#### RESEARCH ARTICLE



# Photocatalytic fixation and oxygenation of NAD<sup>+</sup>/NADP<sup>+</sup> and sulfides using solar light: Exploring mechanistic investigations and their impact on synthetic applications

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#### Abstract

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Sulfur-doped Eosin-B (SDE-B) photocatalysts were synthesized for the first time utilizing sublimed sulfur (S<sub>8</sub>) as a dopant in an in situ thermal copolymerization technique. Sulfur doping not only increased Eosin-B (E-B) absorption range for solar radiation but also improved fixation and oxygenation capabilities. The doped sulfur bridges the S-S bond by substituting for the edge bromine of the E-B bond. The improved photocatalytic activity of SDE-B in the fixation and oxygenation of NAD<sup>+</sup>/NADP<sup>+</sup> and sulfides using solar light is attributed to the photo-induced hole of SDE-B's high fixation and oxygenation capacity, as well as an efficient suppression of electron and hole recombination. The powerful light-harvesting bridge system created using SDE-B as a photocatalyst works extremely well, resulting in high NADH/NADPH regeneration (79.58/76.36%) and good sulfoxide yields (98.9%) under solar light. This study focuses on the creation and implementation of a sulfur-doped photocatalyst for direct fine chemical regeneration and organic transformation.

#### K E Y W O R D S

1,4-NADH/NADPH regeneration, oxygenation reaction, SDE-B, solar light

# INTRODUCTION

Pharmaceutically usable solar fine chemical production, such as NADH regeneration and oxygenation of sulfide under solar light, is very important for the scientific society.<sup>1,2</sup> In this context, oxidation (sulfide) and reduction (NAD<sup>+</sup>) are one of the most captivating transformations of organic compounds<sup>3</sup> and selective regeneration of NADH and have been expansively studied in the previous periods.<sup>4–8</sup> Conventionally, toxic/hazardous reducing and nonreducing agents, such as very toxic expensive metal oxides, methyl viologen, and organic peroxides in stoichiometric quantities, were generally utilized for these chemical conversions in terms of oxidation and reduction.<sup>9-12</sup> Therefore, a photocatalytic, cost-effective, and environmentally friendly reduction and oxidation method is constantly needed through the utilization of solar light as a green<sup>13</sup> and traceless reagent. In this context, photochemistry is a significant and potent synthetic approach that can facilitate numerous functional group transformations<sup>14–22</sup> and regeneration of NADH. In recent years, solar light-driven photocatalysis has emerged as a key area of synthetic methods<sup>23–27</sup> due to the fact that it provides environmentally friendly alternatives to a number of traditional synthetic processes.

Consequently, it has been determined that photocatalysis complies with the ideas of the many methods of Green Chemistry<sup>27</sup> for oxygenation reactions and reduction in NAD<sup>+</sup>. The incorporation of oxygen into a substrate using photosensitized oxygenation has been acknowledged as a contemporary technique. The molecular oxygen activation by a sensitizer's excited state is the foundation of photo-oxygenation. Either singlet oxygen or the electron transfer (ET) process can cause it to happen.<sup>28</sup> However, the use of expensive and dangerous metals severely restricts its practical application. A nonmetal photocatalytic photoreactor offers an environmentally favorable alternative synthetic method for selective oxidation and reduction under mild conditions due to its cheaper cost and widespread availability.<sup>29,30</sup> Since many sulfoxides and NADH are biologically active chemicals and production of energy through redox reactions is frequently utilized in pharmaceutical industries,<sup>31,32</sup> chemo-selective transformation of sulfides to sulfoxides and conversion of NAD<sup>+</sup> to NADH is of great interest (Scheme 1). Sulfoxidation is also advantageous for the synthesis of organic materials, the desulfurization of fossil fuels, the treatment of industrial wastes, and the destruction of chemical weapons.<sup>33–39</sup> However, NADH is also a significant industrial chemicals, which can be utilized in various medicines.<sup>40–42</sup> There is a need for environmentally friendly and gentle sulfide oxidation and NAD<sup>+</sup> reduction processes that produce sulfoxides chemo-selectively without over-oxidation to sulfones and regenerate NADH. As per our group concern, the main problems of using peracids/methyl viologen in industrial processes are the over-oxidation/reduction to sulfones/ NAD<sup>+</sup> and the safety and system corrosion concerns with handling peracids.<sup>32</sup> The photooxidation/reduction of sulfides/NAD<sup>+</sup> was studied using a variety of expensive sensitizers, including organic molecules, inorganic materials,<sup>43–49</sup> and metal complexes.<sup>50–53</sup> Additionally, certain photocatalysts are unstable, which makes it challenging to use them in commercial processes. These factors make a more durable organic photocatalyst that can oxidize and reduce both a wide range of sulfides and NAD<sup>+</sup> particularly desirable. Due to their tunable emission and absorption characteristics, EOSIN-B (E-B) have become a group of fluorescent organic light-harvesting dye molecules, similar to the light-harvesting compounds. Due to their tunable backbone, many researchers are it utilizing in various research fields such as organic photovoltaics, sensor, organic field-effect transistors, supramolecular assemblies, and organic field-effect transistors. There



**SCHEME 1** Pictorial illustration of an artificial photosynthetic system mimicking the natural photosynthetic system for fixation of NAD<sup>+</sup>/NADP<sup>+</sup> into NADH/NADPH along with oxygenation of sulfides via newly designed SDE-B photocatalyst under solar light.

is limited research on the application of SDE-B as solar light-driven photocatalysts for synthetic transformations and NADH/NADPH regeneration,<sup>54</sup> particularly for selective aerobic oxidation, despite these outstanding features of SDE-B such as photosensitizer. Here, we describe a solar light-mediated photo-oxygenation of sulfides to sulfoxides and selective regeneration of cofactor of 1,4-NADH/NADPH using SDE-B as the photocatalyst (Scheme 1).

## **MATERIALS AND METHODS**

### **Materials**

Eosin-B, sublimed sulfur ( $S_8$ ), chloroform (CHCl<sub>3</sub>), dimethylformamide (DMF), triethylamine (TEA), isopropyl alcohol (IPA), ethanol (EtOH), 4-(methylthio) benzaldehyde, 4 chlorobenzene thiol, methyl-p-tolyl sulfide, 2-aminobenzenethiol, 1,3,5-triazine-2,4,6- trithiol, silica gel, hexane, ethyl acetate, ascorbic acid, NAD<sup>+</sup>, NADP<sup>+</sup> pentamethylcyclopentadienyl rhodium (III) dichloride dimer, and 2, 2'bipyridy were used as such and purchased from Sigma-Aldrich.

# Synthesis of sulfur-doped Eosin-B (SDE-B) photocatalysts

The 1.0g Eosin-B and 3.0g sublimed sulfur ( $S_8$ ) were homogeneously mixed by the mortar pastel method, and after that mixed material was collected in the crucible. The crucible was shifted in a muffle furnace for 2 h (ramping rate: 1°C min<sup>-1</sup>) at 160°C. After cooling, the crucible was removed from the same. After that, the gray color product was obtained (1.98g), which is purified by water and acetone (Scheme 2).

# General procedure for photocatalytic oxygenation of sulfides

In a dried vial tube equipped with a small magnetic stir, the initial reactant (sulfides) (0.2 mmol) and SDE-B photocatalyst (5 mg) were dissolved in 4.0 mL of isopropyl alcohol (IPA) under the aerobic situation. After that, the solution was irradiated under solar light for few hours at room temperature in aerobic conditions. The reaction completion condition was examined by the standard thinlayer chromatography (TLC). After the completion of the running reaction, the reaction mixture was concentrated under reduced pressure. The as-obtained final product was refined by using column chromatography based on silica gel (hexane/ethyl acetate: 10:1) to afford the corresponding sulfoxide.<sup>55</sup>

### Photocatalytic fixation of the NAD<sup>+</sup>/ NADP<sup>+</sup> by newly designed SDE-B photocatalyst

The photocatalytic fixation of the NAD<sup>+</sup>/NADP<sup>+</sup> from the SDE-B photocatalyst photocatalysts quickly transfers the excited electrons for NADH/NADPH coenzyme regeneration via ORC. The cofactor regeneration of 1,4-NADH/NADPH was 79.58% and 76.36% in 2h shown in Figure 3. The photocatalytic fixation of NAD<sup>+</sup>/ NADP<sup>+</sup> was performed under solar radiation at room temperature. The reaction was carried in a dried vial tube equipped with a small magnetic stir by mixing the NAD<sup>+</sup>/NADP<sup>+</sup> (1.24 µmol), ORC complex (0.62 µmol), ascorbic acid (AsA) (0.1 mmol) as a sacrificial agent and SDE-B photocatalyst (5 mg) mixed in 3100 µL neutral sodium phosphate buffer solution (100 mM). The photocatalytic output of NADH/NADPH regeneration via SDE-B photocatalysts were monitored by the reported method. 56,57

### **RESULTS AND DISCUSSION**

### Strategy of the artificial photosynthetic photoreactor for mimicking the natural photosynthetic mechanism

In Z-scheme of the natural photosynthetic system contained two types of photosystem (PS) segments, that is, PS-700(I) and PS-680(II) as shown in Scheme 3. Chlorophyll containing PS-680(II) serves as the reaction center for the absorption of solar light. The capture of solar light in the PS-680(II) produces photo-excited electrons, due to which the electron-mediating components, such as the cytochrome complex, move to the plastocyanin (PC) complex. The movement of photoexcited electron via ferredoxin NADP<sup>+</sup> oxidoreductase into NADPH after the PC complex reduces the photooxidized PS-700(I). Therefore, natural photosynthetic PS-700(I) and PS-680(II) systems play an important role in the making of valuable NADH/NADPH coenzymes under solar light radiation.<sup>58-62</sup> On the basis of natural photosynthesis, we design highly efficient SDE-B artificial photosynthetic photoreactor for NADH/NADPH regeneration. The reaction mechanism for the regeneration of NADH/NADPH coenzymes via a photocatalytic



**SCHEME 2** Synthesis of sulfur-doped Eosin-B (SDE-B) photocatalysts utilizing sublimed sulfur ( $S_8$ ) as a dopant in an in situ thermal copolymerization technique.



**SCHEME 3** Pictorial illustration of Z-scheme of the natural photosynthetic system.

route under solar light is shown in Scheme 1. As per Scheme 1, the transfer of electrons between SDE-B photocatalysts and ORC complex is more similar to the electron transfer routes between PS-700(I) and PS-680(II) detected in the natural photosynthesis.<sup>58–62</sup> The highly light-harvesting bridge system captures solar light irradiation-generated photo-excited electrons transfer from SDE-B photocatalyst to ORC complex that easily takes electron and gets reduced. ORC takes proton from aqueous buffer medium and the electrons transferred to oxidized form NAD+/NADP+ and reduces to fine chemicals in the form of NADH/NADPH. In this mechanism, ORC works as electron and proton transfer mediator between SDE-B photocatalysts and NAD<sup>+</sup>/ NADP<sup>+</sup>. Instead, the newly designed SDE-B photocatalyst has also an additional capability for oxygenation reaction under solar light.

# Characterization of newly designed SDE-B photocatalyst

Figure 1A's representation of the UV–visible absorption spectra of SDE-B photocatalyst for solid-state powders shows that SDE-B photocatalyst exhibits wide solar light absorption in 475–500 nm range, which is comparable to that of the Eosin-B (E-B) monomer (Figure S1) and suggests that the SDE-B photocatalyst networks have the



**FIGURE 1** (A) UV-visible absorption spectra of SDE-B photocatalyst along with tau plot for calculation of energy band gap (2.07 eV); (B) FTIR spectra of S<sub>8</sub> (black), E-B (red) monomers and SDE-B (blue) photocatalyst; (C) XRD pattern of E-B (indigo) and SDE-B photocatalyst (red); and (D) cyclic voltammograms of E-B (black), S<sub>8</sub> (red), and mixture of SDE-B + ROC + NAD<sup>+</sup> for mechanistic studies. The potential was scanned at 100 mV s<sup>-1</sup> using glassy carbon as working electrode, Hg/HgCl<sub>2</sub> as a reference electrode, and platinum as a counter electrode in neutral sodium phosphate buffer (100 mM).

ability to absorb light over a broad range or area of the solar spectrum. Therefore, the newly designed SDE-B photocatalyst has superior photocatalytic activity than the E-B monomer. The absence of the bromine bending peak of the C-Br group at about  $772 \text{ cm}^{-1}$  in the FT-IR spectra of the SDE-B photocatalyst recommended that most of the C-Br group in the starting substrate have been utilized to form -C-S- groups in the newly designed networks. Furthermore, a comparison of the FTIR spectra of SDE-B and E-B photocatalysts revealed unique characteristics. The production of S-S bonds was indicated by the observation of a strong and bright band at about  $599 \,\mathrm{cm}^{-1}$ ,<sup>63</sup> which was noticeably lacking in E-B (Figure 1B). Additionally, a new band at roughly  $670 \,\mathrm{cm}^{-1}$  was found, which corresponds to the creation of a C-S bond (Figure 1B).<sup>64</sup> Due to the presence of the carboxylate group, the bond associated with the terminal thiol was not readily evident in the FTIR spectra (Figure 1B). The high degree of spectral of SDE-B photocatalyst demonstrates the structural phenomenon of this material (Figure 1C). XRD patterns of E-B and SDE-B photocatalysts are exhibited in Figure 1C. Power X-ray diffraction measurements indicate that the SDE-B photocatalyst network is amorphous in nature as per reported networks<sup>65</sup> Figure 1C demonstrates the X-ray diffraction for pure E-B dye monomer and SDE-B photocatalysts, respectively. It was noted that various strong peaks appear on the pattern E-B compared with SDE-B photocatalysts. Additionally, the photocatalyst was discovered to be

amorphous and to have a broad peak in the range of 16° to 35° in the PXRD investigation (Figure 1C). In contrast to amorphous chemicals, which often show weak intensity peaks or relatively flat XRD patterns,<sup>66</sup> crystalline substances typically show prominent and sharp peaks in XRD graphs.<sup>67</sup> Long-range atomic disorder in this kind of amorphous material offers them unique mechanical, optical, electrical, and magnetic properties. Charge carriers are trapped by the long-range disorder, making it easier for them to separate, encouraging effective redox reactions.

The SEM image of SDE-B photocatalysts displayed different morphologies than E-B monomer (Figure S3), but rough surfaces and the particles were on the order of micrometers in size (Figure 2C). SEM was used to analyze the surface morphology of the photocatalyst in order to better understand its involvement in photocatalysis. The existence of a dumbbell shape may be shown with localized aggregation<sup>64</sup> in Figure 2C. The elemental composition of the photocatalyst was also evaluated using the SEM-EDS method (Figure S4), which corroborated the presence of carbon, oxygen, sodium, and sulfur and demonstrated that SDE-B photocatalysts form as a result of the absence of bromine. A potent imaging method was used to view the microstructure of materials at a very high-resolution TEM.It appears that TEM was used to evaluate a sample, and the outcomes are shown in Figure 2B. Some details concerning the morphology of the substance seen in Figure 2B are given

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**FIGURE 2** (A) 3D structure of the SDE-B photocatalyst. TEM image of (B) SDE-B, and (C) SEM image of SDE-B along with elemental mapping images of (D) carbon C (E) sodium (F) nitrogen, (G) oxygen, (H) sulfur.



**FIGURE 3** E-B and SDE-B photocatalyst's photocatalytic activity in 3.1 mL of neutral sodium phosphate buffer (100 mM) containing beta-NAD<sup>+</sup>/NADP<sup>+</sup> (1.24  $\mu$ mol), AsA (0.1 mmol), Rh (0.62  $\mu$ mol), and SDE-B photocatalyst (5 mg).

by the term "dumbbell cloth-like flexible agglomerated structure". Dumbbell: Given that a dumbbell is normally made up of two spherical objects, this word implies that the observed structure may have a shape similar to a

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dumbbell, which typically consists of two spherical or ellipsoidal regions connected by a thinner bridge-like structure in the middle. Cloth-like: This adjective suggests that the structure may resemble a fabric or textile, perhaps with a web of intertwined fibers or strands. This can point to a complicated and well-planned arrangement of the material. Flexible: The adjective "flexible" implies that the constituent parts of this structure's material are not inflexible but rather capable of deforming or changing shape. Its special qualities may be connected to this adaptability. Agglomerated: The term "agglomerated" denotes a structure made up of a collection of separate elements or particles. These particles might be nanoparticles or other minute components that have come together to form a more substantial, cohesive assembly. The statement ends by saying that the excellent photocatalytic activity is confirmed by the observed structure. This suggests that the material's ability to efficiently catalyze photochemical processes, which is a desired attribute in different applications, such as environmental clean-up or energy conversion, is connected to the unique shape exhibited in Figure 2B. Overall, the information supplied provides an understanding of the physical structure of the material as revealed by TEM and its relationship to its photocatalytic activity, indicating that the observed morphology is extremely important to the material's functionality.

# Poof of NADH/NADPH regeneration via cyclic voltammetry

Cyclic voltammetry, as seen in Figure 1D, offers an insightful look at the process's mechanics. NAD<sup>+</sup>, ROC, and SDE-B were shown to have reduction potentials of around -0.51 eV, -0.71 V, and -1.01 V (Figure S2). A most important increase in the fixation peak current along with NAD<sup>+</sup> was also seen in the SDE-B-ROC, signifying that the system collected of SDE-B and ROC was able to catalyze the fixation of NAD<sup>+</sup> (Figure 1D). According to a recent publication, the catalytic impact of ROC causes a significantly higher rate of ROC decrease when NAD<sup>+</sup> is present.<sup>40</sup> Further evidence that SDE-B-ROC followed the electrochemistry of ROC came from the absence of an oxidation peak. The catalytic activity of the SDE-B-ROC complex may be attributed to the photoelectric behavior of SDE-B since the excited electron of SDE-B could be forwarded to ROC with ease. Researchers claim that the highest occupied molecular orbital (HOMO) excitation of the lowest occupied molecular orbital (LUMO), followed by the excited electrons transfer into the rhodium ROC, is the source of the hybrid light-harvesting molecule's photoelectrical property. In this instance, the electron photoexcites from HOMO (E = -5.48 eV) to LUMO (E = -3.64 eV) and then cascades into ROC ( $E = -3.96 \,\text{eV}$ ) without emitting radiation. This effective electron transfer from the lightharvesting SDE-B photocatalyst to the electro-catalytic 7511097, 0, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/php.13890 by The Librarian. Wiley Online Library on [27/0]/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

ROC center is made possible by the proximity and potential gradient between them. After being chemically protonated in aqueous environments, the resulting electrically reduced ROC, [Cp\*Rh(bpy)], undergoes a catalytic interaction with NAD<sup>+</sup>/NADP<sup>+</sup> that results in the regeneration of NADH/NADPH (79.58/76.36%).<sup>68</sup>

To investigate E-B and SDE-B photocatalyst for solar light-driven photo-regeneration of NADH/NADPH, photocatalytic experiments were conducted. The starting material E-B's capacity for photocatalytic NADH/NADPH regeneration was also investigated for the comparison sake. In both instances, the amount of photo-regenerated NADH/ NADPH was quantified using UV-visible spectroscopy. As can be seen in Figure 3, SDE-B had notable effectiveness in NADH/NADPH photo-regeneration, accumulating NADH/ NADPH at a steady rate up to 79.58/76.36% with time linearity. In totality, the newly designed photocatalyst is superior than E-B photocatalyst (Figure 3) due to high solar light-harvesting capacity and slow recombination charges. Therefore, the newly designed photocatalyst has additional significant application for organic transformation or oxygenation reaction (Table 1 and Figure 4).<sup>69,70</sup>

Furthermore, Figure S5 depicts the potential energy diagram associated with the generation and transmission of charge through artificial photosynthesis. Primarily, the generation of excited electron–hole pairs within the valence band (V.B.) of SDE-B photocatalyst [with a HOMO energy level of -5.48 eV] is triggered by the illumination of light, and this process is further facilitated by ascorbic acid, which moves the excited electrons into the conduction band (C.B.). Simultaneously, the excited electrons from SDE-B transition to NAD<sup>+</sup> from the C.B. [with a LUMO energy level of -3.64 eV] through the Rh-complex, which acts as an electron mediator, playing a role in the regeneration of NADH. This is attributed to the fact that the LUMO level (-3.64 eV) of

TABLE 1	Optimization	of the oxy	genation	reaction	conditions
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SCH <sub>3</sub> pl CH <sub>3</sub> 1a	$O_2$ , rt, solar light	O <sub>SS</sub> -CH <sub>3</sub> CH <sub>3</sub> 1b	
Entry	Photocatalyst	Solvent	Yield (%)
1.	SDE-B	DMSO	7
2.	SDE-B	DMF	21
3.	SDE-B	CH <sub>3</sub> CN	36
4.	SDE-B	C <sub>2</sub> H <sub>5</sub> OH	25
5.	SDE-B	IPA	99.5
6.	E-B	IPA	35
7.	Without catalyst	IPA	Trace
8.	SDE-B without light	IPA	10



FIGURE 4 SDE-B photo-catalyzed selective oxygenation of sulfides.

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SDE-B is higher than the potential levels of the Rh-complex (-3.96 eV) and NAD<sup>+</sup> (-4.20 eV). Consequently, excited electrons from SDE-B are seamlessly transferred to NAD<sup>+</sup>, resulting in a more efficient regeneration of NADH.<sup>71-73</sup>

The electrochemical impedance spectra (EIS) were scrutinized to assess the behavior of charge carriers' separation/migration and current in a three-electrode system. The analysis was performed over a frequency spectrum spanning from 100 kHz down to 0.1 Hz, employing an AC amplitude of 5 mV. The separation distance between the working and reference electrodes was maintained at a constant 1 cm for all electrochemical assessments. In the figure, we have illustrated the Nyquist plot for both E-B and sulfur-doped eosin-B (SDE-B) photocatalysts. Both samples' Nyquist plots display a flattened and smaller semicircular shape. In line with the results reported in the cited articles,<sup>74–76</sup> the Nyquist plot for SDE-B reveals a reduced radius, signifying a notably improved capacity for the migration and transfer of photo-generated carriers. The structure of SDE-B provides a clear pathway for photo-induced electrons and holes to migrate to the surface, resulting in a further decrease in charge transfer resistance (Rct) for SDE-B. Furthermore, this reduced charge resistance indicates effective electron transfer and current increase during the proton reduction process at the interface between the photocatalyst and electrolyte, primarily attributed to the sulfur doping of E-B. Also, we checked the stability of the photocatalyst in Figure S7.

### Oxygenation reaction via newly designed SDE-B photocatalyst under solar light

We started our research by investigating the oxidation of sulfides (1a) using 5mg of SDE-B for 9h under solar light from a blue LED (5W) at room temperature (Table 1). The reaction was originally carried out in DMSO, but only a very small amount of the desired product was produced (Entry 1). The findings of the solvent optimization showed that solvents are crucial to the oxidation reactions (Entries 2–5). Low yields of products were produced using solvents such as DMF,

CH<sub>3</sub>CN, and C<sub>2</sub>H<sub>5</sub>OH (Entries 2–4), while IPA produced the maximum conversion (99.5%) after 9 h at room temperature (Entry 5), likely as a result of its higher surface area and polarizability than E-B (Entry 6). As a result, we (Entry 5) obtained the best yield (99.5%) and selectivity (100%). No excessive oxidation was seen. A trace amount of product (Entry 7) was produced when SDE-B was not used as the photocatalyst in this reaction because of its incredibly weak UV–Vis absorption in IPA. In this reaction, the SDE-B photocatalyst without light was also investigated, and less product was produced (Entry 8) because of the excitation of the electron. No reaction occurred in the absence of SDE-B (Entry 7) or light (Entry 8), according to the control trials.<sup>69,77</sup>

# SDE-B photo-catalyzed selective oxygenation of sulfides

### Reaction conditions

Sulfides (0.2 mmol), SDE-B photocatalyst (5 mg), and IPA (4.0 mL) equipped with an oxygen balloon under solar light at room temperature.

We explored the substrate scope of this technique after establishing optimal reaction conditions, utilizing 5 mg of SDE-B as a photocatalyst in an aerobic environment at ambient temperature and photo-irradiation with a blue LED  $(1.0 \,\mathrm{mW \, cm^{-2}})$  (Figure 4). The results show that distinct thioethers (1a-4a) had nearly equally acceptable yields and selectivity. All substituted derivatives of thioanisoles having electron donating or withdrawing functional groups at the aryl moiety (2a) were oxidized, although longer reaction durations were required to achieve high conversions (2b). Furthermore, the CH<sub>3</sub>, Cl, and NH<sub>2</sub> groups were well-endured in this reaction (1a, 2a, and 4a), allowing for further functionalization. The rate of sulfoxidation was typically quicker in the aldehyde group containing thioethers (2a). Under these circumstances, the aldehyde group containing sulfides was oxidized to sulfoxides with excellent yields. Sulfidecontaining CH<sub>3</sub>, Cl, and NH<sub>2</sub> groups reacted slowly,



**SCHEME 4** Proposed photocatalytic oxygenation of sulfides into sulfoxides reaction from newly designed SDE-B photocatalyst under solar light in aerobic condition.

presumably because to the less electron density on the sulfur atom.

# Photocatalytic mechanistic investigations of oxygenation reactions

Photocatalytic mechanistic investigation of oxygenation reaction is shown in Schemes 1 and 4. In terms of mechanistic study, the process began with the activation by solar light of the SDE-B photocatalyst "a," which was subsequently transformed into "b." After accepting hydrogen atoms from IPA, the excited form "b" transforms into "c." Further accepting hydrogen atoms from IPA, the intermediate "c" transforms into "d" and produces acetone. The hydrogen acceptor was molecular oxygen, which changed into  $H_2O_2$  after accepting a hydrogen atom from the intermediate "d." Along with the removal of the  $H_2O$  molecule, the generated  $H_2O_2$  oxidizes the sulfides ("e") into their respective sulfoxides ("f"). In order to finish the photocatalytic cycle, the intermediate "d" was once more transformed into its initial state "a."<sup>55</sup>

### CONCLUSION

In conclusion, the allure of natural photosynthesis motivates us. By using Eosin-B and sulfur-doped eosin-B (SDE-B) photocatalysts, we thus showed how to reduce and oxygenate NAD<sup>+</sup>/NADP<sup>+</sup> and sulfides in an environmentally acceptable manner. The SDE-B photocatalyst's photocatalytic performance and important influencing elements for its practical application were scientifically investigated. In comparison with E-B, the SDE-B photocatalyst demonstrated better selective regeneration cofactor 1,4-NADH/NADPH and photocatalytic S=O bond formation, leading to a photocatalytic efficiency that was about sixfold higher under solar light medium. This study offers a simple method for developing an environmentally favorable benign photocatalyst with much higher photocatalytic activity for the production and regeneration of the S=O bond and 1,4-NADH/NADPH in the presence of solar light. Additionally, the SDE-B system may be capable of supporting the 1,4-NADH/NADPH-independent photocatalytic and photoenzymatic system for the widest range of applications.

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## SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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