Meyer rod coating is commonly used for the fabrication of transparent films with low-concentration Cu NWs [4]. From an engineering point of view, this method is ideal for industrial production owing to its simplicity, convenience, and continuous and large-scale manufacturing. Many studies have employed this method to prepare thin films of Ag and Cu NWs to obtain superior transparent electrodes. A precondition for Meyer rod coating is that the metallic NWs with ink formulation must be uniformly dispersed in the solvent. To precisely control the thickness of the NW film, considering the aggregation caused by solvent volatilization, it is important to control various coating parameters such as the concentration of the NW dispersion, coating speed, and shape of the Meyer rod, which directly affect the quality of the film. However, it is difficult to prepare low-concentration metallic NW films with good connection between junctions through this method because of the uncontrollable factor of the dispersion of random metallic NWs by Brownian motion.

Spraying is one of the most practical coating methods which is suitable to prepare metallic NW films for industrial production [27,28]. The main advantage of spraying in a high-end spray equipment is that it can be performed in large areas as a continuous process. During spraying, the metallic NWs are separated by water droplets, such that the aggregation caused by solvent evaporation can also be prevented in a dilute solution. As the spraying time is strongly correlated to the amount of deposition, it is not suitable for the preparation of relatively thick films. More importantly, in the long term, solvent waste and nozzle clogging caused by NWs are some of the technical challenges in this method that still need to be addressed.

Filtration is a traditional deposition method for metallic NW film-making [10,17,21,29]. The main advantage of this method is that the preparation process is simple and fast, and it is suitable for multilayer preparation with a wide range of thicknesses. Although there is no process restriction on the fabrication of opaque NW films, a special transfer film is required to form a transparent film with a low-concentration deposition of the NWs, as the filter membrane is typically not transparent. In comparison to other deposition methods, filtration does not require a solvent evaporation process to minimize the effects of NW aggregation, resulting in high-quality metallic NW films with controllable accuracy of transparency. However, the size of the metal NW film is limited by the suction filter and filter paper, and this method cannot be used in the roll-to-roll process for industrial fabrication.

V. Connectivity of Cu NW network

After the film-making process, the Cu NW film shows poor electrical properties owing to the high contact resistance caused by the oxide layer or organic layer on the Cu NW surface. The connection of Cu NWs requires an additional processing step to effectively remove
these surface layers, which is significantly different from the Ag or Au NWs. The films made from Cu NWs with stable conductive shells are directly conductive. In general, the connectivity of Cu NWs can be classified into the contact mode and welding mode, according to the junction structure.

The most common method of welding involves heating to more than 150 °C in a vacuum or reducing gas environment [10,27]. Welding is the connection of two metals in the form of metallic bonds, which can be accomplished by sufficient energy. However, as metal NWs generally have lower melting points than bulk metals, the junction in NWs is welded by absorbing the energy exceeding their melting temperature. In addition to heating, intense light welding and electrothermal welding methods have been recently reported to connect Cu NWs [30,31]. In the case of intense-light welding, the light energy absorbed from the xenon lamp or laser is highly intense at the junction due to the surface plasmon resonance effect of Cu NWs, resulting in the connection of NWs by percolation at the contact point without the deformation of the NW structure [Fig. 3(a)] [28,32,33]. As intense-light welding can only be performed on the surface of the film with a light source, it is realized by illumination. This imposes significant limitations on the welding of functional electrodes and is not suitable for thick electrodes such as 3D electrodes. Electrothermal welding is based on the principle of Joule heating. Although Cu NW has a highly conductive 1D structure, a high contact resistance is encountered at the junctions of Cu NWs due to surface oxides or organic matter. When a voltage is applied, the high-resistance contact points are first heated to the welding temperature to form metallic bonding, resulting in the connection of Cu NWs. These methods are highly practical with relatively high environmental requirements, such as vacuum or inert gas, because Cu NWs can oxidize or deform during the welding process.

An additional method is the contact mode, in which the oxide layer is removed by a chemical reaction and Cu NWs are connected with a direct contact [34]. Recently, various chemicals including acid, hydrazine, glycerol, and NaBH₄ have been reported to remove the oxide layer from the Cu NW surface, thereby connecting these. The main advantage of the contact mode is that the Cu NWs can be connected in a solution without harsh environmental conditions such as vacuum. Unfortunately, secondary oxidation and contact resistance, which are more serious challenges encountered in this method compared to the welding mode, still remain important bottlenecks that need to be addressed. Recently, Yin et al. reported a new type of solvent-dipped welding method that effectively combined the advantages of the two types of the above-mentioned methods to weld the Cu NWs under a vacuum-free environment [Fig. 3(b)] [35]. Although this method is innovative, long-term improvements are required for its practical applications.

VI. Applications of Cu NWs

1) Flexible transparent electrode for optical devices

Among the electronic display products produced in the past few decades, ITO has been extensively used as a transparent electrode in various devices such as liquid crystal displays and organic light-emitting diodes (OLEDs) [36,37]. ITO exhibits good electrical conductivity with high transparency, and is an indispensable material in displays. Although the use of ITO has significantly promoted the development of electronic devices, the pursuit for alternative materials to ITO has been an ongoing effort since the 1980s because of the scarcity of indium [13]. The high fabrication cost due to harsh engineering conditions is an additional reason to search for these alternatives. In recent years, this demand has become more important with the development of flexible electronics because ITO is a brittle ceramic material that the conductivity was significantly decreased when the film bending [38]. This critical shortcoming makes ITO unsuitable to be used in flexible devices. To replace ITO, various materials such as metal grids, metal NWs, carbon nanotubes (CNTs), graphene, and conductive polymers are some alternatives that can be used to construct transparent electrodes. Among these, Cu NWs are the most promising material for flexible transparent electrodes owing to their low cost, high conductivity, and remarkable mechanical properties.

The fabrication of transparent electrodes by Cu NWs was first reported by Rathmell et al. in 2010 [20]. Although transparent electrodes made of Ag NWs had been reported at that time, this was the first report of fabricating transparent electrodes with Cu NWs, which was a significant development. On the basis of this landmark study, extensive efforts were directed toward improving the optoelectronic performance, and surpassing those of ITO and Ag NW transparent electrodes. The opto-electrical performance of a Cu NW transparent electrode fabricated by Zhang et al. in 2012 was 90 Ω/□ at 90 % of transparency (90 % T) [Figs. 4(a) and 4(b)] [21]. Furthermore, in 2013, Guo et al. reported a value of 51.5 Ω/□ at 93.1 % T for a high-performance transparent electrode using ultrathin Cu NWs, which was comparable to the values for ITO and Ag NW electrodes [10]. These studies laid a solid foundation for the future applications of optical devices. However, a series of technical challenges including roughness still need to be solved for these to be practically applicable to electronic devices such as organic solar cells and OLEDs.

As is well known, the transparent conduction characteristics of Cu NW electrodes are achieved by random nanomesh connections. However, more than 80 % of the electrode area that is not covered by the Cu NWs cannot supply a stable electric field, which is a major shortcoming in their application to optical devices. Sachse et al. used high-conduction Poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS, Clevios PH1000) to fill the electrode portion that is not covered by the Cu NWs, which not only solved the roughness issue of Cu NWs, but also afforded a complete planar electrical conductivity
for the transparent electrode [27]. The authors successfully applied this composite electrode with high transparency to organic solar cells and obtained a relatively good performance, which was slightly inferior to that of ITO. As the first case study for the application of a Cu NW-based transparent electrode to organic solar cells, it was a highly significant report.

In 2014, Im et al. reported the use of a Cu NW film as a flexible transparent electrode in flexible OLEDs [Figs. 4(c)-(e)] [39]. Typically, the requirements for the roughness of OLEDs for transparent electrodes are more severe than those for organic solar cells. The Cu NW film was embedded on a fiber-reinforced transparent plastic film to obtain a high-performance flexible transparent electrode with an ultra-smooth surface. The plastic film was made of a UV-curable matrix resin and glass fabric, and the Cu NW film was monolithically embedded in the film during the curing process. This composite transparent electrode exhibited excellent oxidation stability and low surface roughness ($R_{\text{rms}} < 2 \, \text{nm}$) because the resin matrix tightly encapsulated the Cu NWs with a minimum exposed plane. Interestingly, this Cu NW-based transparent electrode was successfully applied to OLEDs for the first time and achieved comparable performance to that with ITO. These results show the practical application value of Cu NWs in the field of OLEDs and development of flexible displays.

2) 3D Cu NW network for LIBs

After the commercialization of LIBs by Sony in 1991, this innovative invention that changed our lives, has received significant attention [40,41]. LIB is an energy storage device based on an electrochemical reaction and is composed of a positive electrode, a negative electrode, a separator, and an electrolyte, where the electrode is generally divided into the current collector and active materials. With the development of electronic technologies in recent years, the demand for capacity and performance of the battery has gradually increased [42,43]. To achieve these, many research efforts have been focused on the study of active materials that can increase the specific capacity through shape control, doping processes, and compositing [44,45]. Although many studies have achieved breakthrough results in battery performances, the new materials cannot yet be practically applied to replace the traditional active materials because of production costs, safety, and other issues. Except the active material, the modification of the shape of the current collector is also a useful practical method for effectively increasing the actual capacity, energy density, and power density. Among various morphologies, the highly porous 3D current collector connected by the stacking of 1D linear conductive nanomaterials not only provides an appropriate moving path for the electrons and ions, but also increases the loading of the active material based on their high surface areas [46]. In addition, the 1D shape facilitates the fabrication of flexible LIBs for next-generation electronics [47].

CNTs are 1D conductive materials, which have been extensively studied in the field of LIBs. Although CNTs are generally used as conduction agents, which are suitable for reducing the contact resistance of active materials, these are not the preferred materials for a current collector, which collects the current generated by the active material and produces a large current as an external output [48,49]. Therefore, the current collectors must have low internal resistances; this is also an important reason for the use of a metal foil in conventional current collectors. Compared with CNTs, 1D metallic NWs of Al and Cu with high electrical conductivities have identical chemical compositions as those of the conventional current collectors, and are thus more likely to be used in commercial LIBs.

For the negative electrode, studies on the fabrication of current collectors using Cu NWs have been recently reported. As Cu undergoes lithium intercalation at high potentials, the Cu NW electrode can only act as a current collector of the negative electrode. A study on the fabrication of highly conductive electrodes using stacked Cu NWs was reported by Yin et al. in 2014 [17]. However, this study only described some physical properties of these stacked Cu NW electrodes (Fig. 5), and these were not applied to the LIBs. In 2015, Hwang et al. applied the Cu NW electrode as a current collector in the LIBs, where Si NWs were used as the active materials in the anode [50]. Si has a high specific capacity of $> 4,000$ and is an excellent anodic active material in terms of energy storage. However, the deterioration of the LIB
performance caused by the volume change of Si during the charging/discharging process is still an important challenge to be addressed. This study proposed a new composite electrode fabricated by combining Cu NWs and Si NWs. Herein, the junctions were physically entangled by external pressure to improve the adhesion and integrity, which effectively resolved the above-mentioned degradation issues in the LIB performance caused by the expansion of Si. In addition, Lu et al. reported that the use of a 3D Cu NW network as the current collector could more efficiently restrain the growth of lithium dendrites in comparison to the traditional Cu foil [Figs. 6(a) and 6(b)], which was closely related to the important safety issues of Li-based cathode materials. More recently, Yin et al. proposed an all-NW flexible composite anode with a 3D Cu NW network as a current collector and multi-wall carbon nanotubes (MWCNTs) as the active materials, and successfully applied these to fabricate a fast-charging LIB [Figs. 6(c) and 6(d)] [52]. The use of a highly conductive and lightweight Cu NW network overcame the main problem of a high contact resistance between the MWCNTs that made it unsuitable for a full cell. This was the first case that used MWCNTs as the anode active materials to fabricate a full cell with a high energy density. Moreover, as a binder-free electrode, the composite anode could be arbitrarily modified to a free electrode, the composite anode could be arbitrarily modified to a

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been extensively studied in recent years and is the first choice for low-cost and desirable catalysts. Sun et al. reported Cu NW-Ag bimetallic heterostructures for high-efficiency catalytic activity in the reduction of 4-nitrophenol to 4-aminophenol in an aqueous solution [57]. Cu NWs with high roughness were mainly used in this study, showing a superior catalytic activity to that of the smooth Cu NWs owing to a larger specific surface area and more vacancies. The synergy and structures of the two metals played key roles in the catalytic applications. Alia et al. reported that the core-shell structures of Pt/Cu NWs could improve the catalytic activity of the hydrogen oxidation reaction (HOR, Figs. 7(d) and 7(e)) [58]. As the core substrates, Cu NWs exerted a compressive strain on the Pt shell, which was beneficial for the improvement of the HOR activity. Additionally, the surface of Cu in Pt/Cu NWs further aided in the adorption of hydroxyl groups, resulting in an enhanced performance in terms of the HOR activity, which exceeded 3.5 and 1.9 times of the area and mass exchange current densities of the Pt/C electrode, respectively [Fig. 7(f)]. Chen et al. showed that the Cu-Pt core-shell NWs were high-efficiency electrocatalysts for the hydrogen evolution reaction [59]. The mass exchange current density of the Cu-Pt core-shell NW network was more than 8 times that of a typical Pt/C electrode. Interestingly, the transparent film fabricated by the Cu-Pt core-shell NWs with 75% transparency had a comparable catalytic performance to that of the polycrystalline Pt electrode. These remarkable results indicate that Cu NWs have a wide range of applications in the field of catalysis, but further efforts are needed to explore and develop these materials.

VII. Conclusion

Promising applications of Cu NWs in flexible transparent electrodes, 3D network current collectors, and catalysts are comprehensively discussed in this review. The advantages of Cu NWs in terms of the cost and commercial value of their applications are described in detail. By exploiting intrinsic advantages such as excellent electrical conductivity, unique 1D structure, and high activity, Cu NW-based functionalized electrodes can be developed for advanced electrical devices and catalysts, which is not possible with typical metals. For extensive applications of Cu NWs, it is important to select suitable synthetic and film-making methods as each method has some advantages and limitations. Although Cu NWs are cheaper than other metals, the oxidation and aggregation induced by their high surface energies can limit their practical applications. It is necessary to efficiently address these limitations for the fabrication of Cu NW-based functionalized electrodes. The structure of the electrode is typically controlled by the deposition of Cu NWs, which is correlated with physical properties such as porosity, mechanical properties, and electrical conductivity. Additionally, the activity of Cu NWs mainly depends on their sizes, shapes, and compositions. Through precise control of these parameters, functionalized electrodes fabricated by Cu NWs can enable the development of next-generation electronic devices and catalysts.

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