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Authors
Shukla, Sudhanshu
Ager, Joel W
Xiong, Qihua
et al.

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Scientific and Technological Assessment of Iron Pyrite for Use in Solar Devices

Sudhanshu Shukla,[a, b] Joel W. Ager,[c] Qihua Xiong,[d] and Thirumany Sritharan*[a, b]

Iron pyrite (FeS₂) holds an enormous potential as a low cost and non-toxic photoelectrochemical and energy-harvesting material owing to its interesting optical, electronic, and chemical properties along with elemental abundance. In this Review, low cost and scalable processing techniques to synthesize phase-pure pyrite thin films and nanocubes are described, and the application of this material in various energy-harvesting devices such as dye-sensitized solar cells, photodiodes, and heterojunction solar cells is discussed. A detailed analysis of the electron transport in single-crystal iron pyrite is presented to shed light on its bulk- and surface-conduction properties, which could be useful in designing better pyrite solar cells and could be exploited for novel device architectures. Finally, future prospects and directions are discussed.

1. Introduction

Iron pyrite (FeS₂) has drawn significant interest in the field of solar photovoltaics because of its excellent optical absorption in the visible spectrum and suitable energy band gap (≈0.95 eV). In addition, the abundance of Fe and S in the earth’s crust is a favorable situation for terawatt (TW)-scale deployment of pyrite as its supply is nearly inexhaustible. Iron pyrite came into attention primarily in 1980s after the oil crisis, which acted as a catalyst in driving research activities towards finding an ideal solar absorber material.[1–6]

FeS₂ has a simple cubic pyrite type structure and belongs to the Pa₃ crystallographic space group, as shown in Figure 1. Optoelectronic properties of iron pyrite that make it interesting for solar energy conversion are: (i) low minority charge-carrier diffusion length (100–1000 nm), (ii) good electron carrier mobility (μ≈360 cm²V⁻¹s⁻¹) in n-type single crystals and, (iii) high optical absorption coefficient (α>10⁴ for hν>1.3 eV).[7–11] Despite possessing such desirable properties, the success in preparing a working solar cell from iron pyrite has been hampered by a lack of control on the chemistry of the material and by crystal defects that are believed to be responsible for the low photovoltage output from pyrite solar cells. The crystal defects manifest as specific material conditions that include Fe–S phase impurities (troilite, greigite, pyrrhotite, etc.), stoichiometric deviations,[12–14] intrinsic bulk and surface defects,[15–18] reduced surface energy band gaps,[19] Fermi-level pinning,[20] surface-state-induced band bending and ionized deep donors,[9] and surface inversion layers.[21] These issues were extensively investigated in various studies in the literature, yet they are not fully under-
stood. Recently, complex doping mechanisms were developed for iron pyrite, which emphasizes the need of a reassessment of the electronic properties, including the surface versus bulk behavior of films and crystals.\[22\]

Attempts to study these fundamental factors to understand the problem of low output photovoltage, and above-mentioned issues, have led to the utilization of several synthesis and processing schemes, which have resulted in numerous types of thin films and nanostructures in iron pyrite.\[11,23–30\] Early attempts by Tributsch and co-workers to prepare iron pyrite-sensitized TiO$_2$ solar cells showed high external quantum efficiency (up to $\approx 90\%$), but the overall efficiency remained low because of limited photovoltage.\[31,32\] Recent studies on similar device structures also validate these findings.\[33,34\] Interestingly, a pyrite–marcasite mixed-phase thin film performed better than a pure pyrite film in a photoelectrochemical cell, invalidating the belief that marcasite is detrimental to photon conversion. This performance of the mixed phase film was attributed to improved charge separation. Despite the setback in the solar-cell application, iron pyrite has been evaluated in many other optical devices such as high-responsivity photodetectors, near-IR photo- diodes,\[33,35,36\] catalyst in dye-sensitized solar cells (DSSCs),\[37,38\] photoconductors,\[39\] or bulk-heterojunction inorganic–organic hybrid solar cells,\[40\] where appropriate post treatments and custom-designed device architectures were successfully employed. This illustrates that the potential of the material can be harnessed by appropriate processing and device engineering for specific applications other than purely for light absorption.

Several vapor-phase and solution-processing techniques to synthesize iron pyrite were reported, which include sulfurization of iron and iron-oxide thin films\[10,34,41–44\] electrodeposition,\[45\] chemical vapor deposition,\[46–48\] spray pyrolysis,\[49,50\] sputtering,\[51,52\] hydrothermal method,\[53\] and hot-injection method.\[27,29,34,55\] The quality of the pyrite thin film is mostly governed by the sulfurization process in almost all cases whereas organic ligands used in many chemical synthesis methods play an important role in controlling the size of nanosized pyrite particles.\[24,29,56,57\] Bai et al. reported nano-
structured pyrite synthesis in aqueous solution, but the applicability of such pyrite nanostructures is yet to be demonstrated.\[25\] A summary of iron pyrite synthesis is provided in Table ST1 in the Supporting Information. High-quality, low-defect films can be achieved by using a suitable sulfurization treatment. Iron-pyrite single crystals are useful for the scientific understanding of the intrinsic problems of the material but are not practical for commercial usage.\[10,21\] Single crystals provide a good platform for fundamental studies on the electrical charge transport processes within the bulk and the surface. This has prompted some fundamental studies on pyrite single crystals, especially in the context of n-type conduction and surface conductivity. This knowledge would inevitably help in designing better pyrite-based optoelectronic devices. Also, the low cost and phase-pure synthesis of iron pyrite, along with judicious engineering of device architectures, could be promising for various energy-harvesting applications of pyrite.

In this work, we will outline the use of some low-cost processes to produce iron-pyrite thin films and nanostructures and develop suitable post treatments to minimize their deficiencies in specific applications such as a counter electrode in DSSCs, photodiodes, and heterojunction solar cells. We will investigate the structure and relevant properties of the products and natural single crystals, to obtain insights on the charge-carryer conduction mechanisms and to assess their applicability in the technical domain. We will also show results on the carrier conduction across bulk and surface of a natural iron pyrite single crystal through temperature-dependent resistance analysis obtained from a specially designed experimental setup.

2. Preparation of Iron Pyrite Thin Films

Photoactive materials are used in thin-film form in optoelectronic devices. Different thin-film processing methods will yield different microstructures and defect populations. As these will have profound effects on the optical and electronic properties of the film, it is important to examine more than one method of film preparation. Here, we examine two different methods of synthesizing the material and producing thin films and will examine their properties subsequently. The first method is spray pyrolysis where the procedure is to synthesize the iron pyrite phase and produce the thin film simultaneously. The second method is a two-step process where high-purity iron pyrite nanocubes (NCs) are synthesized first and the film is formed in a subsequent step.

2.1. In situ iron pyrite synthesis and film forming by spray pyrolysis

Spray pyrolysis is a cost-effective method to prepare thin films. In a typical process for iron pyrite, the precursor solutions containing iron and sulfur are sprayed on to a hot substrate where they thermally decompose and react to form a coating of FeS\(_2\). Spray pyrolysis is fast and scalable to industrial levels. A detailed synthesis procedure can be found in Ref. [38]. In brief, an aqueous solution of FeCl\(_2\)-H\(_2\)O (\(M_w = 270.30\) g mol\(^{-1}\)) and thiourea \((\text{NH}_2\text{CS})_2; M_w = 76.12\) g mol\(^{-1}\)) mixed in a 1:6 molar ratio was used as the precursor solution. The solution was sprayed onto a substrate at 350 °C. A 50 mL solution typically contained 7 mL 0.1 M FeCl\(_2\)-H\(_2\)O solution, 4.2 mL 0.1 M thiourea solution, and 38.8 mL of deionized water. A thin film of approximate 200 nm thickness was formed after spraying the full amount of the precursor. The as-sprayed films were found to be amorphous. Therefore, the as-sprayed films were subsequently annealed in a sulfur atmosphere to complete the reaction and crystallize FeS\(_2\). Sulfur powder was kept in the tube along with the sample, and an argon carrier gas was slowly flown at \(\approx 20\) scm through the tube during the annealing process to create the sulfur atmosphere in the furnace tube. Experiments were performed using different sulfurization temperatures in the range 300–600 °C for 1 h and it was found that phase-pure films could be formed in the range 400–500 °C, as shown in the X-ray diffraction (XRD) patterns and the Raman spectra in Figure 2g and h. A temperature of 300 °C was not sufficient to form the iron pyrite phase while decomposition occurred above 500 °C.

Figure 2a–f shows the evolution of the grains as a function of sulfurization temperature; larger grains could be observed in the films sulfurized at 400 and 500 °C. An optical band gap of \(\approx 1.04\) eV was found using optical absorption measurements, which is close to the reported values in the literature.\[7\] However, the films were found to be photo-inactive. Electrical measurements revealed the films to be too conducting to be used as a photon absorber. Hall measurements showed the film to be p-type with a high hole concentration of \(\approx 10^{19}\) cm\(^{-3}\) and low mobility. Such high charge-carrier density and relatively low band gap (\(\approx 1\) eV) pushes the iron pyrite semiconductor to the degenerate limit (metal-like).

2.2. Hot-injection synthesis of iron pyrite NCs followed by film forming

Hot-injection solution processing was used to prepare (100)-faceted iron pyrite NCs. The conditions required to produce single-crystal cubes with an approximate 100 nm side length were reported elsewhere.\[29\] The starting materials for the synthesis were 98% anhydrous iron(II) chloride (FeCl\(_2\)), 70% oleylamine (OLA), and sulfur powder from Sigma–Aldrich. For NC synthesis, 0.5 mmol (63.5 mg) FeCl\(_2\) was mixed with 5 mL OLA in a trineck flask and degassed for 30 min. Subsequently, it was heated to 110 °C for 1 h to form the Fe–OLA complex. Thereafter, the temperature was increased to 180 °C and 3 mmol (96 mg) sulfur dissolved in 5 mL OLA was injected into the flask. The temperature was maintained at 180 °C for 24 h to complete the reaction. After the reaction, the solution was cooled to room temperature naturally and a large amount of methanol was added to precipitate the FeS\(_2\) NCs. The product was concentrated by centrifugation and then dispersed in hexane. 50 μL of a suspension with 0.1 M iron pyrite NCs was spin coated on a glass substrate sequentially to obtain an iron pyrite film, which was used for
characterization. As-coated NCs were highly insulating because of residual OLA surfactant ligands on the surfaces from the synthesis process. Subsequent heat treatment was necessary to effectively remove these ligands and make the film more conducting without altering the phase and shape of the NCs. The effects of such a heat treatment in a sulfur atmosphere on the crystal structure and morphology are shown in Figure 3.

Figure 3a shows the XRD patterns of the as-prepared and sulfurized pyrite NCs. All peaks could be indexed to the cubic iron pyrite phase. The phase purity is also evident from the Raman spectra in Figure 3b. The optical band gaps of the iron pyrite NCs were found to be at 0.72 and 1.02 eV, corresponding to indirect and direct excitation, respectively. Unlike spray-pyrolyzed thin films, these spin-coated thin films of NCs were found to be photoactive, making them suitable as a photon absorber in devices. Hall measurements using Van der Pauw geometry was utilized to study the electrical properties of the film. Films were found to be p-type with a high charge-carrier concentration of approximately $10^{18}$ cm$^{-3}$ but with lower hole mobility and conductivity than spray-pyrolyzed film. Scheme 1 shows the spray pyrolysis, hot-injection, and sulfurization processes.

3. Device Application and Novel Properties

3.1. Catalyst in DSSCs

DSSCs are viable alternatives to silicon-based solar cells, especially for indoor applications. Research efforts have been dedicated to reduce the cost and to scale up the technology to commercial level. DSSCs consist of three major components, namely photoanode, photocathode, and electrolyte. At the photoanode, electrons in dye molecules excited by the photons are transferred to a wide band gap semiconductor such as TiO$_2$ or ZnO. The redox couple in the electrolyte reduces the dye back to its ground state and in turn accepts electrons from the counter electrode catalyst. $I_{3}^-/I^-$ based electrolytes are commonly used in DSSCs, with Co-based electrolytes being promising alternatives.

As the position of redox potential of the electrolyte and the work function of the counter electrode affect the kinetics, the choice of the electrolyte and the corresponding catalyst are vital. Pt or C are commonly used as the counter electrode in DSSCs because of their good catalytic activity. Pt, although efficient, increases the cost of the cell whereas C exhibits a lower catalytic performance but at a lower cost. Therefore, development of alternative counter electrode ma-
Materials that have the advantages of both Pt and C would be a notable improvement. Pt performs best with the $I_3^-/I^-$ redox couple whereas poly(3,4-ethylenedioxythiophene) (PEDOT) is the catalyst of choice for Co-based electrolytes. It should be highlighted that PEDOT is one of the very few materials that could perform well with Co-based electrolytes.

Recently, we evaluated iron pyrite to replace Pt and C counter electrodes. Its transition-metal chemistry, Fe–S co-

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**Figure 3.** (a) XRD patterns, (b) confocal micro-Raman spectra, and SEM images of (c) as-prepared and (d) sulfurized iron pyrite NCs. Reprinted with permission from Ref. [8]. Copyright 2016 American Chemical Society.

**Scheme 1.** Representation of the spray pyrolysis, hot-injection, and sulfurization processes. Reprinted with permission.
ordination, and high conductivity are favorable attributes to catalyze the reduction reaction at the counter electrode, enabling faster kinetics in the photoelectrochemical device. Spray-pyrolyzed and subsequently sulfurized thin films exhibit higher conductivity than NC films and hence were chosen for this application as good conductivity will reduce the series resistance in the cell. Catalytic activity and surface roughness play a pivotal role in the overall performance. To assess the catalytic activity, we conducted cyclic voltammetry (CV) for a thin film sulfurized at 400 °C. Figure 4 shows the CV in a three-electrode system (working, reference, and counter electrodes). The electrolyte used was 10 mm LiI, 1 mm I₂ and 0.1 mm LiClO₄ in acetonitrile. The scan rate was fixed at 100 mV s⁻¹. Positive current peaks correspond to the oxidation reaction whereas negative current peaks are the reduction reaction of I₂ / I⁻. The CV curves of the iron pyrite film resemble closely those of Pt, indicating similar activity to catalyze the above reactions in the electrolyte. Notably, the reduction peaks associated with I₂ to I⁻ and I₃⁻ to I⁻ reduction processes are slightly shifted to the right for the case of iron pyrite, by approximately 0.05 V, with respect to the reduction peaks obtained using Pt as counter electrode, signifying that the reaction occurs slightly faster with an iron pyrite counter electrode. Similar CV measurements are shown for the Co⁹⁺/Co⁷⁺ redox electrolytes in Figure 4b. Current densities obtained from CV plots show higher values for iron pyrite with Co⁹⁺/Co⁷⁺ electrolyte in comparison to PEDOT as counter electrode, indicating that iron pyrite can be an efficient counter electrode for this dye system too. Furthermore, higher surface roughness is desirable for catalytic reaction as it provides more possible reaction sites. Figure 4c shows the atomic force microscopy image of pyrite, Pt, and PEDOT surfaces. It is clear that the pyrite surface is rougher than the Pt and PEDOT surfaces. The surface roughness of pyrite is approximately 35 nm.

DSSC devices with iron pyrite counter electrodes were prepared with I₃⁻ / I⁻ and Co(byp)₃⁺ / Co(byp)₂⁺ (byp = 2,2'-bipyridine) electrolytes, and the resulting current density—

![Figure 4. CV scans of (a) FeS₂ and Pt film on FTO substrate in I₃⁻ / I⁻ redox electrolyte, (b) FeS₂ and PEDOT film on FTO (blue) in cobalt-based redox electrolyte. (c) Surface morphology of Pt coated on FTO, FeS₂ thin film on FTO, and PEDOT on FTO. Reprinted with permission from Refs. [38] and [34].](image-url)
voltage ($J-V$) characteristics and the external quantum efficiency (EQE) measured under 1 Sun AM1.5 illumination (100 mW cm$^{-2}$) are shown in Figure 5 and the data are summarized in Table 1. The $J-V$ curve for $I_3/\text{Co}$ electrolyte shows an efficiency ($\eta$) of 7.97% with iron pyrite counter electrode, which is close to 7.54% obtained for the device with Pt as counter electrode. Other pyrite-type binary compounds such as NiS$_2$ and CoS$_2$ and their alloys also demonstrate good catalytic activity, among which metallic CoS$_2$ demonstrates the highest performance in terms of efficiency.$^{[35,40]}$

The major contribution to the efficiency comes from the improvement in current density. The current density increases by about 2%, which manifests in an enhanced EQE spectrum. In summary, the overall lower resistance and higher catalytic activity towards redox species and the higher surface roughness lead to a better performance of DSSC when using a pyrite counter electrode compared to those with Pt or C.

3.2. Photodiode of p-i-n type with the layer configuration ZnO–FeS$_2$–CuI

Solution-processed photoactive iron pyrite NCs could be potential candidates for optical devices such as photodetectors and photodiodes that need a good photon-absorber layer. The low band gap of circa 0.95 eV provides an excellent window for fabricating photodiodes covering the optical spectrum up to the infrared region. In addition, the NCs could be spin coated on any substrate to produce an iron pyrite film. Hence, iron pyrite NCs were chosen for this investigation. Steinhagen et al.,$^{[62]}$ working with different configurations such as Schottky barrier cell and heterojunction solar cell, demonstrated that the solar-cell performance of iron pyrite nanocrystals was poor and their rectification ratio was limited by the large leakage current. However, they did not employ any sulfurization heat treatment on the particles but used a ligand exchange process to remove the organic surface ligands. As iron pyrite is inherently a good photon absorber, the electron- and hole-extraction strategies must be improved to prepare better photodiodes that could exhibit higher rectification ratios. We deployed n-type (ZnO) and p-type (CuI) layers to extract electrons and holes more effi-

<table>
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<tr>
<th>Electrolyte</th>
<th>Counter electrode</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA cm$^{-2}$]</th>
<th>FF</th>
<th>$\eta$ [%]</th>
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<td>$I_3/\text{Co}$</td>
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<td>15.20</td>
<td>0.65</td>
<td>7.97</td>
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<tr>
<td>Pt</td>
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<td>14.77</td>
<td>0.66</td>
<td>7.54</td>
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<tr>
<td>Co(bpy)$_2^{3+}$/Co(bpy)$_2^{2+}$</td>
<td>FeS$_2$</td>
<td>0.78</td>
<td>11.57</td>
<td>0.69</td>
<td>6.34</td>
</tr>
<tr>
<td>PEDOT</td>
<td>0.79</td>
<td>10.83</td>
<td>0.75</td>
<td>6.31</td>
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Figure 5. (a) $J-V$ curve and (b) IPCE of the FeS$_2$ and Pt counter electrode device with $I_3/\text{Co}$ electrolyte. (c) $J-V$ curve and (d) IPCE of the FeS$_2$ and PEDOT counter electrode with Co$^{3+}$/Co$^{2+}$ electrolyte.$^{[34]}$ Reprinted with permission from Refs. [38] and [34].

Table 1. Parameters of solar cells using different counter electrodes and electrolytes.
ciently from the photoactive iron pyrite layer in our ZnO–FeS\textsubscript{2}–CuI heterojunction configuration because their energy bands are favorably positioned.

As-synthesized NCs were subjected to a ligand-exchange treatment by dipping in 0.1 m thioglycolic acid (TGA) in acetonitrile before use in the device to remove any remnant organic ligands on the cube surface. Details of the procedure can be found in Ref. [63]. A scheme of the photodiode configuration is shown in Figure 6a whereas Figure 6b shows the cross-section SEM image of the device. Iron pyrite NCs were spin coated on ZnO microrods grown on Au/SiO\textsubscript{2} substrate. Subsequently, CuI was spin coated on the iron pyrite NCs and ITO was used as a top contact. For comparison, ZnO–CuI and ZnO–FeS\textsubscript{2} bilayer devices were also fabricated and evaluated. Figure 6c shows the I–V characteristics of ZnO–FeS\textsubscript{2}–CuI p–n photodiode under dark and AM1.5 illumination conditions. A rectification ratio of 197 is obtained at a bias of ±1 V for a ZnO–FeS\textsubscript{2}–CuI photodiode. Figure 6d shows the transient response of the photodiode. A short-circuit current density ($J_s$) of 0.5 mA cm\textsuperscript{2} and on–off ratio of 371 with short transient response (<1 s) was achieved under AM1.5 illumination.

These characteristics make our p–n photodiodes potential candidates for use in a self-power mode. The incident photon-to-current conversion efficiency (IPCE) spectra under zero bias voltage of the three devices are shown in Figure 6e. The ZnO–CuI photodiode shows a maximum IPCE at 350 nm that does not change much for wavelengths longer than 500 nm, which matches with the band gap of ZnO and CuI. For ZnO–FeS\textsubscript{2} and ZnO–FeS\textsubscript{2}–CuI photodiodes, the IPCE values increase with decreasing wavelength, which agrees with the absorption spectrum of a FeS\textsubscript{2} film. To study the spectral response, wavelength-dependent responsivity $R(\lambda)$ was obtained (Figure 6f). The ZnO–FeS\textsubscript{2}–CuI p–n photodiode has a larger responsivity in the full wavelength region than the ZnO–FeS\textsubscript{2}/ITO photodiode, which could be attributed to the higher charge-collection probability of photogenerated carriers attributable to the wide depletion region caused by the higher light absorption and lower charge-carrier mobility in iron pyrite. The maximum respon-

![Figure 6](image-url)
sivity of 17 mAW⁻¹ at 400 nm was exhibited by the ZnO–FeS₂–CuI p-i-n photodiode. In addition, there is a broad peak shoulder around 900 nm, which corresponds to the optical absorption characteristics of the FeS₂ NC film. The photoresponsivity of the device is extended to near-IR wavelength, showing its potential for application in infrared light range.

3.3. Heterojunction FeS₂–CdS solar cells

Iron pyrite NC films exhibit high optical absorption and show good photoresponse, which allows it to be used as an absorber layer in a heterojunction solar cell. Judicious engineering of the charge-carrier extraction layers is required to obtain a high voltage output from iron pyrite. We fabricated FeS₂–CdS heterojunction solar cells to demonstrate the potential of iron pyrite NCs in this application. First, the as-synthesized NCs were surface treated or annealed to allow conduction across particle boundaries. We performed sulfurization treatment (described in Section 2.2) on iron pyrite NCs spin coated on a Mo substrate. Thereafter, a CdS film was deposited by chemical-bath deposition and then a transparent conducting layer (aluminum-doped zinc oxide (AZO)) was sputtered followed by thermally evaporating Ag finger electrodes to complete the device architecture.

Figure 7a shows the J–V curve of the solar cell under 1 Sun (100 mWcm⁻²) illumination. A photovoltage of around 94 mV was obtained with a fill factor (FF) of 0.28 and a current density of 0.4 mAcm⁻², showing that an iron pyrite NC film could be used as a solar absorber material. Figure 7b shows the EQE of the FeS₂–CdS heterojunction solar cell where the photocarrier collection band edge is at circa 1.1 eV, close to the band gap of pyrite. Figure 7c shows a scheme of the charge-transfer process in this heterojunction device.

The energy-band position of CdS and Mo with FeS₂ NCs are favorable for charge carriers to be extracted through the electron- and hole-transporting contacts, respectively. A cross-section SEM image of the device is shown in Figure 7d. The active iron pyrite layer and the top and bottom electron- and hole-collecting layers are distinctly visible. Despite the low photovoltage output, this approach proves that solar-cell

![Figure 7](Fig7.png)
devices could be made, in principle, using iron pyrite nanostructures. To improve the photovoltage output, it would be necessary to develop methods for surface treatment and intrinsic defect reduction in iron pyrite. Also, shunting pathways could be blocked by making better junctions, which could result in good current rectification to improve device characteristics.

3.4. Iron pyrite single-crystal device

Photoelectrochemical cells using iron pyrite single crystals have been evaluated with iodine-based redox electrolyte and the highest solar-to-electricity conversion efficiency reported is around 2%."\cite{1,9} This is clearly low; hence, most studies on iron pyrite single crystals have remained fundamental in nature to understand the reasons for the poor performance. Some recent studies on pyrite single crystals revealed the existence of a surface inversion layer and band bending at the surface."\cite{9,21,64} Although no consensus has been reached on the origin of the inversion layer, researchers broadly agree that it is caused by a complex electronic structure of the surface layer. Thus, it would be beneficial to investigate the surface and bulk conduction characteristics to shed some light on this issue. There is no direct experimental method to study the differential surface and bulk conduction. Most researchers rely on a combination of techniques such as photoelectron spectroscopy, surface-potential measurements, thickness-dependent conductivity measurements, or Mott–Schottky analysis to indirectly study the differential conduction behavior of the surface and the bulk of a crystal.

Herein, an attempt is made to directly measure the difference between the bulk and surface conduction through a temperature-dependent investigation of the electrical resistance for some specific geometrical configurations similar to those used by Shekhar et al.\cite{65} and Wolgast and co-workers:\cite{66,67} A natural cube-shaped crystal (from Navajun, Spain) with a side length of approximately 1 cm was cut along the (100) plane using a diamond saw into square wafers of 1 mm thickness. The wafers were polished to remove any surface artefacts caused by the cutting. All characterizations were performed on polished pyrite wafers, as shown in Figure 8. The XRD pattern of the crystal surface shows only a single peak corresponding to the (100) plane (Figure 8a). A sharp peak with a low full width at half maximum (FWHM) reveals the high crystallinity of the sample. To check the phase purity of the crystal, Raman spectroscopy was performed using a 532 nm laser. Figure 8b shows the Raman spectrum of the single crystal. All peaks correspond only to the cubic pyrite phase. No peaks corresponding to other Fe–S phases could be detected, which indicates phase purity of the crystal. The E_g, T_g(1), A_g, and T_g(3) phonon modes can be clearly seen in the spectra. Also, a high Raman intensity and narrow peaks (FWHM) are indicators for the high crystallinity.

Figure 8. (a) XRD of the polished crystal surface in thin-film arrangement, (b) Raman spectra of the pyrite single crystal, (c) Four probe I–V measurement configurations to measure resistances along different current pathways.
Using Hall measurements, the sample was confirmed to be n-type with a high mobility, in contrast to thin films that often show p-type conductivity and low carrier mobilities. For electrical transport measurements, contacts were prepared on both sides of the pyrite wafer (Figure 8c). Temperature-dependent electrical transport measurements were made on the crystal using three different four-probe configurations, namely top, bottom, and hybrid (Figure 8c) in the temperature range 30–350 K.

A constant, direct current source was used to apply a steady current across two terminals, and the potential difference generated across different terminals was measured, which permitted the determination of the apparent resistance. The resistance measured at different temperatures in this manner is shown in Figure 9. Resistances measured in the top, bottom, and hybrid configurations will be referred as \( R_{T} \), \( R_{B} \), and \( R_{H} \), respectively. The measured resistances \( R_{T} \) and \( R_{B} \) were approximately equal whereas \( R_{H} \) started to increase as the temperature decreased to below 130 K. A previous study by Law and co-workers on synthetic iron pyrite crystals showed an increase in the surface resistance at a similar temperature, which they argued was caused by a surface inversion layer.\(^{[21]}\) The above observed difference for bulk and surface conductivity seem to indicate that surface conduction dominates at temperatures below 130 K. The higher resistance measured in hybrid configuration may be attributable to a longer conduction path along the surface when the surface conductivity dominates. However, above 130 K, the resistance in all three configurations were similar and no difference was observed between the surface and bulk resistances. At temperatures below 130 K, the electrical transport is a complex function of both the surface and the bulk resistances. If there were no differences between the bulk and the surface conductivities, then \( R_{T} \) and \( R_{B} \) would be similar whereas \( R_{H} \) would be higher because of the longer conduction path. The order for the resistances at low temperatures is \( R_{H} \geq R_{T} \geq R_{B} \), which implies that surface conduction dominates as the bulk becomes more and more insulating as the temperature decreases. Hence, the trend \( R_{H} \geq R_{T} \geq R_{B} \) is obtained. As the major conduction path would be the surface, \( R_{H} \) would dominate.

A scheme of the current flow in hybrid configuration is shown in Figure 9b. When the current flows through the surface, the total resistance is given by the surface resistance \( (R_{surf}) \) whereas in the case of bulk conduction, the conduction would be governed by the bulk resistance \( (R_{bulk}) \). However, the data in Figure 9a show a higher resistance at low temperature, which could be attributed to the dominance of \( R_{surf} \) as the current flows through a longer path (in the top configuration) at the surface. The reason why \( R_{surf} \) measured in the top configuration would be higher than that measured in the bottom configuration is because the current in the top configuration would be higher across \( V_{s} \) and \( V_{b} \) terminals than in the case of bottom configuration for \( R_{B} \). These results are direct experimental proof of the surface and bulk conductivity difference in iron pyrite single crystals at low temperatures. In addition, the simplicity of this experiment can be applied to the study of surfaces in other semiconductors.

### 4. Summary and Future Perspective

We have presented an overview of the application potential of iron pyrite in specific devices for energy harvesting. Iron pyrite thin films prepared by spray pyrolysis can be operated efficiently as a counter electrode in dye-sensitized solar cells (DSSCs). Iron pyrite could be a potential low-cost solution for counter electrodes in DSSCs for large-scale application. Photodiode and heterojunction applications of solution-processed iron pyrite nanocubes demonstrate that phase-pure iron pyrite could be synthesized and used in these devices for energy-harvesting applications through judicious engineering of device architectures and interfaces. Finally, we showed the difference in surface and bulk conduction in natural pyrite single crystals at temperatures <130 K. The results were provided by performing direct experimental measurements that could be deconvoluted to derive surface and bulk conductivities in iron pyrite single crystals. This would be extremely useful to study the surface of iron pyrite and

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**Figure 9.** (a) Resistance vs. temperature for three configurations. (b) In hybrid configuration, current applied across \( I_{s} \) and \( I_{b} \) terminal and voltage is measured at terminal \( V_{s} \) and \( V_{b} \). When the surface conduction dominates, current flows through the surface whereas for a homogeneously conducting sample current flows through the bulk. Blue arrows indicate the flow of current.
could serve as a platform to directly analyze the effect of surface treatment and passivation. These results would help in designing future pyrite photovoltaic and related devices.

The interesting properties of pyrite films arise from their morphology, crystallinity, and S/Fe atomic ratio. Control of these parameters could open up the window for novel energy-harvesting applications in many devices. Sulfurization treatment protocols could be useful to manipulate defect populations and phase purity in pyrite thin films, giving opportunities to achieve desirable electronic and transport properties. Significant focus is required to understand some fundamental issues to enable successful photovoltaic device applications. Some fundamental issues that need to be understood are the doping effects on defects, phase instability/im purities, and the differences in surface and bulk conduction. These issues have hampered the development of pyrite-based optoelectronic devices for a long time. Therefore, future research is expected to focus on (i) defect passivation studies, (ii) improved heterojunction formation with better band offsets, (iii) device architectures, and (iv) surface studies on single crystals and nanostructures. Success in understanding the fundamentals and the ability to mitigate inherent defects coupled with suitable device architectures could make iron pyrite a significant photoactive material in the industry because of its low cost and industrially amenable film-formation techniques.

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Conflict of interest

The authors declare no conflict of interest.

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