CuS Nanoparticles Trigger Sulfite for Fast Degradation of Organic Dyes under Dark Conditions

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ABSTRACT: CuS nanoparticles (CuS NPs) were synthesized by a simple precipitation method using rice starch water as a capping and reducing agent. The phase composition, morphology, absorbance, chemical bonds, and chemical states of the CuS NPs were investigated systematically and then examined for dye degradation catalytic activity with or without sulfite (SO$_4^{2−}$) under dark conditions. Herein, we observed two reaction trends after the addition of SO$_4^{2−}$ in a CuS NPs/dye system, first substantially enhanced dye degradation and second greater degradation activity between reaction time interval “t” 0–12 min. The redox cycling of Cu(II)/Cu(I) and oxidized sulfur (SO$_2^{−}$) species on the surface of CuS NPs played a major role for the activation of SO$_3^{2−}$ and generation and transformation of a sulfite radical (•SO$_3$) into a sulfate radical (•SO$_4$). Scavenging studies of reactive oxygen species (ROS) revealed that •SO$_4$ was major reactive species involved in dye degradation. Our study showed that SO$_3^{2−}$ acted as a source and CuS NP surface acted as an SO$_3^{2−}$ activating agent for the generation of •SO$_4$, which degrades the dyes. The activation pathway of SO$_3^{2−}$ and generation pathway of relevant ROS were proposed.

1. INTRODUCTION

Water moves endlessly by the hydrological cycle and controls various natural processes. Endless desire of humans for better lifestyle has a great impact on the hydrological cycle. A great environmental concern is with synthetic organic dyes, which not only harm humans but do more harm to the aquatic ecosystem. Advanced oxidation processes (AOPs), including Fenton, ozonation, chlorination, and •SO$_4$−, have drawn much interest because of efficient destruction of organic contaminants, such as dyes, pesticides, perfluoro compounds, pharmaceuticals, and others. SO$_4^{−}$ is a strongly oxidizing species owing to high redox potential ($E_0 = 2.5−3.1$ V vs NHE, $4< \text{pH} < 9$) and longer half-life (30−40 $\mu$s) as compared to the hydroxyl radical (•OH) which has low redox potential ($E_0 = 2.18$ V vs NHE, pH = 7) and half-life (less than 1 $\mu$s). Furthermore, SO$_4^{−}$ reactivity is less influenced by pH and organic matter in real water as compared to the reactivity of •OH. Generally, SO$_4^{−}$ is generated by the activation of persulfate precursors, such as peroxydisulfate and peroxymonosulfate. Homogeneous transition metal ion catalysis, photolysis by UV light, alkaline pH, and photocatalysis.

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using transition metals including Fe(II/III), Mn(II), Co(II), Cr(VI), and Cu(II) exhibited excellent auto-oxidation of SO₄²⁻ to *SO₄· via *SO₅⁻. However, homogeneous transition metal ion-catalyzed SO₄²⁻ auto-oxidation suffers from drawbacks, such as the potential hazard of free metal ions, generation of sludge, and need for post-treatment. Research efforts have been made to explore an SO₃²⁻ activation method, which is environmentally friendly, illumination-free, and nontoxic.

It is well-established that the tailored heterogeneous nanocatalyst surface can be employed for environmental remediation. In addition, activation of SO₃²⁻ on the carefully designed heterogeneous catalyst surface is an important aspect of study pursued by researchers. Chen et al. demonstrated SO₃²⁻ activation over the NiFe₂O₄ nanomaterial surface for estriol removal. Ahmed et al. reported enhanced degradation of organic dyes due to the multifunctional surface impacts of silver, graphene oxide, and cellulose acetate on the nanocomposites. Zhang et al. demonstrated that solid NiS showed Fenton dye degradation catalytic activity due to the transformation of the S=O bond on the catalyst surface to *SO₄⁻ and *OH⁻. It is reported that surface SO₃ anchored on polystyrene NPs acts as a nanopromoter for methane hydrate formation. The presence of the SO₃ group on nano-ZrO₂ exhibited enhanced sorption of lead ions. Furthermore, SO₄ species bonded to SnO₂ NPs were found to be favorable for stabilization and growth of NPs. Iron oxide NPs functionalized by SO₄ species showed enhanced decomposition of refractory contaminants via a radical transfer reaction. Modified Fe₃O₄ acted as an excellent heterogeneous Fenton catalyst because of the conversion of surface SO₄ into *SO₄⁻. From the literature, it is evident that SO₃²⁻ on the surface of NPs promotes stabilization, degradation of contaminants, and metal ion sorption. Furthermore, the redox cycle of cupric [Cu(II)] and cuprous [Cu(I)] on the CuS NP surface exhibited enhanced activation of persulfate and dye degradation. The redox cycle of Fe³⁺/Fe²⁺ and Cu²⁺/Cu⁺ in the CuFe-LDH/PS/Vis system accounted for the activation of persulfate and degradation of azo dye. Therefore, utilization of redox reactions of metal ions and SO₄²⁻ species on the nanocatalyst surface is an attractive idea for the following processes: activation of SO₃⁻, generation of *SO₅⁻, and conversion of *SO₄⁻ into *SO₅⁻.

Transition metal sulfides, such as NiS, FeS, CoS, MoS₂, CuS, and so forth, have attracted interest in diverse fields including solar cells, batteries, thermoelectric energy harvesters, supercapacitors, water purification, and others. CuS, a unique p-type semiconductor, is a potential candidate owing to nontoxic nature and tunable properties, such as a direct band gap of 1.2–2.0 eV, crystal structures, stoichiometric composition, and localized surface plasmon resonance (LSPR). Chalcocite (Cu₂S) exhibits no LSPR peak, whereas CuS exhibits an LSPR peak in the near-infrared (NIR) region due to high concentration of free carriers. Zhu et al. demonstrated that CuS acts as an excellent co-catalyst with K₂S₂O₈ under visible light conditions for the generation of *SO₄⁻ which degraded orange II. However, *SO₄⁻ generation via SO₃²⁻ activation over the CuS NP surface for degradation of both cationic and anionic dyes under dark conditions is rarely studied.

Starch, a natural biodegradable polymer, is the major constituent in Oryza sativa (rice). Generally, rice starch water is prepared after soaking or boiling rice; however, the rice starch water is discarded during the food preparation procedure. Rice starch water has been explored as a capping and reducing agent in the synthesis of nanoparticles.

In the present study, CuS NPs were synthesized by a facile precipitation method using rice starch water as a capping and reducing agent. The crystalline phase, morphology, absorbance, and surface properties of the prepared CuS NPs were explored and applied for the generation of *SO₄⁻ via activation of SO₄²⁻ under dark conditions. The highly reactive *SO₄⁻ degraded the organic dyes. The CuS NP catalytic activity was evaluated under dark conditions for degradation of cationic methylene blue (MB) and anionic methyl orange (MO) and bromophenol blue (BB) as sample dyes. The experimental results demonstrated that surface chemistry of heterogeneous CuS NPs played a major role in dye degradation. The redox cycling of Cu(II)/Cu(I) triggered SO₄²⁻ and generated *SO₅⁻, which further grabbed dissolved oxygen and transformed to *SO₅⁻. SO₅⁻ species on the surface of CuS NPs efficiently transformed *SO₅⁻ to highly reactive *SO₄⁻, which degrades organic dyes.

2. RESULTS AND DISCUSSION

The synthesis of starch-capped CuS NPs was achieved by a simple precipitation method (Scheme 1).

The crystalline phase, purity, and composition of the CuS NPs were confirmed by powder X-ray diffraction (XRD) analysis (Figure 1). The XRD patterns revealed that the particles were crystalline and phase-pure. The diffraction peaks corresponding to (103), (006), (110), and (102) planes were well-consistent with the standard card of CuS (JCPDS 060464) and indicated the hexagonal phase of CuS NPs. The average crystallite size of CuS NPs measured using a well-known Debye–Scherrer formula was 8.87 nm.

The morphology information of the synthesized CuS sample was investigated by transmission electron microscopy (TEM) and high-magnification TEM (HRTEM) images. Apparently, the recorded TEM images (Figure 2a,b) revealed that the CuS NPs were slightly agglomerated, nanosized, and spherical in morphology. From the TEM image (Figure 2b), the particle

Scheme 1. Schematic Representation of the Formation of CuS NPs

Starch

Starch enriched with copper ions

Formation of CuS nanoparticles

Cu²⁺

CuS NPs

1. NH₃

2. Na₂S

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diameter histogram analysis was performed and the average particle diameter was about 11.60 nm (Figure 2c). The HRTEM image (Figure 2d) shows different periodic atom arrangements of the CuS NPs. The interlayer lattice spacing of 0.28 and 0.32 nm are unambiguously ascribed to the (103) and (101) plane of crystallite, respectively. Thus, HRTEM analysis was in agreement with powder XRD analysis. Next, the fast Fourier transform (FFT) image spot array (Figure 2e) and lattice averaged image (Figure 2f) obtained from the area indicated by hexagon in Figure 2d was also well-consistent with the hexagonal CuS of the [101] zone axis. Furthermore, energy-dispersive X-ray spectroscopy (EDX) revealed the purity of the sample and showed that the ratio of copper to sulfur was approximately 1:1. All XRD, TEM, HRTEM, and EDX analyses depicted the formation of CuS NPs by a simple precipitation method.

The absorbance property of CuS NPs was investigated by UV−visible−near-infrared (UV−vis−NIR) spectroscopy (Figure 3a). CuS NPs exhibited strong absorption in the entire visible region, and the LSPR peak was observed in the NIR region at wavelength ~760 nm. Furthermore, the absorption tail reached to ~1645 nm in the NIR range. The strong absorption in the visible region implied that CuS NPs might act as an excellent visible light harvester. Moreover, the absorption tail observed in the NIR range was attributed to excess holes in the valence band.33 Using the absorbance data, the optical band gap energy was calculated using eq 1.

\[(\alpha h\nu)^n = A(h\nu - E_g)\]  

(1)

where $\alpha$, $h\nu$, $A$, $E_g$, and $n$ are the absorption coefficient, photon energy, constant, and band gap and the value of $n$ is 2 for the direct transition, respectively. The optical band gap was determined by extrapolating the plot of $(\alpha h\nu)^n$ versus $h\nu$, and the band gap of CuS NPs was calculated to be 1.75 eV (Inset of Figure 3a).

The chemical bonds present in the CuS NPs were demonstrated by Fourier transform infrared spectroscopy (FTIR) analysis (Figure 3b). The characteristic vibration peaks at 520, 608, and 1065 cm$^{-1}$ were assigned to disulfide (S=S or S$_2^{2-}$), Cu−S stretching modes, and asymmetric valence S=S stretching vibration, which reflected the presence of disulfide, metal sulfi de, and S=O bonds, respectively.34 The characteristic bands at 867 and 2100 cm$^{-1}$ were attributed to C−H and C−C bending vibrations of aromatics, respectively.35 The absorption band between 900 and 1100 cm$^{-1}$ was attributed to the C−O−H bending vibration of starch.36 The vibrations at

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**Figure 1.** XRD patterns of CuS NPs.

**Figure 2.** (a,b) TEM images, (c) histogram of particle size distribution, (d) HRTEM image, (e,f) corresponding FFT and lattice averaged image from the area indicated by a hexagon in panel (d), (g) SAED pattern, and (h) EDX spectrum of CuS NPs.
1670 and 2365 cm\(^{-1}\) were attributed to the O–H bending mode of the water molecule. Furthermore, the band at 3000–3100 cm\(^{-1}\) was assigned to C–H stretching vibration. Thus, FTIR studies clearly indicated the presence of Cu–S, S–S, and S=O bonds on the surface of CuS NPs.

The chemical and electronic states of CuS NPs were investigated by X-ray photoelectron spectroscopy (XPS) (Figure 4). The Cu 2p region was dominated by two typical peaks at around 934.8 and 954.8 eV originating from Cu(II) 2p\(_{3/2}\) and Cu(II) 2p\(_{1/2}\), respectively (Figure 4a). The binding energy gap between the Cu(II) 2p\(_{3/2}\) and 2p\(_{1/2}\) peaks was 20 eV, which was in agreement with a previous report for the presence of CuS species on the surface.\(^3\) Generally, in the Cu 2p spectrum, the two shakeup satellite peaks at higher binding energy than those of Cu 2p\(_{3/2}\) and 2p\(_{1/2}\) peaks at around 944.2 and 962.3 eV likely arise from the paramagnetic divalent Cu species.\(^3\) The dominant Cu(II) 2p peaks accompanied by two shoulder peaks at lower binding energies at around 932.5 and 952.8 eV were assigned to Cu(I) 2p\(_{3/2}\) and Cu(I) 2p\(_{1/2}\), respectively, which denoted the presence of Cu\(^+\) in CuS.
Moreover, the Cu 2p XPS results clearly indicated the coexistence of Cu(II) and Cu(I) species in CuS NPs. Furthermore, oxidation of the sulfur species was observed from the S 2p spectrum (Figure 4b). The peaks at 162.2 and 163.7 eV were assigned to sulﬁde (S\(^{-2}\)) and disulﬁde (S\(^{2-}\)) species, respectively. The S\(^{2-}\) species was credited to the presence of Cu−S−S−Cu and S−S bonds. It is noteworthy that the crystal structure of CuS is complicated where a layer of triangular CuS\(_3\) units is sandwiched between two layers of CuS\(_4\) units by interlinking disulﬁde bonds.\(^{39}\) The important feature to be noted in the S 2p spectrum was the prominent peak at about 169.2 eV, which is ascribed to SO\(^{-2}\) species.\(^{40}\) Thus, surface analysis data obtained from the S 2p XPS and FTIR spectrum clearly indicated the presence of Cu−S, S−S, and S==O bonds on the surface of CuS NPs. The O 1S spectrum (Figure 4c) exhibited a symmetric peak at 532.1 eV, which was assigned to organic C−O bonds resulting from the capping molecule (i.e., starch). The C 1S spectrum (Figure 4d) was deconvoluted into three peaks: (i) 284.6 eV assigned to C−C and C−H bonds of sp\(^{3}\) hybridization, (ii) 285.3 eV ascribed to C−O−C bonds, and (iii) 285.6 eV attributed to C−OH, C==O, and O−C−O bonds, which further conﬁrmed the presence of starch, the capping molecule.\(^{41}\) The N 1S spectrum (Figure 4e) exhibited two peaks at about 400.1 and 401.4 eV, which was ascribed with the amine group (C−NH\(_2\)) and protonated amine group (C−NH\(_3\)\(^+\)) suggesting the interaction of starch and ammonia.\(^{42,43}\)

Under dark conditions, the catalytic activity of CuS NPs was evaluated for the degradation of sample dyes (MB, MO, and BB) with or without SO\(^{2-}\). We observed that the CuS NPs/SO\(^{2-}\) system was capable of enhancing the degradation of sample dyes. The time-resolved UV−vis absorbance spectra showed a decrease in characteristic UV−vis peaks of MB, MO, and BB, with SO\(^{2-}\) (20 mM SO\(^{2-}\)) for MB and 30 mM SO\(^{2-}\) for both MO and BB) under dark conditions for 20 min (Figure 5a−c). Notably, prominent decrease in absorbance was observed during the reaction time interval “t” 0−12 min. The relative concentration of MB, MO, and BB in different systems under dark conditions for 20 min was measured, which highlighted the signiﬁcant concentration change in dyes in the CuS/SO\(^{2-}\) system (Figure 5d−f). The percentage degradation of the organic dye was calculated using eq 2 given below

\[
\% \text{ degradation (}\xi\text{)} = \left(\frac{A_0 - A_t}{A_0}\right) \times 100
\]

where \(A_0\) and \(A_t\) represent the initial and time-dependent absorbance of dye solutions, respectively. In the presence of CuS NPs and in the absence of SO\(^{2-}\), 12.2, 11.0, and 12.0% of MB, MO, and BB were degraded, respectively. Next, in the presence of SO\(^{2-}\) and in the absence of CuS NPs, the degradation percentage of MB, MO, and BB was 8.7, 7, and 6.4%, respectively. However, in the case of the CuS NPs/SO\(^{2-}\) system under dark conditions for 20 min, the degradation percentage of MB, MO, and BB was 86.9, 78.3, and 76.0%, respectively. Thus, it was evident that the degradation percentage of the CuS NPs/SO\(^{2-}\) system was signiﬁcantly higher as compared to dye, CuS NPs, and SO\(^{2-}\) systems. The higher degradation activity was attributed to the synergistic eﬀect of CuS NPs and SO\(^{2-}\).

The scavenging studies of ROS were performed to gain insights into the predominant ROS involved in the dye degradation activity of the CuS NPs/SO\(^{2-}\) system (Figure 6). Specific ROS scavengers, namely, ethylenediamine tetraacetic acid (EDTA), isopropanol alcohol (IP), sodium nitrate, p-benzoquinone (BQ), and methanol, were spiked in the suspension as scavengers for holes (h\(^+\)), \(\cdot\text{OH}\), aqueous electron, superoxide radical (O\(_2\)\(^-\)), and both \(\cdot\text{OH}\) and \(\cdot\text{SO}_\text{4}\)\(^-\), respectively.\(^{44}\) We observed that the addition of EDTA, IP, sodium nitrate, and BQ had no signiﬁcant eﬀect in dye degradation, which revealed that h\(^+\), \(\cdot\text{OH}\), aqueous electron, and \(\cdot\text{O}_2\) were not dominant ROS (Figure 6). We designed the ROS scavenging experiments using methanol as an eﬃcient scavenger and the relative Degradation percentage was shown in Figure 6.
scavenger of both •OH and •SO4−, whereas IP as a preferential scavenger of •OH.44 Notably, on the addition of methanol, the degradation efficiency of MB, MO, and BB was reduced to 18.9, 22.4, and 23.8%, respectively, indicating that the CuS NPs/ SO3− system can indeed generate •SO4− which can degrade the dye molecules into small molecules. It is noteworthy that the redox potential of the •SO4− radical (E0 = 2.5–3.1 V vs NHE, 4 < pH < 9) was higher as compared to •OH (E0 = 2.18 V vs NHE, pH = 7), •O2− (E0 = 0.15 V, pH = 7), •SO4− (E0 = 0.75 V vs NHE, pH = 7), and •SO3− (E0 = 0.81 V).5 Hence, enhanced dye degradation in the CuS NPs/SO3− system can be attributed to the generation of highly reactive •SO4−.

To illustrate the catalytic mechanism of CuS NPs, we performed two experiments. In the first experiment, CuII and SO2− were added to the MB dye without CuS NPs and the MB degradation percentage was only 3% after 20 min. In the second experiment, a definite quantity of CuS NPs and 10 mM sodium sulfate (Na2SO4) were added to MB which showed a degradation percentage of around 4%. These experimental results demonstrated that the peculiar surface of CuS NPs triggered SO2− for dye degradation.

Based on the dye degradation experimental results obtained from the CuS NPs/SO2− system, we observed two reaction trends with regard to degradation activity. First, substantially enhanced degradation with the CuS NPs/SO2− system as compared to without SO2− was observed. Second, greater catalytic activity was apparently observed during reaction time interval “t” 0–12 min. The first reaction trend was attributed to the activation of SO2− by redox cycling of Cu(II)/Cu(I) and sequential generation of •SO4− via reaction with SO2− species on the surface of CuS NPs. Typically, Cu(II) species on the CuS NP surface reacted with SO2− to create Cu(I) and •SO3−, as shown in eqs 3 and 4. Cu(I) further grabbed oxygen to create Cu(II) and •O2−, as shown in eq 5. On the CuS surface, the cycle of redox reactions as illustrated in eqs 3–5 activated SO2− and generated •SO4−. The resultant •SO4− was able to grab oxygen and further evolved to •SO5−, as represented in eq 6. The •SO5− reacted with SO2− species on the CuS NP surface to get further evolved to highly reactive •SO4−, as represented in eq 7. Finally, •SO4− degraded the dyes as represented in eq 8. Thus, several reactive species, namely, •SO5−, •O2−, •SO3−, and •SO4− radicals, were generated in the reaction medium. Nevertheless, ROS scavenging studies confirmed the contribution of •SO4− in the dye degradation process. Hence, it was evident that the synergistic effect of the redox cycle of Cu ions and SO2− species on the CuS NP surface triggered SO2− and generated •SO4− which ultimately degraded the dyes. The aforementioned degradation processes are represented below as eqs 3–8 and Scheme 2.

\[
\begin{align*}
\text{Cu(II) + Na}_2\text{SO}_3 & \rightarrow \text{Cu(II)} - \text{OSO}_2^- \\
\text{Cu(II)} - \text{OSO}_2^- & \rightarrow \text{Cu(II)} + *\text{SO}_3^- \\
\text{Cu(I)} + \text{O}_2 & \rightarrow \text{Cu(II)} + \text{*O}_2^- \\
*\text{SO}_3^- + \text{O}_2 & \rightarrow *\text{SO}_4^- \\
*\text{SO}_4^- + \text{SO}_2^- & \rightarrow *\text{SO}_4^- + \text{SO}_2^{2-} + 1 \\
*\text{SO}_4^- + \text{Dyes} & \rightarrow \text{Degraded products}
\end{align*}
\]

When considering the second reaction trend for greater reactivity during reaction time interval “t” 0–12 min. The degradation percentage for MB, MO, and BB was 82.84, 73.2, and 71.1%, respectively, under dark conditions for the first 12 min. During the reaction time interval “t” 60–20 min, the degradation percentage for MB, MO, and BB was marginally increased to 86.9, 78.3, and 76.0%, respectively. Thus, it is evident that the degradation activity was higher during reaction time “t” 0–12 min. It is reported that •SO3− can be rapidly oxidized by dissolved oxygen into •SO4− with an approaching-diffusion rate of 1.5 × 107 M−1 S−1.45 Furthermore, •SO3− obtained from even 0.5 mM SO2− was sufficient to completely deplete dissolved oxygen.46 Our experiments with requisite SO2− dosage was sufficient for rapid oxidation of •SO3− to •SO5−. However, as the degradation process progressed, it can be speculated that dissolved oxygen content in the system might be insufficient for the occurrence of the chain reaction, as illustrated in eqs 6–8. Thus, after the addition of SO2−, the initial faster degradation rate during the first 12 min was attributed to higher generation of •SO4− and the later slower degradation rate was attributed to insufficient generation of •SO4−. Furthermore, we studied the effect of SO2− dosage (0, 10, 20, 30, 40, and 50 mM) for degradation of MB, MO, and BB, respectively (Figure 7a–c). The experimental results of the catalytic degradation of MB, MO, and BB were used for calculating the reaction rate and rate kinetics using the second-order model, as represented in eq 9

\[
\frac{1}{C_t} - \frac{1}{C_0} = kt
\]

where \(C_0\), \(C_t\), \(k\), and \(t\) represent the concentration of the dyes at time \(t\), initial concentration of dyes, rate constant (L mg−1 min−1), and time, respectively. The plots of the observed second-order rate constant were calculated by the slopes of the
straight lines in the linearized plots of \((1/C_t \rightarrow 1/C_0)\) versus time. These experimental results obeyed the linear relation implying that the catalytic degradation followed second-order kinetics (Figure 7d–f). We observed a nonlinear change in the rate constant of the CuS NPs/SO\(_3^{2−}\) system under dark conditions for dye degradation with different concentrations of SO\(_3^{2−}\) (Table 1).

**Table 1. Rate Constant of the CuS NPs/SO\(_3^{2−}\) System Under Dark Conditions for Dye Degradation with Different Concentrations of SO\(_3^{2−}\)**

| Dyes | CuS catalytic degradation rate \((L \text{mg}^{-1} \text{min}^{-1})\) on Na\(_2\)SO\(_3\) addition | 0 mM | 10 mM | 20 mM | 30 mM | 40 mM | 50 mM |
|------|-------------------------------------------------|-----|-----|-----|-----|-----|-----|
| MB   |                                                 | 0.0075 | 0.2028 | 0.4494 | 0.3533 | 0.2818 | 0.2417 |
| MO   |                                                 | 0.0015 | 0.1413 | 0.1660 | 0.2443 | 0.1856 | 0.1486 |
| BB   |                                                 | 0.0095 | 0.1392 | 0.1684 | 0.2049 | 0.1073 | 0.1499 |

The apparent second-order rate constant values increased to 0.2028 and 0.4494 L mg\(^{-1}\) min\(^{-1}\) with 10 and 20 mM SO\(_3^{2−}\) for MB; 0.1413, 0.1660, and 0.2443 L mg\(^{-1}\) min\(^{-1}\) with 10, 20, and 30 mM SO\(_3^{2−}\) for MO; and 0.1392, 0.1684, and 0.2049 L mg\(^{-1}\) min\(^{-1}\) with 10, 20, and 30 mM SO\(_3^{2−}\) for BB degradation, respectively. These degradation experiments validate that SO\(_3^{2−}\) dosage had a considerable impact on dye degradation. The rate constant of MB increased by about 27, 60, 47, 37, and 32 times upon the addition of 10, 20, 30, 40, and 50 mM sulphite. The rate constant of MO increased by about 94, 110, 162, 123, and 99 times and that of BB increased by about 15, 18, 22, 11, and 16 times upon the addition of 10, 20, 30, 40, and 50 mM sulphite, respectively. Notably, the rate constant increased linearly at lower SO\(_3^{2−}\) concentration but the rate of enhancement was less prominent at a higher concentration. We speculate three rate-limiting factors at a higher SO\(_3^{2−}\) concentration. The first rate-limiting factor can be attributed to the fate and quenching of the intermediate \(\cdot\text{SO}_5^{−}\), as shown in eqs 10–12.

\[
\cdot\text{SO}_5^{−} \rightarrow \text{SO}_3^{−} + \cdot\text{O}_2^{−} \tag{10}
\]

\[
\cdot\text{SO}_5^{−} + \text{SO}_3^{2−} \rightarrow \text{SO}_5^{2−} + \cdot\text{SO}_3^{−} \tag{11}
\]

\[
\cdot\text{SO}_5^{−} + \text{SO}_3^{2−} + \text{H}_2\text{O} \rightarrow \cdot\text{OH}^{−} + 2\text{SO}_4^{2−} + \text{H}^{+} \tag{12}
\]

The fate of \(\cdot\text{SO}_3^{−}\) is still uncertain, it may get quenched as shown in eq 10 or react with excess SO\(_3^{2−}\) as mentioned in eqs 11 and 12. The second rate-limiting factor can be attributed to the depletion of dissolved oxygen in the reaction medium due to the oxygen-mediated conversion of SO\(_3^{2−}\) to \(\cdot\text{SO}_5^{−}\); notably, the rate constant of eq 6 is \(< 10^9 \text{M}^{-1} \text{S}^{-1}\). The third rate-limiting factor can be attributed to the influence of SO\(_3^{2−}\) concentration in the redox chemistry of Cu ions and stability of SO\(_x^{2−}\) species on the surface of CuS NPs. Further studies are needed to ascertain these limiting factors.

Generally, recycle numbers denote the stability, potential, and sustainability of the catalyst in dye degradation. CuS NPs showed significant dye degradation catalytic effects for three cycles (Figure 8). After three cycles, the degradation percentages of MB, MO, and BB were 45.2, 38.4, and 31.3%, respectively. The decrease in degradation percentage after three cycles was attributed to the change in the surface composition of CuS NPs. We performed FTIR analysis to demonstrate the change in surface chemical composition on the CuS NPs after three degradation cycles. The FTIR spectra (Figure 9) of CuS NPs before catalysis and after three cycles revealed that the Cu\(−\)S and S\(=\)O stretching vibrations exhibited intense decrease, which validated the pivotal role of Cu and SO\(_x^{2−}\) species in dye degradation.

Catalytic dye degradation by CuS NPs under dark conditions is scarce. We found that CuS NPs exhibited excellent degradation efficiency for both cationic and anionic dyes. 

![Figure 7. (a–c) Plot of \((C_t/C_0)\) vs time and (d–f) plot of \((1/C_t \rightarrow 1/C_0)\) vs time for the CuS NPs/SO\(_3^{2−}\) system for dye degradation with different concentrations of SO\(_3^{2−}\).](https://pubs.acs.org/journal/acsodf)
Dissolved oxygen in the medium and SO₃ degradation of organic dyes under dark conditions. The two conditions.

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3. CONCLUSIONS

In summary, we have synthesized starch-capped CuS NPs by a simple precipitation method using rice water as a capping and reducing agent. In a typical synthesis, 200 mL of rice starch water was warmed to 70 °C, and then, 3.19 g (0.1 M) of copper sulfate pentahydrate (CuSO₄·5H₂O) was dissolved in hot rice starch water and made up to 200 mL using DW. The resultant solution was made basic by adding 10 mL of ammonia (0.1 M) and heated to 60 °C for 10 min. Next, sodium sulfide (Na₂S) solution was prepared by dissolving 1.56 g (0.1 M) of Na₂S in 200 mL of DW. The Na₂S solution was added dropwise to CuSO₄·5H₂O-enriched starch solution at a flow rate of 5 mL/min under mechanical stirring. The reaction mixture turned to green via brown and the formation of green color solution indicated the formation of CuS NPs. The resultant mixture was allowed to react for 2 h at 60 °C under mechanical stirring and then cooled to room temperature. The blackish green precipitate was filtered and washed thrice with DW. Finally, the precipitate was dried at 60 °C in an oven overnight.

4. MATERIALS AND METHODS

4.1. Materials. All the chemicals were purchased from commercial sources and used without further purification. Rice was purchased from local market. All aqueous solutions used in the experiments were prepared using single distilled water (DW).

4.2. Preparation of Rice Starch Water. A total of 200 g of rice was washed three times with DW to remove dust particles and impurities. Then, rice was soaked in water for 30 min and thereafter cooked in an open vessel with 600 mL of DW for 30 min. Rice starch water was filtered through cotton filter cloth and stored in sterile conical flasks.

4.3. Synthesis of CuS NPs. CuS NPs were synthesized by a simple precipitation method using rice starch water as a capping and reducing agent. In a typical synthesis, 200 mL of rice starch water was warmed to 70 °C, and then, 3.19 g (0.1 M) of copper sulfate pentahydrate (CuSO₄·5H₂O) was dissolved in hot rice starch water and made up to 200 mL using DW. The resultant solution was made basic by adding 10 mL of ammonia (0.1 M) and heated to 60 °C for 10 min. Next, sodium sulfide (Na₂S) solution was prepared by dissolving 1.56 g (0.1 M) of Na₂S in 200 mL of DW. The Na₂S solution was added dropwise to CuSO₄·5H₂O-enriched starch solution at a flow rate of 5 mL/min under mechanical stirring. The reaction mixture turned to green via brown and the formation of green color solution indicated the formation of CuS NPs. The resultant mixture was allowed to react for 2 h at 60 °C under mechanical stirring and then cooled to room temperature. The blackish green precipitate was filtered and washed thrice with DW. Finally, the precipitate was dried at 60 °C in an oven overnight.

4.4. Characterization. The crystallinity and phase composition of CuS NPs were analyzed by XRD analysis performed on a PANalytical, Netherlands, instrument using Cu Kα (λ = 1.54060 Å) irradiation at 40 kV and 15 mA. Powder XRD patterns were obtained in the 2θ range of 10.00 to 79.97° with a step size of 0.0220. The morphology of the sample was

Table 2. Comparison of Degradation Efficiency of CuS NPs Reported in the Present Work with Other CuS-Based Studies Reported in the Literature

| catalyst | catalytic condition | dye conc. (mg L⁻¹) | ROS | degradation (%) | time (min) | reference |
|----------|---------------------|--------------------|-----|-----------------|------------|-----------|
| starch-capped CuS NPs | dark and Na₂SO₄ | 6 of MB, 6.5 of MO, 3.35 of BB | SO₄²⁻ | 86.9 of MB, 78.3 of MO and 76.0 of BB | 20 | present work |
| CuS NPs | visible light and K₂S₂O₄ | 60 | SO₄²⁻ | 98.88 of orange II | 120 | 24 |
| CuS porous aggregate | sunlight and H₂O₂ | 10 | OH⁻ | 100 of MB | 10 | 37 |
| CuS@L-Cys NPs | visible light | 10 | OH⁻ | 99 of MO | 35 | 48 |
| CuS-functionalized aerogel | visible light and H₂O₂ | 20 | OH⁻ | 97 of MO | 6 | 49 |
| starch-capped CuS NPs | visible light and H₂O₂ | 10 | OH⁻ and O₂⁻ | 100 of MB; 99 of rhodamine B, 95.2 of MO and 94.4 of BB | 30 | 34 |
| RGO/CuS | sunlight | 10 | OH⁻ and O₂⁻ | 97.6 of malachite green | 90 | 50 |
4.5. Dye Degradation Experiments. The CuS NPs were evaluated for the degradation of MB, MO, and BB with or without sodium sulfite (Na2SO3) under dark ambient conditions. Na2SO3 was used as a source of SO₄²⁻. In a typical process, 25 mg of the CuS catalyst was added to 50 mL of aqueous solution of 2 × 10⁻⁵ M MB or MO and 5 × 10⁻⁶ M BB. The suspension of organic dyes and CuS NPs were stirred under dark conditions for 60 min to establish adsorption–desorption equilibrium. A certain amount of Na2SO3 was then added and the suspension was allowed to react under dark conditions. At regular time intervals, a certain volume of the reaction mixture was extracted for concentration or degradation analysis. Using a UV–vis spectrophotometer, the degradation of MB, MO, and BB was analyzed by measuring the characteristic absorbance maxima at 663, 463, and 591 nm, respectively. The same parameters were followed for the degradation experiments without Na2SO3. The procedure for recycling experiments was the same as the degradation experiments.

4.6. Detection of ROS. The relevant ROS involved in the degradation of sample dyes using the CuS NPs/SO₄²⁻ system under dark conditions were identified by scavenging experiments. Specific ROS scavengers, namely, ethylenediamine tetraacetic acid (EDTA), isopropyl alcohol (IP), sodium nitrate, p-benzoquinone (BQ), and methanol, were spiked in the suspension as scavengers for holes (h⁺), ·OH, aqueous electron, ·O₂⁻, and both ·OH and ·SO₄⁺, respectively. The experimental process was similar to the dye degradation experiment described above.

## REFERENCES

1. Hodges, B. C.; Cates, E. L.; Kim, J.-H. Challenges and Prospects of Advanced Oxidation Water Treatment Processes Using Catalytic Nanomaterials. Nat. Nanotechnol. 2018, 13, 642–650.
2. Guo, Y.; Lou, X.; Fang, C.; Xiao, D.; Wang, Z.; Liu, J. Novel Photo-Sulfite System: Toward Simultaneous Transformations of Inorganic and Organic Pollutants. Environ. Sci. Technol. 2013, 47, 11174–11181.
3. Deng, W.; Zhao, H.; Pan, F.; Feng, X.; Jung, B.; Abdul-Wahab, A.; Batchelor, B.; Li, Y. Visible-Light-Driven Photocatalytic Degradation of Organic Water Pollutants Promoted by Sulfite Addition. Environ. Sci. Technol. 2017, 51, 13372–13379.
4. Yang, Y.; Jiang, J.; Lu, X.; Ma, J.; Liu, Y. Production of Sulfate Radical and Hydroxyl Radical by Reaction of Ozone with Peroxymonosulfate: A Novel Advanced Oxidation Process. Environ. Sci. Technol. 2015, 49, 7330–7339.
5. Liu, Y.; Fan, X.; Qian, X.; Fan, Y.; Chen, S.; Zhao, X. Enhanced Perofluorocarboxylic Acid Degradation by Electrochemical Activation of Sulfate Solution on B/N Codoped Diamond. Environ. Sci. Technol. 2019, 53, 5195–5201.
6. Xia, X.; Zhu, F.; Li, J.; Yang, H.; Wei, L.; Li, Q.; Jiang, J.; Zhang, G.; Zhao, Q. A Review Study on Sulfate-Radical-Based Advanced Oxidation Processes for Domestic/Industrial Wastewater Treatment: Degradation, Efficiency, and Mechanism. Front. Chem. 2020, 8, 1–16. 
7. Wang, Z.; Jiang, J.; Pang, S.; Zhou, Y.; Guan, C.; Gao, Y.; Li, J.; Yang, Y.; Qiu, W.; Jiang, C. Is Sulfate Radical Really Generated from Peroxysulfate Activated by Iron(II) for Environmental Decontamination? Environ. Sci. Technol. 2018, 52, 11276–11284.
8. Wei, Z.; Villamena, F. A.; Weavers, L. K. Kinetics and Mechanism of Ultrasonic Activation of Persulfate: An in Situ EPR Spin Trapping Study. Environ. Sci. Technol. 2017, 51, 3410–3417.
9. Qi, C.; Liu, X.; Lin, C.; Zhang, H.; Li, X.; Ma, J. Activation of Peroxysulfate by Microwave Irradiation for Degradation of Organic Contaminants. Chem. Eng. J. 2017, 315, 201–209.
10. Wang, L.-D.; Ma, Y.-L.; Hao, J.-M.; Zhao, Y. Mechanism and Kinetics of Sulfite Oxidation in the Presence of Ethanol. Ind. Eng. Chem. Res. 2009, 48, 4307–4311.
11. Li, Q.; Guo, B.; Yu, J.; Ran, J.; Zhang, B.; Yan, H.; Gong, J. R. Highly Efficient Visible-Light-Driven Photocatalytic Hydrogen Production of CdS-Cluster-Decorated Graphene Nanosheets. J. Am. Chem. Soc. 2011, 133, 10878–10884.
12. Zhang, J.; Zhu, L.; Shi, Z.; Gao, Y. Rapid Removal of Organic Pollutants by Activation Sulfite with Ferrate. Chemosphere 2017, 186, 576–579.
13. Xu, Y.; Gocze, Z.; Cabooter, D.; Dewil, R. Efficient Reduction of Carbamazepine Using UV-Activated Sulfite: Assessment of Critical Process Parameters and Elucidation of Radicals Involved. Chem. Eng. J. 2021, 404, 126403.
14. Chen, Y.; Li, M.; Tong, Y.; Liu, Z.; Fang, L.; Wu, Y.; Fang, Z.; Wu, F.; Huang, L.-Z. Radical Generation via Sulfite Activation on NiFeOₓ Surface for Estriol Removal: Performance and Mechanistic Studies. Chem. Eng. J. 2019, 368, 495–503.
15. Yuan, Y.; Zhao, D.; Li, J.; Wu, F.; Brigante, M.; Mailhot, G. Rapid Oxidation of Paracetamol by Cobalt(II) Catalyzed Sulfite at Alkaline pH. Catal. Today 2018, 313, 155–160.
16. Zhou, D.; Chen, L.; Li, J.; Wu, F. Transition Metal Catalyzed Sulfite Auto-Oxidation Systems for Oxidative Decontamination in Waters: A State-of-the-Art Minireview. Chem. Eng. J. 2018, 346, 726–738.
(17) Ahmed, M. K.; Shalan, A. E.; Afifi, M.; El-Desoky, M. M.; Langeros-Méndez, S. Silver-Doped Cadmium Selenide/Graphene Oxide-Filled Cellulose Acetate Nanocomposites for Photocatalytic Degradation of Malachite Green toward Wastewater Treatment. ACS Omega 2021, 6, 23129–23138.

(18) Zhang, A.; Huang, X.; Nan, Z. Facile Synthesis of 3D-Structured NIS as an Excellent Fenton-like Catalyst under Various pH through Different Mechanisms. Inorg. Chem. 2019, 58, 14136–14144.

(19) Wang, F.; Guo, G.; Luo, S.-J.; Guo, R.-B. Preparation Of *SO₃⁻*-Coated Nanopromoters for Methane Hydrate Formation: Effects of the Existence Pattern of *SO₃⁻* Groups on the Promotion Efficiency. J. Mater. Chem. A 2017, S, 2640–2648.

(20) Zhang, Q.; Du, Q.; Hua, M.; Jiao, T.; Gao, F.; Pan, B. Sorption Enhancement of Lead Ions from Water by Surface Charged Polystyrene-Supported Nano-Zirconium Oxide Composites. Environ. Sci. Technol. 2013, 47, 6536–6544.

(21) Gutiérrez-Báez, R.; Toledo-Antonio, J. A.; Cortés-Jácome, M. A.; Sebastian, P. J.; Vázquez, A. Effects of the SO₃⁻ Groups on the Textural Properties and Local Order Deformation of SnO₂ Rutile Structure. Langmuir 2004, 20, 4265–4271.

(22) Kim, J.; Choe, Y. J.; Kim, S. H.; Jeong, K. Enhancing the Decomposition of Refractory Contaminants on SO₃⁻-Functionalized Iron Oxide to Accommodate Surface SO₃⁻ Generated via Radical Transfer from OH. Appl. Catal., B 2019, 252, 62–76.

(23) Li, T.; Wang, X.; Chen, Y.; Liang, J.; Zhou, L. Producing "OH, SO₄²⁻, and "O₂" in Heterogeneous Fenton Reaction Induced by Fe₆O₇-Moderated Schwertmannite. Chem. Eng. J. 2020, 393, 124735.

(24) Zhu, B.; Cheng, H.; Qin, Y.; Ma, J.; Kong, Y.; Komarneni, S. Copper Sulfide as an Excellent Co-Catalyst with K₂SO₄ for Dye Decomposition in Advanced Oxidation Process. Sep. Purif. Technol. 2020, 233, 116057.

(25) Ma, Y.; Chen, F.; Yang, Q.; Zhong, Y.; Xu, Y.; Xie, T.; Li, X.; Wang, D.; Zeng, G. Sulfate Radical Induced Degradation of Methyl Violetazo Dye with CuFe Layered Double Hydroxide as Heterogeneous Photoactivator of Persulfate. J. Environ. Manage. 2018, 220, 406–414.

(26) Abdel Maksoud, M. I. A.; Fahim, R. A.; Shalan, A. E.; Abd Elkodous, M.; Olojede, S. O.; Osman, A. I.; Farrell, C.; Al-Muhtaseb, A. H.; Awed, A. S.; Ashour, A. H.; et al. Advanced Materials and Technologies for Supercapacitors Used in Energy Conversion and Storage: A Review. Environ. Chem. Lett. 2021, 19, 375–439.

(27) Sanad, M. F.; Shalan, A. E.; Abdelatif, S. O.; Sere, E. S. A.; Adly, M. S.; Alsham, M. A. Thermoelectric Energy Harvesters: A Review of Recent Developments in Materials and Devices for Different Potential Applications. Top. Curr. Chem. 2020, 378, 48.

(28) Roy, P.; Srivastava, S. K. Nanostructured Copper Sulphides: Synthesis, Properties and Applications. CrystEngComm 2015, 17, 7801–7815.

(29) Raj, S. I.; Jaiswal, A.; Uddin, I. Ultrasmall aqueous starch-capped CuS quantum dots with tunable localized surface plasmon resonance and composition for the selective and sensitive detection of mercury(II) ions. RSC Adv. 2020, 10, 14050–14059.

(30) Mathew, S.; Raveendran, A.; Mathew, J.; Radhakrishnan, E. K. Antibacterial Effectiveness of Rice Water (Starch)-Capped Silver Nanoparticles Fabricated Rapidly in the Presence of Sunlight. Photochem. Photobiol. 2019, 95, 627–634.

(31) Singh, M. K.; Manda, P.; Singh, A. K.; Mandal, R. K. Localized Surface Plasmon Behavior of Ag-Cu Alloy Nanoparticles Stabilized by Rice-Starch and Gelatin. AIP Adv. 2015, 5, 107108.

(32) Mousavi-Kamazani, M.; Zarghami, Z.; Salavati-Niasari, M. Facile and Novel Chemical Synthesis, Characterization, and Formation Mechanism of Copper Sulfide (Cu₂S, Cu₂S/CuS, CuS) Nanostructures for Increasing the Efficiency of Solar Cells. J. Phys. Chem. C 2016, 120, 2096–2108.

(33) Putnis, A. The Transformation Behaviour of Cuprous Sulphides and Its Application to the Efficiency of Cu₂S-CdS Solar Cells. Philos. Mag. 1976, 34, 1083–1086.