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Shock wave-driven phase transition of iron sulphide for enhanced photocatalytic application: a combined experimental and DFT approach†

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In the present investigation, we systematically investigate how acoustic shock waves induce a phase transition from FeS to α -Fe₂O₃ and how this transition influences the material's structural, morphological, optical, and photocatalytic properties. The findings from X-ray diffraction (XRD), scanning electron microscopy (SEM), ultraviolet differential reflectance spectroscopy (UV-DRS), and X-ray photoelectron spectroscopy (XPS) studies unequivocally demonstrate a complete phase transition from FeS to α -Fe₂O₃ at 600 shock pulses. The control sample has an uneven morphology. The material exhibits moderate morphological changes but maintains its fundamental FeS phase after 400 shock pulses. On the other hand, the material undergoes a notable structural and morphological change at 600 shock pulses, assuming a distinct needle-like shape that is suggestive of phase transition and improved crystallinity. UV-DRS analysis reveals an increase in optical reflectance and a noticeable blue shift in the energy band gap under 600-shock conditions, further supporting the formation of a new phase with altered electronic structure. Density Functional Theory (DFT) calculations further support these findings, revealing a reduction in the electronic density of states (DOS) near the Fermi level upon phase transition, indicative of the enhanced charge separation crucial for improved photocatalytic performance. As a result, for FeS subjected to 600 shock pulses, transition to α -Fe₂O₃ exhibits superior photocatalytic efficiency and reaction rates compared to the control and other shock-treated samples.

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1. Introduction

The incredible versatility of phase transition in materials has led to a surge in studies in recent years, with researchers from all corners of the scientific spectrum looking for interesting materials.¹ The intriguing journey of studying phase change reactions in materials is always yielding new information about crystal structures and their functions.² We can gain valuable insight into and direct evidence of the mechanism by studying materials' behaviour during phase transitions when subjected to extreme conditions. This understanding could pave the way for developing materials for various applications.³ Likewise, because certain materials have the potential to contribute to

astounding applications, these kinds of phase transition experiments carried out on materials have significant importance not only in the research area but also in the world of industrialization.^{4,5} Such study also offers a different approach to finding breakthrough materials for future use in industry.⁶ It is possible to induce phase transformation by heat treatment, processing of the material, and by altering the parameters during synthesis, such as chemical composition, oxidation, reduction, *etc.*⁷ An additional potential option is to induce modifications to materials by employing external factors, such as pressure, temperature, a magnetic field, an electric field, or epitaxial strain.^{8,9} Moreover, applying pressure is a great way to fine-tune electrical, magnetic, structural, and vibrational characteristics for practical and theoretical analysis.¹⁰ Implications of significant importance can be discovered across the whole field of physical research, including the biological sciences.¹¹ As a result of high pressure, virtually all materials undergo a transformation into distinct phases, which alters material crystallographic structures.¹² In light of the fact that the crystal structure plays a preponderant role in determining the qualities of materials and their performance, it is of the utmost importance to increase our understanding of their crystal structure.² Since the molecular volume of high-pressure phases is low, subjecting materials to high pressure is a useful technique for

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obtaining phase transitions.¹³ Theoretically, the equivalence criteria of matching Gibbs energies determine individual phase boundaries. There is a noticeable discrepancy between the phase equilibrium lines and the real transformation line at the start of the experiments. Therefore, partial pressure transitions (PTs) to high-pressure phases take place at pressures greater than the equilibrium pressure.¹⁴ Considerable experimental research has been conducted over the course of many years to investigate the phase transition of a variety of materials under static and dynamic pressure conditions.^{15,16} Apart from contributing to the investigation of static high-pressure and high-temperature observations, dynamic shock-induced phase transition experiments carried out on materials might offer essential details for the scientific community to aid in the understanding of the behaviors of molecules and atoms.^{17,18} In recent years, dynamic shock-induced phase transition experiments have emerged as one of the most promising areas of scientific inquiry. Many fascinating findings have been achieved in environments of extreme pressure in the past few decades, all because of advancements in experimental methods and computer models.^{19–21} Sivakumar *et al.* investigated using dynamic shock wave to induce a switchable phase change in Li_2SO_4 samples, switching them from an amorphous-glassy-crystalline to an amorphous phase.²² Furthermore, sodium sulphate crystals with a switchable phase transition were synthesised and displayed to work under shock conditions. The pattern of phase transitions, where changing to the sequence of shock pulses is 0, 1, 2, 3, and 4.²³ Shock impact studies can employ these kinds of observations to infer the thermal-kinetic and thermodynamic states. At the same time, it is fascinating to accomplish phase transitions of materials under shocked conditions, where the results are similar to those of static high-pressure studies. In contrast to traditional thermal or chemical synthesis techniques, shock waves provide an extremely quick and non-equilibrium way to create phase transitions, which frequently lead to metastable structures, increased defect densities, and improved surface reactivity, all without the need for harsh chemicals or time-consuming processing.²⁴ Contributing to enhanced photocatalytic performance, these characteristics offer a new and energy-efficient method of material engineering.²⁵ In this particular case, we have opted to investigate the crystallographic phase stability of iron sulphide (FeS) under a shock wave flow environment for photocatalytic application. Iron sulphides are minerals that exist naturally and may be found in a wide range of geological formations.²⁶ Additionally, FeS has a narrow band gap, excellent adsorption characteristics, and a unique capacity to transport electrons.²⁷ The initial finding of a high-pressure phase of FeS was made by Taylor and Mao.²⁸ According to previous reports, FeS exists in five stable phases: troilite (with parameters $a = 3a_f$ and $c = 2c_f$), hexagonal phase (with parameters $a = 2a_f$ and $c = c_f$), NiAs type phase (with parameters $a = a_f$ and $c = c_f$), and high-pressure phase (which remains stable at pressures more than 7 GPa).^{29,30} Ming *et al.* analysed FeS *in situ* resistance and reported four anomalous alterations during compression, which is evidence that the phase transition of semiconductor-semimetal occurs, and two of these happen at pressures of 4.7 GPa

and 62.3 GPa.³¹ To the best of our knowledge, all high-pressure measurements carried out on FeS were on static conditions; studies on the dynamic pressure of FeS are difficult to find. Consequently, it is possible that FeS NPs present a considerable opportunity for use in a variety of applications with extreme conditions. Specifically, photocatalysts for the breakdown of harmful organic compounds are seeing a rise in the utilisation of metal chalcogenides. A major environmental concern is the utilisation of visible light to initiate thermodynamically undesirable processes to break down organic hazardous dyes. Chemical and structural changes can control the surface atomic coordination and structure, which in turn control the catalytic efficiency of FeS.³² Maji *et al.* reported that, when exposed to light, FeS NPs enhance photocatalytic activity through the catalytic breakdown of MB. Furthermore, it follows standard Michaelis–Menten kinetics and demonstrates exceptional catalytic efficiency.³³ Tan *et al.* analysed the photoactivity of FeS/WS₂ nanosheets; research findings demonstrate that the FeS/WS₂ heterojunction outperforms a pure WS₂ catalyst due to its promotion of charge separation, which in turn enhances photocatalytic activity.³⁴ Dutta *et al.* investigated nanocrystalline FeS/FeSe and reported that, unlike FeSe NPs, the rate constants for dye degradation when exposed to FeS NPs are higher.³⁵ While all prior studies on FeS NPs were carried out in static or ambient pressure conditions, this study discusses the morphological, structural, optical, and chemical properties of FeS subjected to dynamic shock waves. Additionally, photocatalytic dye degradation using MB dye tests was performed on the control and the shock wave-loaded FeS samples.

2. Experimental details

2.1 Synthesis procedure

The elemental source materials Fe (99.5%) and S (99.5%) were obtained from SRL (Sisco Research Laboratories Pvt. Ltd, India) and used for the milling process. Fe and S powders were added to the milling jar at a stoichiometric ratio of 1 : 2, along with process control agent (PCA) toluene. Planetary milling was performed utilising the Fritch Pulversitte P-6 classical line, with a hardened steel milling jar with a tungsten carbide inner wall and a volume of 250 mL. The balls were made of tungsten carbide and had two different diameters/weights (10 mm/8 g and 15 mm/26.2 g). A ball-to-powder ratio (BPR) of 15 : 1 and a milling speed of 500 rpm were maintained for 24 hours of milling. For every one hour of run time, 10 minutes of pause time was given.³⁶ Further, the 24-hour milled samples were subjected to shock wave treatment for phase transitions analysis.

2.2 Characterization details

The shock wave experiments were conducted using a Tabletop Reddy shock tube. Using a Rigaku X-ray diffractometer with a Bragg–Bretano focusing geometry and monochromatic $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$), powder X-ray diffraction (PXRD) patterns were collected throughout the experiment. A JASCO V-530 UV-vis spectrophotometer was utilised to carry out



photocatalytic research as well as research on reflectance spectra. Sample morphology was examined using a scanning electron microscope (SEM, VEGA TESCAN 3 variant). X-ray photoelectron spectroscopy, also referred to as XPS, was carried out with the assistance of a Thermo ESCALAB 250.

2.3 Computation details

To characterise the relationship between core and valence electrons, density functional theory (DFT) calculations were carried out using the Vienna *Ab initio* Simulation Package (VASP) in the projector-augmented wave (PAW) method.^{37,38} The exchange–correlation energy was treated using the Perdew–Burke–Ernzerhof (PBE) functional in the generalised gradient approximation (GGA).³⁹ The conjugate gradient approach was used to minimise the total energy for structural relaxation, with a force convergence criteria of 10^{-3} eV Å⁻¹. Using a Monkhorst–Pack *k*-point grid and an energy cutoff of 600 eV for the plane-wave basis set, the Brillouin zone was sampled. For electronic occupation, 0.1 eV Gaussian smearing was used. The energy difference barrier of 10^{-6} eV per atom was reached *via* the electronic self-consistency cycle. To analyse the pressure-induced phase transition, the total energy as a function of volume was fitted to the universal equation of state (EOS). For band structure calculations, the irreducible part of the first Brillouin zone was sampled along high-symmetry *k*-points. The density of states (DOS) and electronic band structures were computed with a denser *k*-point mesh to ensure accurate electronic properties.

2.4 Photocatalytic degradation of methylene blue

The photocatalytic activity of shock wave-loaded FeS NPs was assessed in this study. The purpose of this study was to explore the degradation of Methylene Blue (MB) in an aqueous solution in the presence of sunlight.^{40,41} With the objective of achieving an ideal adsorption–desorption equilibrium amongst the solution containing the MB dye and the catalyst, 10 mg of FeS catalyst powder was dispersed in 100 mL of aqueous methylene blue (MB) solution with a dye concentration of 10 mg L⁻¹. In order to eliminate pH-induced artifacts in dye degradation, the photocatalytic studies were carried out in neutral pH settings (~7). Following that, the resulting solutions were exposed to sunlight,

and specimens were collected at regular intervals of fifteen minutes to determine the absorbance at a wavelength of 665 nm of the substance being studied. As the length of the reaction progressed, the findings showed that there was a decrease in the concentration of dye in the solution itself. This finding suggests that the photocatalysts worked well in the degradation of MB in an aqueous solution when exposed to sunlight.^{42,43}

2.5 Shock wave loading

The intricacies of the propagating shock created within the shock tube and the parameters required to generate a shockwave were better understood by means of the evaluation of the shock tube.^{44,45} There are three parts to it: the driver, the driven, and the diaphragm sections. With an interior diameter of 1.5 cm in the driver as well as driven sections, the tubes of the driver (48 cm) and driven (33 cm) parts are made of seamless steel. To generate shock waves, atmospheric air was utilised in the driver and driven parts as the working resource, as shown in Fig. 1. Through the diaphragm part, the driver and driven sections are separated. With the assistance of pneumatic cylinders, diaphragms were introduced into the area dedicated to the diaphragm. During the process of compressing the air from the atmosphere into the driver section, the diaphragm was breached at the critical pressure.⁴⁶ This caused a shock wave to form, which then travelled along the driven tube and struck the FeS sample.

For the purpose of this experiment, a shock wave with a Mach number of 1.7 was used to repeatedly strike the test sample with 200, 400, and 600 shock pulses, maintaining a two-second interval between consecutive pulses. It is worth noting that the duration of each pulse (test time) is 2.5 milliseconds. The pressure generated in the current investigation was 0.59 MPa, and a transient temperature of 520 K was calculated using the standard Rankine–Hugoniot (R–H) relation.⁴⁵ Both the control samples and the shock wave loaded samples were sent for analytical tests once the experiment involving shock wave loading had been completed.⁴⁷

3. Results and discussion

3.1 PXRD analysis

The PXRD has been measured for the control and various shocked samples, which exhibit a hexagonal crystal structure

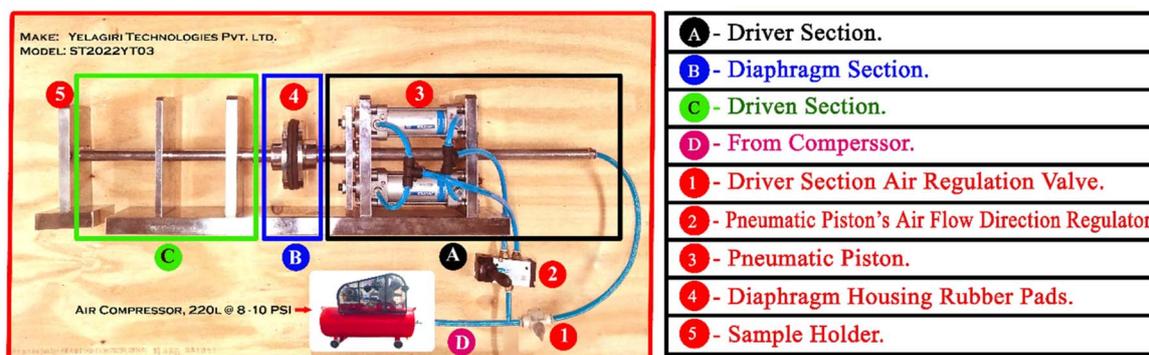


Fig. 1 Schematic illustration of semi-automatic Reddy tube.



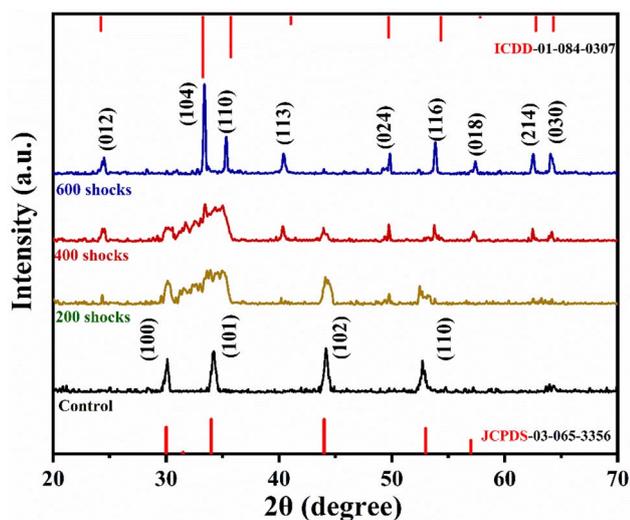


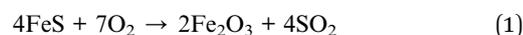
Fig. 2 XRD pattern of control, 200, 400 and 600-shocked FeS sample.

with space group $P\bar{6}2c$ (190), in accordance with the existing literature.⁴⁸ The lattice parameters for this material are $a = 5.89$ Å, $b = 5.90$ Å, and $c = 11.42$ Å.⁴⁹ Fig. 2 illustrates the PXRD pattern of FeS as well as the phase transition that occurs at the 600-shock. In accordance with the standard JCPDS card no. 89-6926, the peaks in the controlled FeS diffraction pattern that have been identified are (100), (101), (102), and (110).⁵⁰ It has been noticed that there are significant variations in the context of diffraction peak intensity and peak position under shocked conditions. Under 200 shocks, the intensity of the existing peaks was reduced, and the diffraction peak (101) broadened.

Further, moving on to 400 shock pulses, a few peaks vanished, and a new diffraction peak appeared. Additionally, increasing the shock pulses number to 600 revealed more peaks, such as (012), (104), (110), (113), (024), (116), (018), (214), and (030), strongly indicating the onset of a new α -Fe₂O₃ phase with rhombohedral structure. Using the JCPDS number 01-071-0053 as a reference, we found that all of the identified peaks were in good agreement with the typical hematite α -Fe₂O₃ (rhombohedral, $R\bar{3}c$) (167).⁵¹ It is common for FeS to have a hexagonal crystal shape in its initial form. Troilite is a mineral composed of iron (Fe) and sulphur (S) atoms organised in a precise pattern within a lattice.⁵²

The acoustic shock pulse deforms the FeS lattice by creating a high-pressure and temperature environment upon impact. This pressure causes oxygen atoms from the surface to enter the FeS lattice. Once inside the lattice, the oxygen atoms react with sulphur atoms because the oxygen has a higher electronegativity (3.44) than those of sulphur (2.58) and iron (1.83). Because of oxygen's stronger electronegativity, it is more likely to form sulphur–oxygen bonds than iron–sulphur bonds. Therefore, sulphur dioxide (SO₂) gas is produced and released. At the same time, iron oxides are formed as a result of the reaction between oxygen and iron atoms (see Fig. 3).

The formation reaction is given below



Each time an α -Fe₂O₃ molecule forms, two SO₂ molecules are generated and escape from the lattice, creating vacancies. These empty spaces allow more oxygen atoms to penetrate the lattice, facilitated by the material being in a molten state. Additionally,

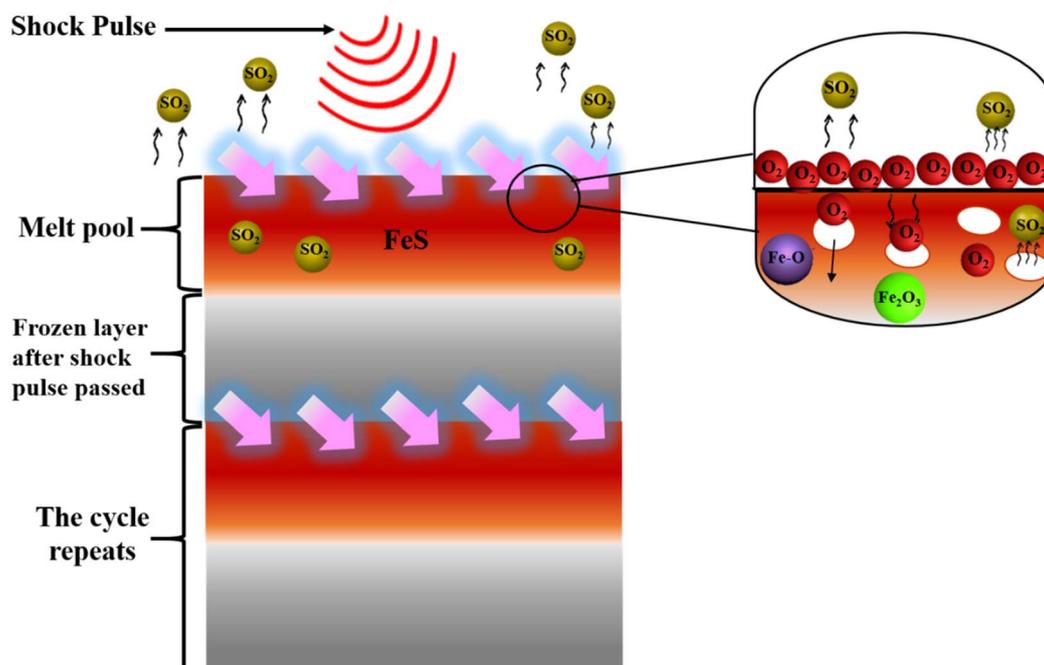


Fig. 3 Schematic representation of FeS nanoparticles undergoing structural transformation under shock wave treatment. The inset shows atomic-level rearrangement illustrating the replacement of S by O and the formation of Fe–O bonding.



the shock pulse generates high pressure, drastically reducing the activation energy required for these processes.

As a result, the peak broadened and decreased intensity occurs, as seen in Fig. 2. Iron sulphide is represented by the chemical formula FeS; it combines S^{2-} anions with Fe^{2+} cations. Octahedral coordination is a common feature of FeS crystal structures. The transition from FeS to α -Fe₂O₃ occurs along a pathway affected by the severe physical and chemical conditions when the material is subjected to a high dynamic pressure and temperature environment. Because of the compressive force of high dynamic pressure, the crystal lattice might undergo the above-mentioned adaptations. Iron undergoes an oxidation reaction, whereas the oxidation of iron results in the transition of oxidation state from Fe^{2+} in FeS to Fe^{3+} . The rates of most chemical reactions, including oxidation, are known to increase as pressure and temperature increase. Whenever the temperature rises, the molecules of the reactants gain energy, which speeds up the process and causes more frequent collisions. Overcoming an activation energy barrier is probably involved in the oxidation of hexagonal FeS. This barrier may be more easily overcome under higher temperatures, which speed up the rate of oxidation. The formation of α -Fe₂O₃ is the result of a reaction between FeS and oxygen, which functions as an electron acceptor. Over the course of these processes, electron transfer takes place. The presence of electron acceptors makes it easier for electrons to travel around, which in turn increases the number of oxidation states of iron. Similarly, Li *et al.* investigated the phase transitions as well as reactions of non-oxidized

alongside mackinawite (FeS) in hydrogen sulphide and helium gas. An intermediate phase, known as greigite (Fe₃S₄), can be formed through the reaction of FeS. In addition, greigite can undergo an exothermic reaction, which results in the formation of pyrite (FeS₂), a process that emits heat. The complete process wherein pyrite is produced when electron acceptors are present.⁵³ However, in the current investigation, there is no formation of an intermediate phase up to 600-shock pulses. The availability of electron acceptors, high pressure and temperature conditions are some of the overarching parameters that greatly influence the reaction pathways, which in turn cause the phase transformation of FeS into α -Fe₂O₃.

3.2 Morphological analysis

SEM analysis was undertaken to offer significantly persuasive evidence for the shock wave triggered phase transformation taking place in the FeS NPs, alongside the resulting microscopy images presented in Fig. 4. The figure shows that FeS is composed of tiny, irregularly shaped nanoparticles.⁵⁴ As a result of the reduction in shape at the 200 shock condition, most of the spherical-shaped particles are transformed into coral reefs with petals. The picture that corresponds to this transformation can be found in Fig. 5. Following 300 shocks, the spherical shape is virtually eliminated; as a result, flowers with petal shapes are formed with nanoneedles (Fig. 5). A deep magnification view of the 300-shocked sample is shown in Fig. 5, which shows the nanoneedle formation. This is due to the dynamic recrystallisation induced by the shock waves.⁵⁵ The oxidation

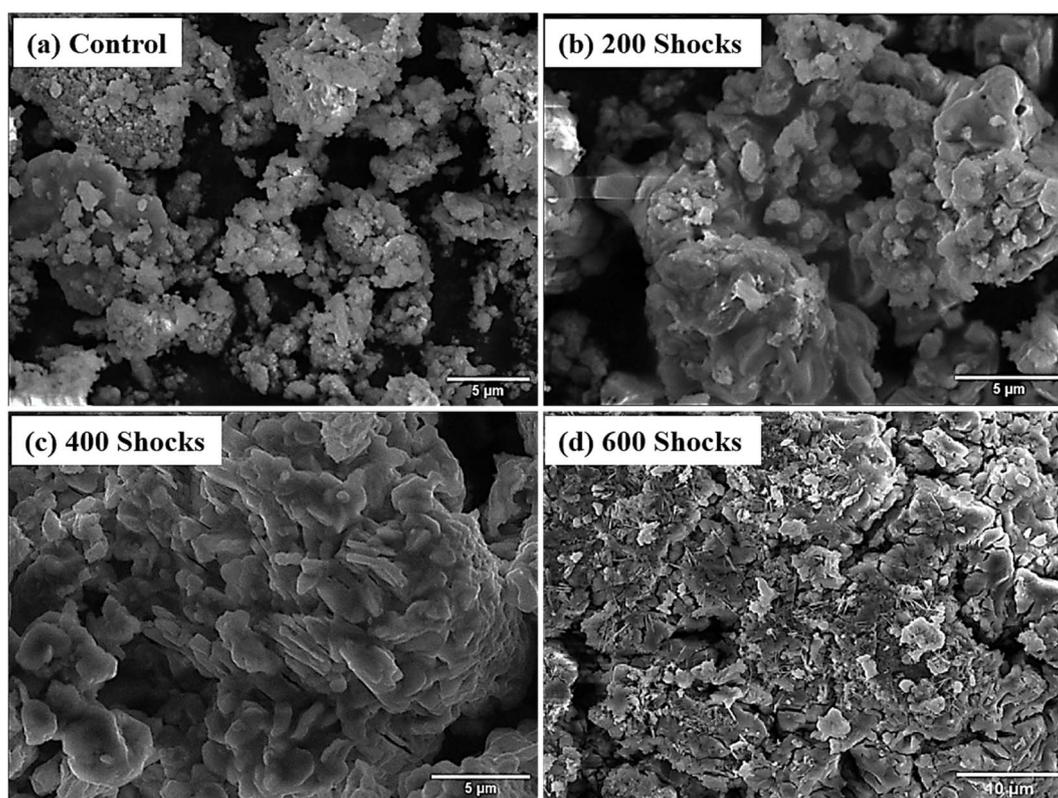


Fig. 4 SEM images of (a) control, (b) 200-shocks, (c) 400-shocks, and (d) 600-shocks treated FeS sample.



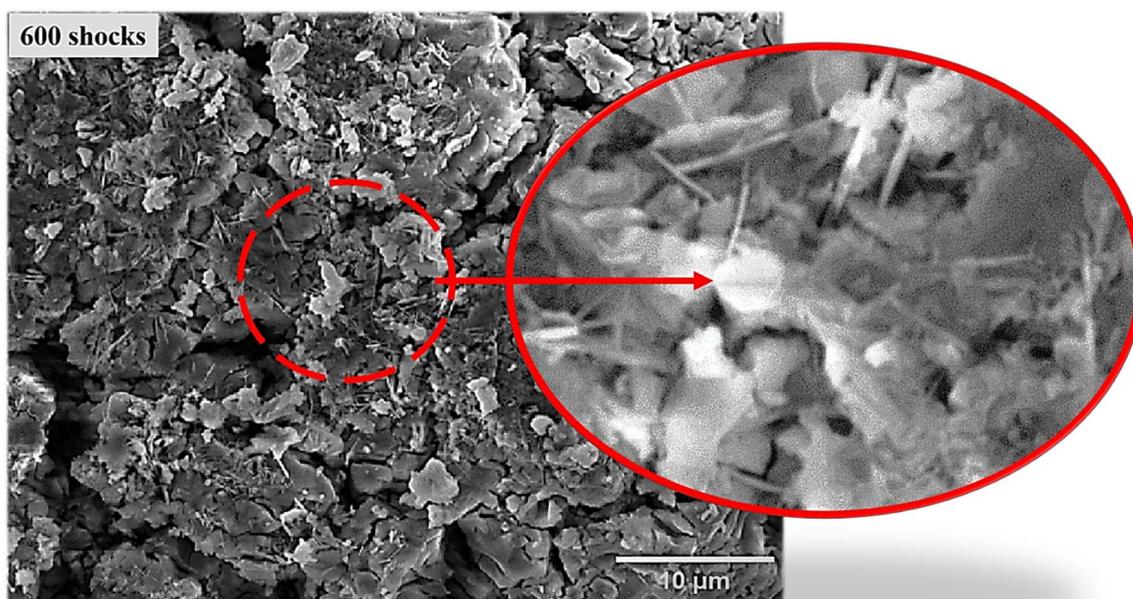


Fig. 5 Magnified view of the needle-like structure formed in the 600-shock flow exposure.

rate and dynamic recrystallisation process, which are significantly related to the thermal parameters of FeS, are responsible for all of the morphological changes of FeS. In this particular scenario, recrystallisation holds the potential to result in the creation of hexagonal and rhombohedral crystal structures of FeS to α -Fe₂O₃, respectively. A significant amount of work has been put into influencing the shapes of these materials, which include microboxes,⁵⁶ nanorods,⁵⁷ nanoneedles,⁵⁸ and hollow spheres⁵⁹ during synthesis. Yet, the chemical techniques that are now available for altering the morphology of compounds are often either difficult to implement or not economically viable. For instance, J. Wang *et al.* investigated the synthesis of FeS/Fe₂O₃ by solvothermal oxidation technique. In this experiment, the FeS nanoparticles were introduced into the tube furnace and subjected to temperatures of 450 °C and 550 °C, at a heating rate of 1 °C per minute, for 10 hours. Finally, pristine Fe₂O₃ was produced when the temperature was lowered to the ambient temperature.⁶⁰ Nevertheless, in our present case, within milliseconds, the FeS surface area was subjected to overheating effects as a consequence of transient temperature (520 K) and pressure (0.59 MPa). As a result, the oxidation phase α -Fe₂O₃ was seen in the material being examined. In addition, the majority of NPs incurred morphological distortions and alterations of their initial forms when subjected to shock pulse; only a relatively small percentage of the components maintained their initial physical characteristics. However, there have been a great number of shock wave studies that have considered tailoring the morphology in positive ways for synthesis or application purposes.^{55,61} In agreement with the findings of the XRD analysis, the phase transition from FeS to α -Fe₂O₃ exhibits a significant degree of resonance from a morphological perspective.

3.3 UV-DRS analysis

The UV-DRS spectra of the control and shock-wave loaded test material are shown in Fig. 6. There is a slight decrease in the absorbance percentage after 200 and 400 shock wave exposures. This is possibly because of the dislocations, surface defects, and distortions generated by the shock pulse, which in turn contribute to a reduction of optical absorbance.⁶² Furthermore, when the number of shock pulses is increased, a significant increase in the percentage of optical absorbance results, as can be seen in Fig. 6. One potential justification for the increase in absorbance at 600 shocks is the structural phase transition from hexagonal (FeS) to rhombohedral (α -Fe₂O₃) crystal structure, triggered by shock waves. Similarly, Sivakumar *et al.* utilised

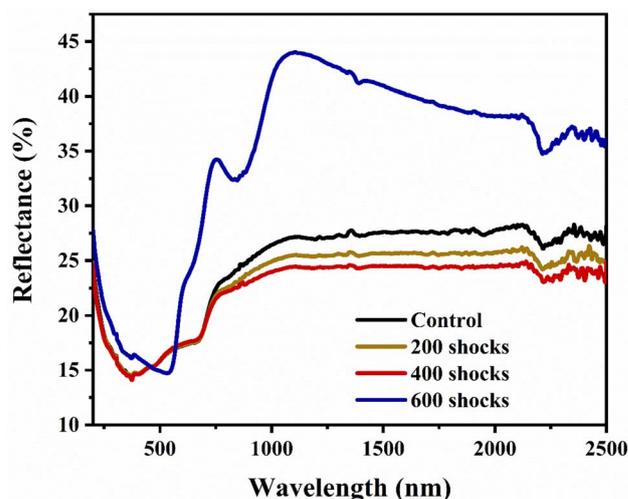


Fig. 6 UV-DRS spectra of control and shocked FeS samples.

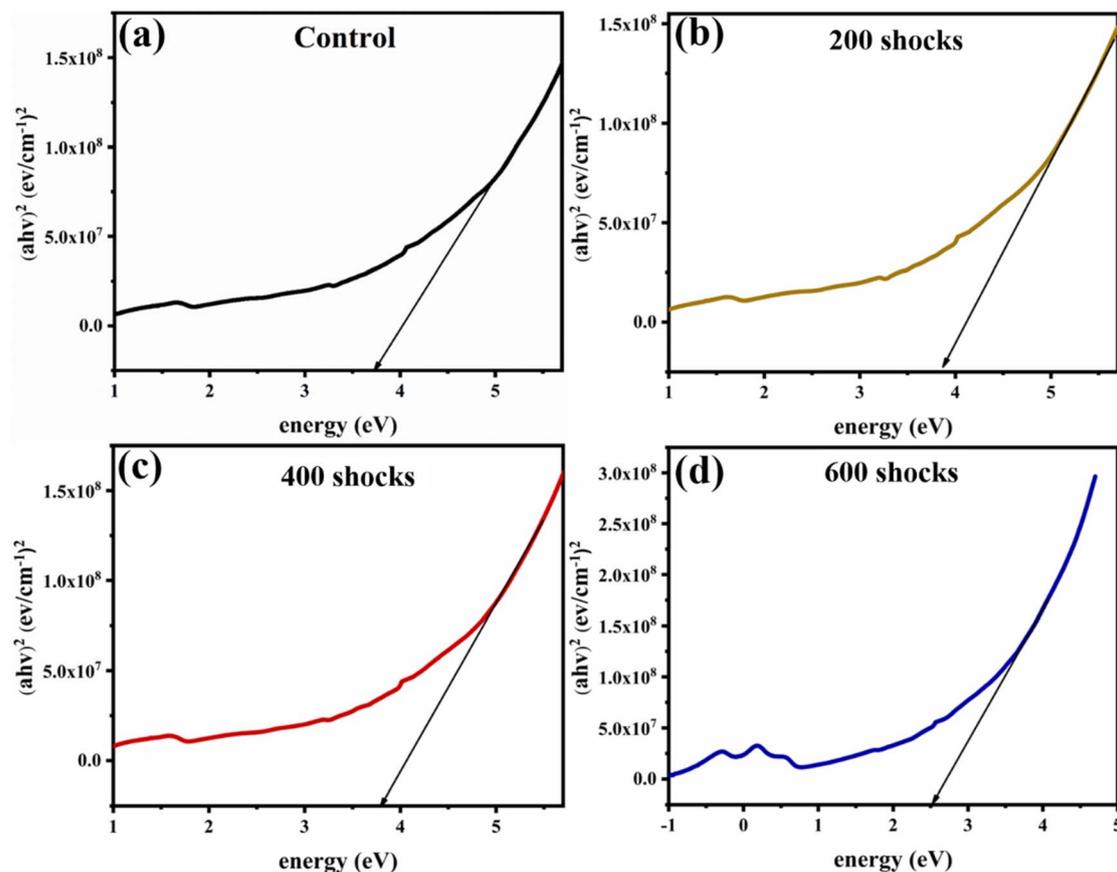


Fig. 7 Tauc plot for (a) control, (b) 200 shocks, (c) 400 shocks, and (d) 600 shock treated FeS specimens.

K_2SO_4 crystals and reported a red shift for the first shock; for the second shocks, the transmittance percentage returned to its initial position, indicating the reversible phase transition.⁶³ Now, in the present case, it is evident that the 200 and 400 shock wave-treated XRD patterns were well distorted and deformed. With the further increase to 600 shock pulses, the FeS phase transformed into α -Fe₂O₃ with good crystalline peaks. UV-DRS results validate this by showing a slight drop in 200 and 400 reflectance % and a substantial increase in 600 optical reflectance %. Moreover, as the number of shock pulses increases, the XRD data show that increased lattice strain and the creation of defects decrease the crystalline nature. Similar to this, the UV reflectance spectra undergo a red shift following exposure to 200 and 400 shock waves. In agreement with the XRD results, this decreased optical absorbance signifies a reduced degree of crystalline nature and an increase of structural disorder.⁶⁴

Taking into consideration that the optical reflectance values rely on the optical energy gap values, the band structure change might be validated based on the acquired data. Due to this particular rationale, the Tauc plot was plotted, as shown in Fig. 7(a–d), to identify the indirect optical band gap for control and shocked FeS samples.⁶⁵ The calculated energy gap values are 3.7 eV, 3.8 eV, 3.8 eV, and 2.5 eV for the control, 200, 400 and 600 shocked samples, respectively. The drastic shift from 3.7 eV to 2.5 eV is due to the shock pulse-induced phase

transformation from FeS to α -Fe₂O₃. In addition, through a discussion of pressure-induced electronic reconstruction, research into hexagonal FeS by Craco *et al.* provides insight into the basic principles of electronic transitions within materials under extreme conditions.⁶⁶ The research also shows that electronic transitions in FeS at moderate pressures are caused by spin state shifts, which in turn cause orbitally selective Kondo quasiparticle electronic reconstruction at low energies. The complex interactions among electronic correlations and external stimuli like pressure are illustrated by the pressure-induced metal-insulator transition in FeS. Similarly, a wide bandgap is obtained as a consequence of these changes in electronic band structure and crystal-field splitting. Shock wave-induced phase transitions from FeS to α -Fe₂O₃ also include intricate electronic rearrangements driven by changes in the spin state and dynamic spectral weight transfer. Therefore, the band gap increased due to these changes in the material's electronic band structure.

3.4 XPS analysis

X-ray photoelectron spectroscopy was carried out on the FeS sample to determine its surface chemical nature and the respective valence states of the Fe and S ions. The survey spectra of control and shock-loaded samples are depicted in Fig. 8. From the survey-scanning spectrum of control FeS, it can be



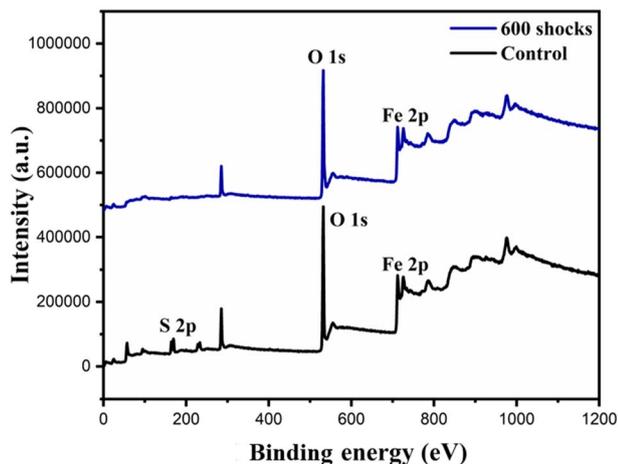


Fig. 8 XPS spectra of control and 600 shock treated FeS samples.

observed that the primary component elements are Fe 2p, S 2p, and O 1s, representing FeS in its pure phase. It would be plausible to relate the peaks that were found at around 708.99 and 721.59 eV to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively, which indicates the presence of Fe²⁺ in FeS NPs.⁴⁸ On the other hand, the peaks deconvoluted at 711.3 and 724.8 eV affirm the presence of Fe³⁺ in the control FeS, as shown in Fig. 9(a). In the case of the S 2p core level, the XPS spectra are displayed in Fig. 9(c). There are two signals at 164.5 and 169.2 eV that are associated with distinctive peaks S 2p_{3/2} and S 2p_{1/2}, respectively. A significant peak associated with O 1s can be seen in Fig. 9(b); it is positioned at 530.2 eV. This peak can be ascribed to the formation of oxygen in FeS. After execution of the 600-shock

pulse, the survey spectra reveal the presence of Fe and O, indicating the formation α -Fe₂O₃, as can be seen in Fig. 9(a-c). The peaks that were discovered at 711.4 and 724.7 eV, respectively, correspond to Fe 2p_{3/2} and Fe 2p_{1/2}, which show the existence of Fe³⁺ in α -Fe₂O₃. This indicates the transition in oxidation states from Fe²⁺ to Fe³⁺, clearly validating the previous analysis that showed the formation of α -Fe₂O₃, as can be seen in Fig. 9(a).⁶⁷ For additional confirmation, there are two satellite peaks found in Fe 2p around 718.5 eV and 732.5 eV, showing the phase transformation of α -Fe₂O₃.⁶⁸ Fig. 9(c) displays the O 1s spectra of the 600 shock wave loaded FeS. The deconvolution peaks of the O 1s spectra are at 530.4 eV, and are attributed to crystal lattice oxygen; the peak at 531.8 eV corresponds to hydroxyl oxygen; that at 532.6 eV denotes adsorbed water.⁶⁹ Consequently, the findings provide evidence that hydroxyl is present on the surface of the α -Fe₂O₃ particles. An additional faint peak developed at 533.4 eV when FeS was loaded with 600 shock pulses. This peak is attributed to the OIII component of surface oxygen atoms and may be seen at that energy level. In the control FeS nanoparticles, the atomic percentages remained at 14.7% for Fe 2p, 4.6% for S 2p, and 50.6% for O 1s. However, after incorporating shock waves, distinct atomic percentages were observed, with 8.78% for Fe 2p and 58.3% for O 1s. This clearly indicates the phase transformation of α -Fe₂O₃ and also indicates that, after the shock wave experiment, oxygen vacancies formed, which were the cause of the modifications that have been seen.

3.5 DFT analysis

3.5.1 Phase stability and reaction energetics. To evaluate the oxidation pathways of FeS under varying conditions, Density

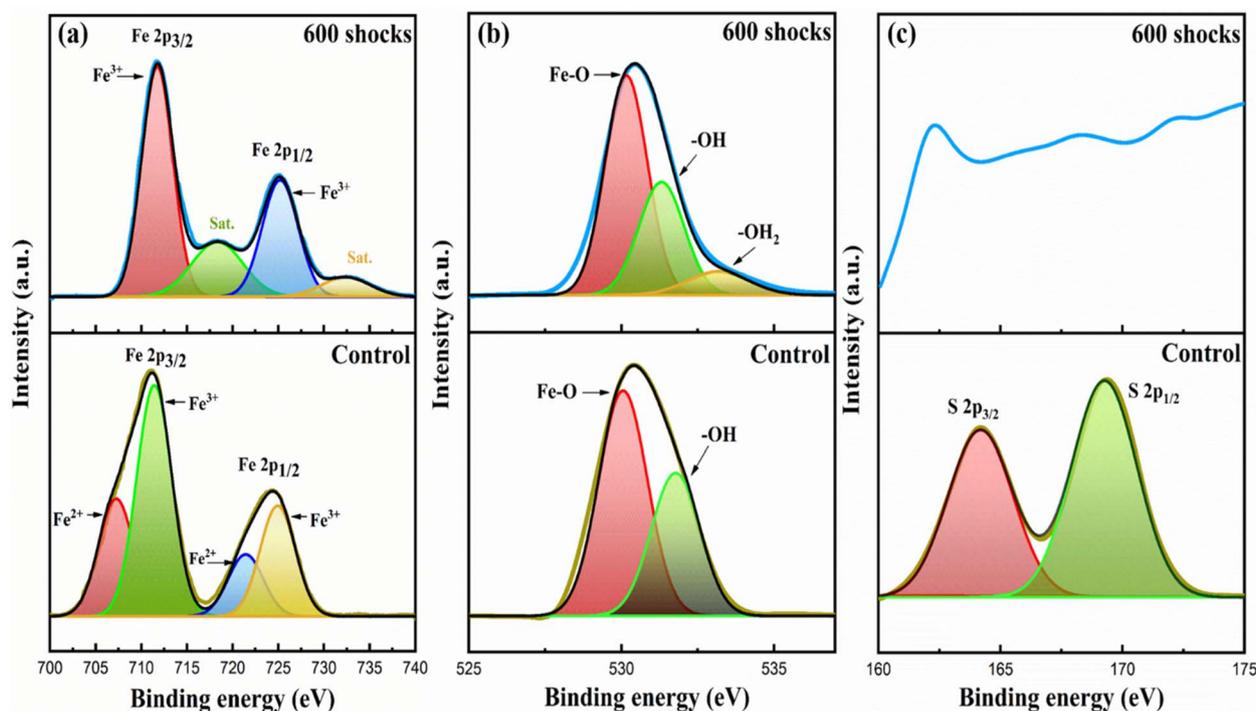


Fig. 9 XPS deconvolution for (a) Fe 2p, (b) O 1s, and (c) S 2p for control and 600 shock treated FeS samples.



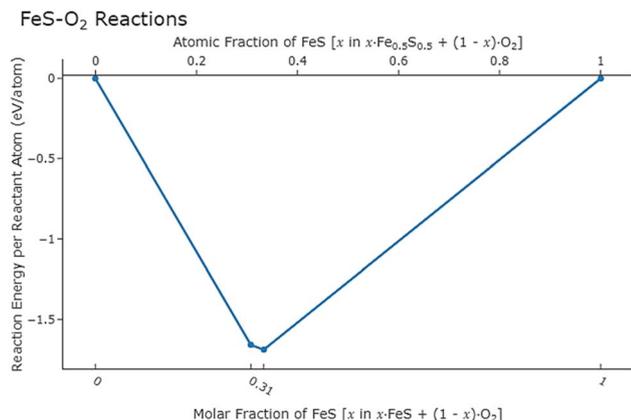
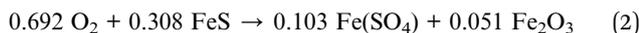


Fig. 10 Reaction energy per reactant atom as a function of molar fraction of FeS in FeS–O₂ system.

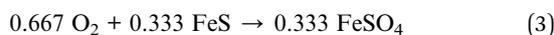
Functional Theory (DFT) calculations were performed to determine the phase stability and reaction energetics of the oxidation products (refer to Fig. 10). The reaction energetics were analysed by computing the total energies of FeS, O₂, α -Fe₂O₃, and FeSO₄ to establish their relative thermodynamic stability. Upon exposure to oxygen, FeS undergoes oxidation, leading to the possible formation of α -Fe₂O₃ or FeSO₄. The stability of these oxidation products is assessed through their respective reaction energies:

Reaction 1 (α -Fe₂O₃ formation):



Calculated reaction energy (ΔE) = $-320.1 \text{ kJ mol}^{-1}$.

Reaction 2 (FeSO₄ formation):



Calculated reaction energy (ΔE) = $-326.0 \text{ kJ mol}^{-1}$.

Both reactions exhibit strongly negative reaction energies, indicating that oxidation is thermodynamically favourable. However, the difference in ΔE between these two oxidation pathways is only 6 kJ mol^{-1} , suggesting that both α -Fe₂O₃ and FeSO₄ can coexist under specific conditions. The small energy gap implies that minor variations in external factors such as temperature, pressure, or reaction environment could shift the preferred oxidation pathway (Table 1).

3.5.2 Energy–volume relationship and structural stability.

The energy–volume (E – V) curves of FeS and its oxidation products provide further insights into phase stability. The computed E – V curves, plotted for multiple phases, show local minima corresponding to stable crystal structures. α -Fe₂O₃ and FeSO₄

exhibit closely spaced local minima, indicating that their relative stability is highly dependent on external thermodynamic conditions, as shown in Fig. 11. The phase transition from FeS to α -Fe₂O₃ is associated with a noticeable volume reduction, which suggests densification of the material upon oxidation. The formation of FeSO₄ exhibits a more gradual energy change with respect to volume, indicating that its structural stability is less sensitive to compression effects. From these observations, it is evident that shock wave compression, external pressure, and high-temperature conditions could influence the relative stability of α -Fe₂O₃, making phase selection tunable. This is particularly relevant for applications in which controlled phase formation is required, such as in photocatalysis.⁷⁰

3.5.2.1 Implications for oxidation mechanisms. The small energy difference between the competing oxidation pathways suggests that kinetic factors, such as diffusion and activation barriers, could dictate the dominant phase formation, rather than thermodynamic stability alone. Under rapid oxidation conditions, FeSO₄ formation may be preferred due to lower activation energy, whereas α -Fe₂O₃ formation may dominate under equilibrium conditions.

3.5.3 Electronic structure and bonding analysis. To gain deeper insight into the oxidation mechanisms and electronic behaviour of FeS and its oxidation products, we performed Density of States (DOS) calculations and charge density analysis. The oxidation process significantly alters the electronic structure, which in turn affects material properties such as conductivity, bandgap, and photocatalytic performance.

3.5.3.1 DOS analysis. The electronic structures of the parent FeS and the Fe₂O₃ (corresponding to 600 shocks) were investigated through spin-polarized projected density of states (PDOS) calculations, shown in Fig. 12(a and b).

3.5.3.1.1 FeS. In the parent FeS system, the PDOS plot reveals significant spin asymmetry between the spin-up and spin-down states, indicating the system's magnetic character. The Fe 3d states dominate across the entire valence band region (from approximately -6 eV to the Fermi level), while S 3p states contribute notably closer to the Fermi level. A strong hybridization is observed between Fe 3d and S 3p orbitals, especially in the range of -4 eV to 0 eV , implying strong Fe–S bonding interactions.

The Fermi level intersects the Fe 3d states, indicating metallic behaviour for pristine FeS. The finite density of states at the Fermi level confirms its conductivity, consistent with the known semimetallic nature of FeS.

3.5.3.1.2 α -Fe₂O₃. For the shock-treated sample, which leads to the formation of α -Fe₂O₃, the PDOS shows clear signs of electronic structure modification. A noticeable band gap opens

Table 1 Analysis of FeS oxidation under different molar fractions of O₂

Molar fraction	Reaction equation (normalized to reflect molar fraction)	E_{rxn} of eqn (kJ mol^{-1})
0.000	$\text{O}_2 \rightarrow \text{O}_2$	0
0.308	$0.692 \text{ O}_2 + 0.308 \text{ FeS} \rightarrow 0.103 \text{ Fe}_2(\text{SO}_4)_3 + 0.051 \text{ Fe}_2\text{O}_3$	-320.1
0.333	$0.667 \text{ O}_2 + 0.333 \text{ FeS} \rightarrow 0.333 \text{ FeSO}_4$	-326.0



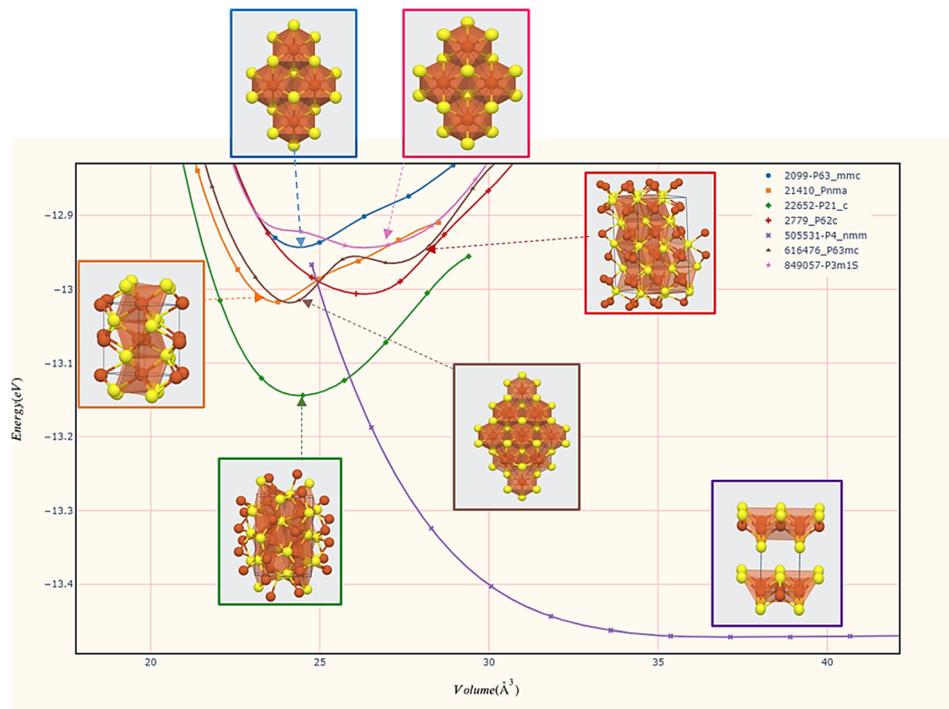


Fig. 11 Energy vs. volume curves for different structural phases of FeS, with corresponding atomic structures overlaid.

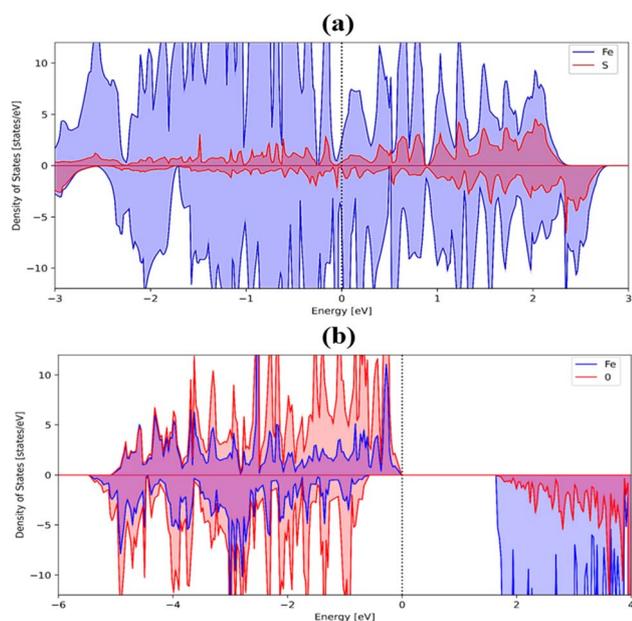


Fig. 12 Projected density of states for (a) FeS and (b) α -Fe₂O₃. The contributions from FeS and α -Fe₂O₃ are shown, indicating hybridisation and electronic states near the Fermi level.

up at the Fermi level, and the DOS near the Fermi level significantly decreases compared to FeS, indicating a transition to semiconducting behaviour. The Fe 3d states are more localised and separated from the O 2p states, though moderate hybridisation still exists between -6 eV and -2 eV. The oxygen 2p states dominate the deeper valence band region, while Fe 3d

contributes closer to the conduction band edge. This suggests that under high-energy shock treatment (600 shocks), FeS undergoes significant oxidation, leading to the formation of α -Fe₂O₃ with reduced conductivity and modified magnetic and bonding characteristics.

3.5.3.2 Charge density and bonding characteristics. Charge density distribution maps were computed to visualise the bonding nature in FeS, Fe₂O₃, and FeSO₄. The charge density plots show strong covalent bonding between Fe and S atoms, with significant charge accumulation along the Fe–S bonds. The charge transfer between Fe and S is indicative of the partial ionic character, but FeS remains largely metallic in nature. The oxidation process leads to stronger Fe–O ionic interactions as oxygen atoms withdraw electron density from Fe. The charge density maps exhibit localized charge accumulation around O atoms, confirming the increased ionicity in Fe₂O₃. The Fe atoms exhibit a high-spin state due to unpaired 3d electrons, which influences magnetic properties. The Fe–O bonding in FeSO₄ is also highly ionic, with a homogeneous charge distribution, making FeSO₄ structurally stable under different conditions. Compared to α -Fe₂O₃, FeSO₄ exhibits weaker Fe–O bonding, which may impact its catalytic efficiency.

3.6 Photocatalytic study

It is important to note that crystallographically induced structural phase transitions, as well as variation in morphology and band gap of the shocked FeS samples, significantly influence the photocatalytic property, which includes the degradation efficiency.^{71,72} These parameters play significant roles in enhancing or diminishing the photocatalytic activity of



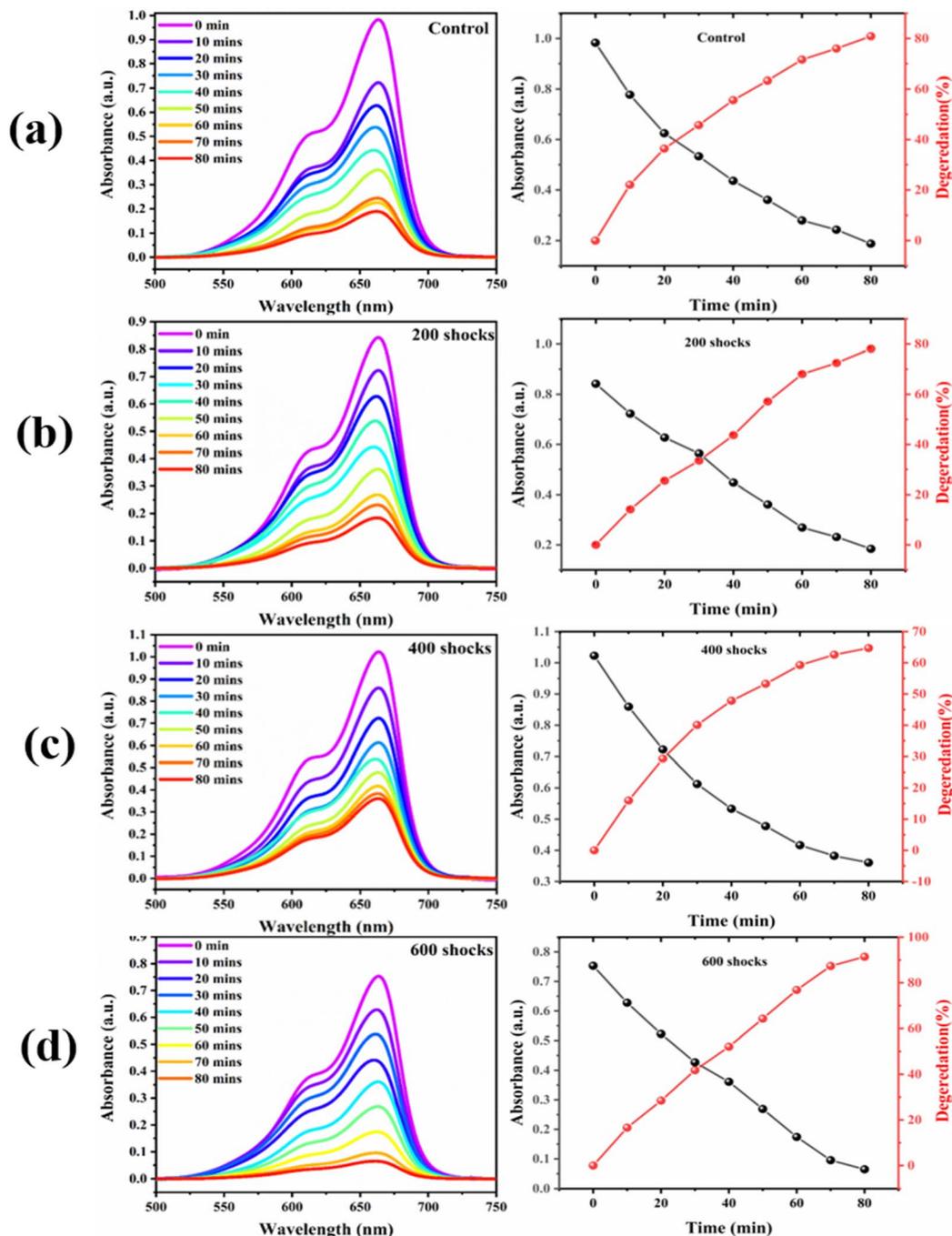


Fig. 13 Photocatalytic dye degradation of (a) control, (b) 200 shocks, (c) 400 shocks, and (d) 600 shock treated FeS samples.

materials, notably in processes such as the degradation of pollutants and the creation of hydrogen.^{73,74} There is a strong possibility that the catalytic property of the FeS nanoparticles might undergo a significant degree of transformation due to the remarkable morphological variations and the formation of a new phase under a 600-shock pulse. Fig. 13(a-d) shows the reflectance spectra of the control and shock-loaded FeS sample.

$$\text{Degradation efficiency}(\eta)\% = \frac{(A_0 - A_t)}{A_0} \times 100 \quad (4)$$

Through the course of the experiment, the beginning absorbance, which was marked as A_0 , and the end readings, which were labelled as A_t , were recorded. The degrading efficiency estimates of the control, 200, 400, and 600 shock pulses were 78.4%, 77.1%, 64.7%, and 98.41%, according to eqn (2). The efficiency of the shock wave-treated FeS decreases for the 200 and 400 shock pulse samples, and dramatically, the efficiency increases for the 600 shock-treated FeS. The low efficiency obtained for the 200 and 400 shocked FeS samples is due to defects;⁷⁵ these defects serve as recombination centres for



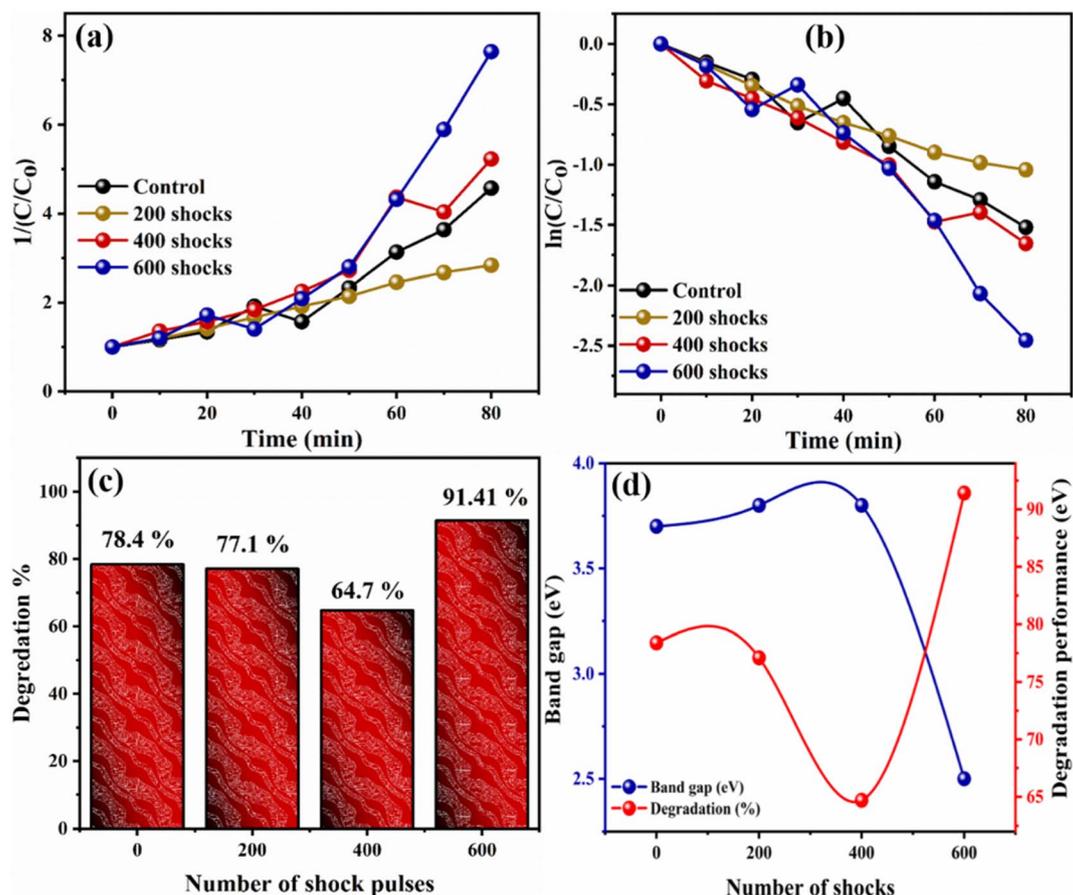


Fig. 14 Catalytic performance (a and b) pseudo-first-order kinetics, (c) efficiency histogram, (d) band gap and efficiency comparison for control and shocked FeS samples.

electrons and hydrogen ions. When FeS undergoes deformations such as stress and strain due to shock impulsion, this in turn affects the photocatalytic property. Jarvin *et al.* investigated the photocatalytic activity of SnO₂ NPs under the effects of shock waves and reported that the photocatalytic efficiency of the parent SnO₂ NPs in the degradation of VB dye is greater than that of the shock-treated samples. Further, the degradation efficiency decreased due to the variations in the bond length, as well as other factors such as stress and strain.⁷⁵ Interestingly, for 600 shock wave-treated samples, the efficiency increased to 91.2%. This increased efficiency is due to the phase transformation from FeS to α -Fe₂O₃ induced by the shock waves. Moreover, the enhancement is due to the following factors:

when FeS undergoes a phase transition to α -Fe₂O₃, the change modifies the optical properties *via* changes in the material's energy gap. A narrow bandgap means that more visible light photons are absorbed by α -Fe₂O₃ than by FeS. This extended reflectance spectrum enables a more effective use of solar energy by improving the photocatalytic activity under exposure to visible light; conversely, the reduction in reflectance % in the 200 and 400 shocked samples is responsible for the lower efficiency rate. In contrast to the control and the 200- and 400-shock wave-treated FeS nanoparticles, the 600-shock-treated FeS sample exhibits superior photodegradation activity. To quantify this performance, a pseudo-first-order kinetic model was applied to evaluate the degradation rate of MB dye. The

Table 2 FeS photocatalytic performance comparison

Material	Dye	Catalyst dosage	Dye conc.	Solution pH	Source	Performance (%)	Ref.
Ag-Fe ₂ O ₃	MB	0.4 g L ⁻¹	10 mg	7	Sunlight	96.33	77
α -Fe ₂ O ₃	MB	1 g L ⁻¹	3.2 mg	~3	UV	65	78
α -Fe ₂ O ₃ NPs	MB	0.4 g L ⁻¹	10 mg	6.5	Sunlight	78.68	79
α -Fe ₂ O ₃ NPs	RY	0.4 g L ⁻¹	10 mg	~6.5	UV	75	80
Fe ₂ O ₃ /TiO ₂	MB	0.3 g L ⁻¹	10 mg	6.5	UV	97	81
600 Shock treated α -Fe ₂ O ₃	MB	0.1 g L ⁻¹	10 mg	~7	Sunlight	91.2	Present study



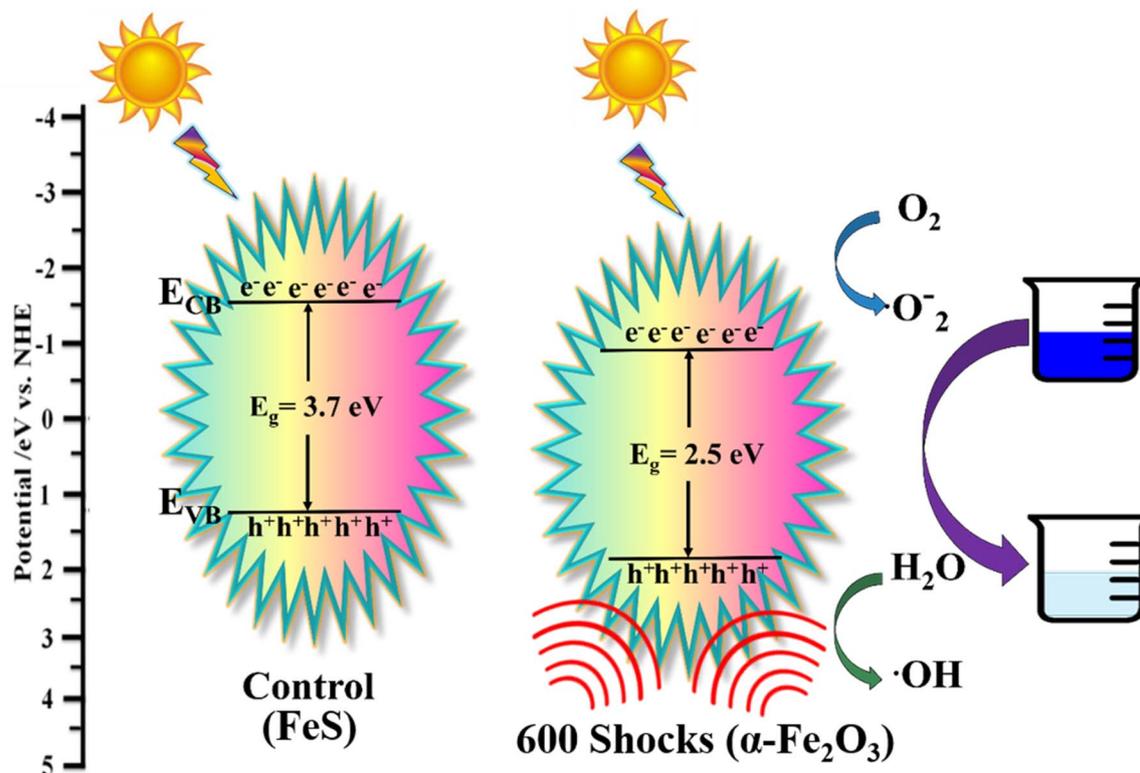


Fig. 15 Schematic representation of the dye deprecation mechanism of control FeS and 600 shock-treated α -Fe₂O₃.

corresponding rate constants, derived from linear fits of $\ln(C_0/C)$ versus time (as shown in Fig. 14(a and b)), are as follows: control: $0.063 \times 10^{-2} \text{ min}^{-1}$, 200 shocks: $0.053 \times 10^{-2} \text{ min}^{-1}$, 400 shocks: $0.041 \times 10^{-2} \text{ min}^{-1}$, 600 shocks: $0.078 \times 10^{-2} \text{ min}^{-1}$, these results Fig. 14(a and b) clearly indicate that the 600-shock wave-treated FeS sample demonstrates the highest photocatalytic activity, as reflected by the highest rate constant.⁷⁶ Table 2 provides a clear visual representation of the current research findings and of the photodegradation efficiency found in this study in comparison to values in previous research works. It is possible to tailor the structural, optical, morphological, and photocatalytic characteristics of FeS by altering the number of shocks. This leads us to a potential versatile material for accelerating wastewater degradation in the textile sector.

3.6.1 Possible photocatalytic mechanism. The possible mechanism for the enhanced photocatalytic activity is shown in Fig. 15.

3.6.2 Initial shock exposure (200 and 400 shocks). Shock initialisation (200 and 400 shocks) causes nanoparticles to develop structural defects and dislocations at 200 and 400 shock wave-loaded conditions. Vacancies, interstitials, and dislocations are examples of defects that can serve as sites for non-radiative recombination of photogenerated electrons and holes. As a result of the existence of these defects and wider band gap, the chance of electron-hole recombination is increased, which in turn reduces the number of charge carriers that are accessible for photocatalytic processes. Due to the fact

that fewer electrons and holes are involved in producing reactive species that eliminate pollutants, the effectiveness of photocatalytic degradation drops.

3.6.3 600 Shock pulse exposure. At 600 shocks, there is an apparent shift in the phase of the α -Fe₂O₃ nanoparticles, which potentially indicates that they have become crystalline and have a better crystal structure. Crystalline enhancements lessen the number of recombination centres caused by defects and dislocations.⁸² In situations in which there are fewer recombination centres, the rate at which photogenerated electron-hole pairs recombine is likely to decrease, increasing the visible light reflectance. More electron-hole pairs are produced by this increase in light reflectance. As a result, the photocatalytic degradation is improved in the 600-shocked FeS sample.

4. Conclusion

Our study effectively deduced the phase transformation of FeS to α -Fe₂O₃ induced by acoustical shock waves. The oxidation of FeS with oxygen from the atmosphere, which takes place during 600 shock pulses, is responsible for the transition of troilite into the hematite crystal structure. XRD patterns prove that the α -Fe₂O₃ phase was formed under the 600-shock condition. Furthermore, the results obtained from SEM and UV-DRS fully concur with the XRD data. Interestingly, with a 600-shock pulse, a nanoneedle-like structure formed. Moreover, the XPS analysis validates the current research by confirming that sulphur ceased to exist in 600 shock-loading conditions. DFT-based



electronic structure analysis confirms that oxidation transforms FeS from a metallic state to a semiconducting oxide (α -Fe₂O₃ or FeSO₄) with altered band gaps and charge distributions. The ionic Fe–O bonding in both oxidation products stabilises their crystal structures, but α -Fe₂O₃ remains the more promising phase for photocatalytic applications due to its optimal electronic properties. Photocatalytic study provides a clear representation of the increase in degradation efficiency compared to the control, and the 200 and 400 shock treated samples. The reaction rate constants were $0.063 \times 10^{-2} \text{ min}^{-1}$, $0.053 \times 10^{-2} \text{ min}^{-1}$, $0.041 \times 10^{-2} \text{ min}^{-1}$, and $0.078 \times 10^{-2} \text{ min}^{-1}$. The efficiency significantly diminished when the number of shock pulses increased to 200 and 400 because of distortions and defects that occurred throughout the process. These defects served as recombination centres for e[−] and h⁺. Further, at 600 shock pulses, the efficiency increased to 91.2% due to the phase transformation. Therefore, shock wave-treated FeS can be utilised in photocatalytic applications in future.

Data availability

All the data used in the manuscript are within the manuscript.

Conflicts of interest

The authors declare that they have no conflicts of interest.

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