Photoelectrochemical Properties of Fe₂O₃-Cu₂O Heterojunction Nanowire Prepared on Anodic Aluminum Oxide Template by Sequential Electrodeposition

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ABSTRACT

Fe₂O₃-Cu₂O heterojunction nanowire arrays are a promising photoelectrode technology for solar fuel production because of their increased absorption ability as well as the enhanced separation and transfer rate of the charge carriers. Here, we report on the preparation of a Fe₂O₃-Cu₂O heterojunction nanowire photoelectrode by sequential electrodeposition and we investigate its photoelectrochemical properties. The Fe₂O₃-Cu₂O heterojunction photoelectrode is successfully prepared using an anodic aluminum oxide (AAO) membrane as a template material. One side of a double-pass AAO membrane is covered with conductive Ag paste and then Fe and Cu are sequentially electrodeposited in the metal salt electrolyte for constructing the heterojunction nanowire arrays. The sequentially deposited Fe-Cu nanowire arrays are converted into Fe₂O₃-Cu₂O nanowire photoelectrodes by a post-annealing process. The front side of the crystallized Fe₂O₃-Cu₂O heterojunction nanowire photoelectrode undergoes a photoelectrochemical reaction upon illumination with solar light, and its improved photoelectrochemical properties are investigated intensively. In summary, we propose a facile electrodeposition method to prepare a p-n heterojunction electrode with high charge separation efficiency and improved charge transport efficiency for artificial photosynthesis through solar water splitting and the hydrogen evolution reaction.

Keywords: Heterojunction, Photoelectrode, Sequential deposition

1. Introduction

Thus far, solar energy has been widely studied as a desirable source of renewable and sustainable energy [1-3]. Among various approaches for utilizing solar energy, artificial photosynthesis, which imitates the process of natural photosynthesis, has been highlighted as a promising strategy for producing valuable chemicals such as hydrogen, formic acid, and alcohols [4,5]. In recent decades, the development of the solar-energy-driven water splitting reaction, which splits water molecules into hydrogen and oxygen through a photoelectrochemical process, has been intensively studied because water splitting by solar energy is a basic reaction for realizing an efficient artificial photosynthetic system [6,7]. H₂ (hydrogen), which is a storable and transportable fuel and feedstock, is an ecofriendly resource in the modern chemical industry.

Since Fujishima and Honda discovered the solar-energy-driven water splitting reaction using TiO₂ as a photocatalyst through photochemical (PC) and photoelectrochemical (PEC) processes, various types of metal oxide materials such as Fe₂O₃, BiVO₄, ZnO, and WO₃ have been used to produce hydrogen through water splitting [8-11].

Strategies for achieving efficient solar energy conversion have focused on three fundamental processes: light absorption, charge separation, and charge transport. Valence band potential engineering, introducing a dopant into a host, using solid solutions, and combining surface plasmon resonance with other technologies have been reported as effective strategies for enhancing physicochemical and photophysical performances. Moreover, together with morphology control of photocatalysts for achieving a large surface area and highly reactive properties, Z-scheme configurations such as composite structures of double-species metal oxide photocatalysts and combining carbon-based materials with photocatalysts have been recognized as prospective strategies [12-14].

Compared with PC systems, morphology structuring from nano- to micro-scale dimensions has attracted considerable attention in the field of PEC systems. One-dimensional (1D) manipulation, such as that of wire-, tube-, and rod-shaped nanomaterials, has been successfully demonstrated to enhance their PEC characteristics. For instance, Yang *et al.* [15] demonstrated that 1D geometrical parameter manipulation increased the electron transport rate considerably. Furthermore, Frank *et al.* [16] succeeded in achieving a low recombination rate in 1D structured nanomaterials, which resulted in a high photoconversion

efficiency. Grimes *et al.* [17] reported that introducing a 1D TiO₂ nanotube into a dye-sensitized solar cell remarkably improved its photovoltaic performance [17]. The above-mentioned results indicate that vertically oriented 1D structured materials exhibit highly improved light energy conversion efficiency with favorable electron and ion diffusion between their interfaces.

However, in spite of the advantages of vertically oriented 1D structured electrodes for solar-energy-driven water splitting in PEC systems, it remains challenging to not only construct a suitable heterojunction of metal-oxide-based photocatalysts with higher chemical stability in a wide range of pH of the electrolyte solution but also maintain the vertically oriented 1D rod/wire structure. Hematite (α -Fe₂O₃ phase), one of the most abundant minerals on Earth, has high corrosion resistivity in both alkaline and acidic media as well as an optimum band position for high-efficiency solar energy absorption and utilization [18]. Cu₂O, which is another abundant mineral, is non-toxic and involves a low-cost fabrication process; hence, it is also capable of good PEC performance [19]. Moreover, it has a band gap of 2.0 eV, which is suitable for high solar energy utilization. Although both Cu₂O and hematite have favorable band energy positions for solar water splitting, there are challenges that restrict their application as efficient and durable photoelectrodes for solar fuel production. The major challenges are the unfavorable ratio between the carrier diffusion length and the light absorption depth in the photoelectrode [20,21]. For instance, theoretically, the film thickness of a Cu₂O electrode should be at least 1000 nm so that it can absorb sunlight efficiently. However, owing to the short carrier diffusion length of Cu₂O (~200 nm or less), it is not possible to increase the thickness of the Cu₂O film to the optimal value [22,23]. Hence, it is necessary to construct a p-n junction of a photocatalyst exhibiting much higher photoactivity than bare materials by facilitating the separation and transfer of charge carriers through an internal electric field established at the interface of the heterojunction [24].

To solve the above-mentioned problems, here, we demonstrate the preparation of a Fe₂O₃-Cu₂O heterojunction nanowire photoelectrode by sequential electrodeposition with an anodic aluminum oxide (AAO) membrane as a template material. Through our template-mediated method for constructing a p-n junction structured electrode of hematite and Cu₂O with a 1D nanowire structure, we realize high charge separation efficiency and improved charge transport efficiency. In addition, the photoelectrochemical properties for solar fuel production are investigated in detail.

2. Experimental details

2.1. Materials

AAO membranes were purchased from InRedox Ltd. Conductive Ag paste, iron (II) sulfate heptahydrate (FeSO₄·7H₂O), copper (II) sulfate pentahydrate (CuSO₄·5H₂O), boric acid (H₃BO₃), and NaOH were purchased from Sigma-Aldrich. All the chemicals used as received. Distilled water was produced using a Millipore Milli-Q purification system (resistivity ≥ 18.2 M Ω ·cm).

2.2. Preparation of Fe₂O₃ and Cu₂O nanowire arrays by electrodeposition

Typically, one side of the double-pass AAO wafer was covered

with conductive Ag paste. After the conductive Ag paste dried, the AAO membrane was immersed in 0.2 M iron (II) sulfate heptahydrate and 0.1 M boric acid solution as an electrolyte solution. A three-electrode system was configured, where the AAO membrane covered with Ag paste was the working electrode, a coiled platinum wire was the counter electrode, and Ag/AgCl (3 M KCl saturated) was the reference electrode. Electrochemical deposition was performed using a PL-9 (KST-P1) potentiostat at room temperature (RT). Fe wire arrays were electrodeposited at -4 V for 4 h into the AAO column.

After the deposition, the AAO substrate was cleaned with distilled water and ethanol. Then, the AAO substrate was heat-treated at 723 K for 4 h under air conditioning for crystallization. The annealed AAO substrate was immersed in 2 M NaOH solution to remove the AAO membrane. For the preparation of Cu₂O nanowire arrays, electrodeposition was performed in 0.2 M copper (II) sulfate and 0.1 M boric acid solution at -4 V for 0.5 h.

2.3. Preparation of Fe₂O₃-Cu₂O nanowire arrays by sequential electrodeposition

Similarly, the electrodeposition of the Fe-Cu metallic bilayers followed the above-mentioned method. Fe wire arrays were deposited on AAO as the first layer under an iron source electrolyte and Cu wire arrays were then sequentially deposited on the Fe wire arrays on AAO under a copper source electrolyte. The sequentially electrodeposited AAO substrate was cleaned and annealed at 723 K for 4 h under air conditioning for the conversion to metal oxide phase crystallization. Finally, it was treated with NaOH to remove the AAO template.

2.4. Characterization

The morphology and elemental mapping of the prepared samples were investigated using a scanning electron microscopy (Hitachi Horiba S300) with attached energy dispersive spectroscopy (EDS) equipment. For transmission electron microscopy (TEM) observations, the samples were prepared by placing one drop of the colloidal solution onto 200-mesh carbon-coated copper grids and dried for a few minutes. The crystallinity and crystal structure were measured by X-ray diffraction (XRD, Rigaku D'Max 2200V) with Cu K α radiation ($\lambda = 1.5406$ Å). Linear sweep voltammetry (LSV) of each electrode was conducted using a PL-9 (KST-P1) potentiostat with 0.1 M NaOH electrolyte in the three-electrode system. The AAO membrane was the working electrode, a coiled platinum wire was the counter electrode, and Ag/AgCl (3M KCl saturated) was the reference electrode. All the curves were measured under chopped 1-sun illumination (AM 1.5 G, 100 mW/cm²) using a solar simulator (Newport, 300 W Xe source).

3. Results and discussion

In the present study, we demonstrated the preparation of 1D binary wire arrays as a heterojunction photoanode by sequential deposition for solar fuel production. A heterojunction of Fe₂O₃-Cu₂O binary wire arrays was prepared in three steps: 1) binary layer deposition of Fe and Cu wires onto an AAO membrane covered with conductive Ag paste, 2) heat treatment for the conversion of the metal wires into metal oxides, and 3) removal of the AAO membrane by treatment with NaOH. A schematic for the preparation of the Fe₂O₃-Cu₂O binary wire arrays by electrodeposition on the AAO membrane

Figure 1. Preparation of nanowire arrays using alumina membrane by sequential electrodeposition. (a) Commercial alumina membrane, (b) AAO membrane covered with Ag conductive paste, (c) first deposition of Fe nanowires onto alumina electrode, (d) second deposition of Cu nanowires, and (e) heat-treated electrode after removing alumina membrane.

Figure 2. Field emission SEM (FE-SEM) and elemental mapping images of (a) alumina membrane and (b) Fe_2O_3 - Cu_2O heterojunction nanowire on alumina membrane.

is shown in Fig. 1. First, the double-pass AAO membrane was used [Fig. 1(a)]. One side of the AAO membrane was covered with conductive Ag paste for the preparation of the electrode substrate [Fig. 1(b)]. After the conductive Ag paste dried, FeOOH was electro-deposited inside the column of the AAO membrane using FeSO_4 solution in boric acid as the deposition electrolyte [Fig. 1(c)]. The formation of FeOOH is given by [25,26]

As the second wire array, $\text{Cu}(\text{OH})_2$ was sequentially electro-deposited on FeOOH nano-rods in CuSO_4 -boric acid electrolyte solution [Fig. 1(d)]. The formation reaction of Cu_2O is given by [27]

The morphology of the Fe and Cu precursors deposited into the column of the AAO membrane was investigated by scanning electron microscopy (SEM). Figure 2(a) shows the top-view and cross-sectional SEM images of the bare AAO membrane. It appears that the AAO template has the morphology of typical nano-tubular/column arrays. Compared with the SEM images of the bare AAO template, Fig. 2(b) shows the top-view and cross-sectional SEM images of the sequentially electrodeposited samples. It indicates that the electrodeposited wires filled the column of the AAO substrate. Interestingly, the cross-sectional SEM image with the EDS mapping results shows that the Fe-based wire arrays were grown from the Ag paste substrate on the bottom of the AAO membrane. As the second deposition layer, Cu-based wire arrays were formed on the Fe-based wire arrays inside the AAO nanotube arrays [Fig. 2(b)].

The Fe-Cu nanowire arrays sequentially deposited on the AAO

Figure 3. FE-SEM and elemental mapping images of Fe_2O_3 - Cu_2O heterojunction nanowire on Ag substrate after removing the template. (a) Top-view image, (b) cross-sectional image, and elemental mapping images of (c) selected area, (d) Fe, (e) Cu, and (f) O.

substrate were heat-treated for conversion into Fe_2O_3 - Cu_2O nanowire photoelectrodes. During the annealing process, the electrodeposited Fe-based wires were expected to convert into Fe_2O_3 and the crystallinity of Cu_2O was expected to increase as follows [28,29]:

To free the binary wire arrays, the Ag-covered AAO substrate was immersed in NaOH solution and then removed. Their wet-etching reaction is expressed as

As the above-mentioned wet-etching reaction occurs drastically in NaOH solution, the sequentially deposited products were treated with NaOH [Fig. 1(e)]. After dissolving the AAO membrane in NaOH solution, the morphology of the free-standing binary wire arrays was observed via SEM analysis (Fig. 3). Figure 3(a) shows the top-view SEM image of the structured nanowires with a diameter of around 100 nm, where the pore diameter of the AAO nanotube template was maintained after sequential deposition of the nanowire structure. The array of deposited nanowires was also observed with a length of around 5 μm in the cross-sectional SEM image [Fig. 3(b)]. The selected area of the prepared nanowire arrays was observed via EDS mapping analysis [Fig. 3(c)]. The upper part of the individual nanowires consisted of Cu [Fig. 3(d)], while Fe was detected in the lower part [Fig. 3(e)] and oxygen was detected in all parts of the nanowires [Fig. 3(f)]. Thus, the binary stacked nanowire arrays were well deposited and freely stood on the Ag substrate in spite of annealing and NaOH treatment.

Microscopic observation of individual wires in the sequentially deposited nanowire structure was performed via TEM with EDS analysis (Fig. 4). Figure 4(a) shows a typical TEM image of the individual wires in the deposited product. The selected area electron diffraction (SAED) pattern of the individual nanowires was compared among three zones of nanowires. The SAED pattern of the first zone [red box in Fig. 4(a)] showed typical crystalline Fe_2O_3 with the (110) plane lattice structure in which the d-spacing was 0.2521 nm [Fig. 4(b)] [30]. The SAED pattern of the second zone [blue box in Fig. 4(a)] showed typical crystalline Cu_2O with the (311) plane lattice structure in which the d-spacing was 0.4266 nm [Fig. 4(c)] [31].

Figure 4. (a) Typical TEM image and SAED pattern of (b) bottom zone and (c) upper zone of Fe_2O_3 - Cu_2O heterojunction nanowire. (d) EDS spectrum and (e) SAED pattern of middle zone of Fe_2O_3 - Cu_2O heterojunction nanowire.

Interestingly, the EDS result for the middle zone [green box in Fig. 4(a)] in the individual nanowires shows that both Fe and Cu exist concurrently [Fig. 4(d)]. Together with EDS analysis, the SAED pattern of the middle zone of the nanowires showed typical SAED patterns of a multi-crystal structure, which is different from the SAED pattern of single crystal phase materials. This indicates that the middle part of the heterojunction nanowire consisted of a mixed/combined crystal structure of Cu_2O and Fe_2O_3 phases after the post-annealing process of the heterojunction of Fe_2O_3 - Cu_2O binary wire arrays [Fig. 4(e)]. These results are consistent with previous SEM-EDS analysis results in which Cu_2O and Fe_2O_3 exist simultaneously in the middle zone of the Fe_2O_3 - Cu_2O heterojunction nanowire arrays.

To determine the effect of the post-annealing process on the conversion into metal oxide phases after sequential electrodeposition, the crystal structures of the nanowire arrays were compared according to different post-annealing treatments with XRD patterns (Fig. 5). When the binary stacked nanowire array was heat-treated at 300 °C, only two peaks were dominantly observed at 2θ values of 25° and 74° [Fig. 5(a)]. They matched with the (012) plane of the Fe_2O_3 phase and the (311) plane of the Cu_2O phase, respectively. As the annealing temperature was increased to 400 °C, hidden peaks of other planes appeared in both the Fe_2O_3 phase and the Cu_2O phase. The observed peaks at 25°, 42°, 50°, and 64° correspond to the (110), (113), (024), and (300) planes of the hematite phase, respectively. Other peaks at 37°, 44°, 62°, and 77° were assigned to the (111), (200), (220), and (222) planes of the Cu_2O phase, respectively. This indicates that the crystallinity of the Fe_2O_3 - Cu_2O heterojunction increased with the post-annealing temperature [Fig. 5(c)].

Based on the previously reported band energy position of Cu_2O and Fe_2O_3 as a visible-responsive photocatalyst, the suggested energy band diagram of the Fe_2O_3 - Cu_2O heterojunction nanowire is presented as a scheme in Fig. 6(a). Specifically, the band position of the Cu_2O photocatalyst ranges from 1.3 V vs. NHE for the valance band energy level to -0.7 V vs. NHE for the conduction band energy level, while the band position of Fe_2O_3 ranges from 2.4 V vs. NHE for the valance band energy level to 0.3 V vs. NHE for the conduction band energy level [22,32]. Considering the intrinsic properties of these photocatalysts, i.e., Fe_2O_3 has n-type semiconductor properties and Cu_2O has p-type semiconductor properties, constructing a p-n junction of both materials

Figure 5. Comparison of typical XRD patterns of Fe_2O_3 - Cu_2O heterojunction nanowire electrode by heat treatments at (a) 300, (b) 400, and (c) 500 °C for 4 h.

Figure 6. (a) Schematic diagram of energy band of Fe_2O_3 - Cu_2O heterojunction nanowire and (b) LSV curves of Fe_2O_3 , Cu_2O , and Fe_2O_3 - Cu_2O heterojunction nanowire electrode under 1-sun illumination.

facilitates a more favorable hole-charge separation and diffusion of the generated holes and electrons owing to the inner electric field induced by the p-n junction [33]. This is proved by LSV measurements of the Fe_2O_3 - Cu_2O heterojunction nanowire photoelectrode, as shown in Fig. 6(b). The LSV curve of the pure Fe_2O_3 electrode is a typical LSV curve of an n-type semiconductor, with an onset potential (V_{onset}) of 0.45 V vs. Ag/AgCl, and the 1-sun illumination response starts at 0.5 V vs. Ag/AgCl in the anodic direction. The bare Fe_2O_3 photoanode exhibited a current density of 0.16 mA/cm^2 at 1.23 V vs. Ag/AgCl under the standard reaction potential for the water oxidation reaction. In addition, no light response was observed at a potential lower than 0.5 V vs. Ag/AgCl. Further, pure Cu_2O shows typical LSV curves of a p-type semiconductor, with a V_{onset} of 0.2 V vs. Ag/AgCl, and the 1-sun illumination response starts at 0.2 V vs. Ag/AgCl in the cathodic direction. In addition, the bare Cu_2O photoelectrode showed a current density of 0.1 mA/cm^2 at -0.3 V vs. Ag/AgCl and no light response was observed at a potential higher than 0.2 V vs. Ag/AgCl. However, interestingly, the Fe_2O_3 - Cu_2O nanowire showed 1-sun illumination responses in the whole range of the LSV curves, with an anodic current density of 0.23 mA/cm^2 at 1.23 V. Compared with that of bare Fe_2O_3 , the current density of the Fe_2O_3 - Cu_2O heterojunction nanowire was 60 % greater at 1.23 V vs. Ag/AgCl. Moreover, the Fe_2O_3 - Cu_2O heterojunction nanowire showed a cathodic current of 0.8 mA/cm^2 at -0.3 V, which was not observed in the case of the bare Fe_2O_3 photoelectrode. It is worth noting that the effect of the p-n junction

was obvious in the case of the Fe_2O_3 - Cu_2O heterojunction nanowire structure with the shift of the anodic onset potential from 0.45 to 0 V vs. Ag/AgCl . These remarkable enhancements in the photoelectrochemical activity of the Fe_2O_3 - Cu_2O nanowire structure were realized by constructing a heterojunction structure consisting of both the photocatalysts. This strongly suggests that their hole-charge separation are more favorable and the charges are readily diffused owing to the p-n junction structure of the Fe_2O_3 - Cu_2O binary nanowire.

4. Conclusions

In this study, a facile approach for enhancing the photoelectrochemical properties of Fe_2O_3 and Cu_2O nanowire array photoelectrodes was investigated by constructing a p-n heterojunction structure of both the materials. The Fe_2O_3 - Cu_2O heterojunction nanowire was prepared by electrodeposition on an AAO membrane as a template for the photoelectrode. Through a post-annealing process, high crystallinity was achieved for improving the charge transport efficiency of the photoelectrode. As a result, the sequentially deposited binary wire arrays exhibited enhanced PEC performance compared to the individual materials. Moreover, a significant V_{onset} shift of the Fe_2O_3 - Cu_2O heterojunction nanowire array electrode was observed. In summary, we proposed a facile method for preparing a p-n heterojunction electrode by sequential electrodeposition, with high charge separation efficiency and improved charge transport efficiency for artificial photosynthesis through solar water splitting and the hydrogen evolution reaction.

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References

- [1] N. S. Lewis and D. G. Nocera, *PNAS* 103, 15729 (2006).
- [2] V. G. Gude, N. Nirmalakhandan, and S. Deng, *Energy* 36, 78 (2011).
- [3] N. S. Lewis, *Science* 351, aad1920 (2016).
- [4] M. J. Kang, C. W. Kim, A. U. Pawar, H. G. Cha, S. Ji, W. B. Cai, and Y. S. Kang, *ACS Energy Lett.* 4, 1549 (2019).
- [5] C. W. Kim, M. J. Kang, S. Ji, and Y. S. Kang, *ACS Catal.* 8, 968 (2018).
- [6] H. W. Seo and J. S. Kim, *Appl. Sci. Converg. Technol.* 27, 61 (2018).
- [7] T. Nakamura, *Sol. Energy* 19, 467 (1977).
- [8] H. S. Kim, *Appl. Sci. Converg. Technol.* 28, 122 (2019).
- [9] S. H. Nam and J. H. Boo, *Appl. Sci. Converg. Technol.* 22, 138 (2013).
- [10] C. W. Kim, S. Ji, M. J. Kang, H. Park, F. Li, H. M. Cheng, and Y. S. Kang, *Mater. Today Energy* 13, 205 (2019).
- [11] A. Fujishima and K. Honda, *Nature* 238, 37 (1972).
- [12] H. G. Cha, H. S. Noh, M. J. Kang, and Y. S. Kang, *New J. Chem.* 37, 4004 (2013).
- [13] J. Low, J. Yu, M. Jaroniec, S. Wageh, and A. A. Al-Ghamdi, *Adv. Mater.* 29, 1601694 (2017).
- [14] C. W. Kim, M. J. Kang, T. K. Van, and Y. S. Kang, *J. Ind. Eng. Chem.* 53, 341 (2017).
- [15] M. Law, L. E. Greene, J. C. Johnson, R. Saykally, and P. Yang, *Nat. Mater.* 4, 455 (2005).
- [16] K. Zhu, N. R. Neale, A. Miedaner, and A. J. Frank, *Nano Lett.* 7, 69 (2007).
- [17] G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese, and C. A. Grimes, *Nano Lett.* 6, 215 (2006).
- [18] K. Sivula, F. Le Formal, and M. Grätzel, *ChemSusChem* 4, 432 (2011).
- [19] J. Luo, L. Steier, M. K. Son, M. Schreier, M. T. Mayer, and M. Grätzel, *Nano Lett.* 16, 1848 (2016).
- [20] A. Paracchino, J. C. Brauer, J. E. Moser, E. Thimsen, and M. Graetzel, *J. Phys. Chem. C* 116, 7341 (2012).
- [21] K. P. Musselman, A. Marin, L. Schmidt-Mende, and J. L. MacManus-Driscoll, *Adv. Funct. Mater.* 22, 2202 (2012).
- [22] A. Paracchino, V. Laporte, K. Sivula, M. Grätzel, and E. Thimsen, *Nat. Mater.* 10, 456 (2011).
- [23] P. E. de Jongh, D. Vanmaekelbergh, and J. J. Kelly, *J. Electrochem. Soc.* 147, 486 (2000).
- [24] M. Yan, Y. Hua, F. Zhu, W. Gu, J. Jiang, H. Shen, and W. Shi, *Appl. Catal. B: Environ.* 202, 518 (2017).
- [25] J. L. Leibenguth and M. Cohen, *J. Electrochem. Soc.* 119, 987 (1972).
- [26] G. Rahman and O. S. Joo, *Mater. Chem. Phys.* 140, 316 (2013).
- [27] G. Wu, W. Zhai, F. Sun, W. Chen, Z. Pan, and W. Li, *Mater. Res. Bull.* 47, 4026 (2012).
- [28] M. J. Kang and Y. S. Kang, *J. Mater. Chem. A* 3, 15723 (2015).
- [29] M. J. Kang, H. Yu, W. Lee, and H. G. Cha, *J. Phys. Chem. Sol.* 130, 93 (2019).
- [30] D. R. Cummins, H. B. Russell, J. B. Jasinski, M. Menon, and M. K. Sunkara, *Nano Lett.* 13, 2423 (2013).
- [31] T. D. Golden, M. G. Shumsky, Y. Zhou, R. A. VanderWerf, R. A. Van Leeuwen, and J. A. Switzer, *Chem. Mater.* 8, 2499 (1996).
- [32] M. Barroso, S. R. Pendlebury, A. J. Cowan, and J. R. Durrant, *Chem. Sci.* 4, 2724 (2013).
- [33] M. Wang, Y. Hu, J. Han, R. Guo, H. Xiong, and Y. Yin, *J. Mater. Chem. A* 3, 20727 (2015).