CuS nanoparticles decorated MoS$_2$ sheets as an efficient nanozyme for selective detection and photocatalytic degradation of hydroquinone in water

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The development of cost effective and efficient nanomaterials with enzyme mimetics and photocatalytic activity has achieved tremendous research interest in the quantitative detection as well as removal of toxic environmental pollutants. CuS nanoparticles decorated MoS$_2$ sheets were successfully synthesized adopting a simple hydrothermal technique and using low-cost materials. The nanocomposite was successfully used as an efficient catalyst for the selective detection and removal of a toxic phenolic compound like hydroquinone (HQ). The CuS–MoS$_2$ nanocomposite catalyzed the oxidation of different chromogenic substrates like 3,3',5,5'-tetramethylbenzidine, 2,2'-azino-bis(3-ethylbenzo-thiazoline-6-sulfonic acid)diammonium salt, and o-phenylenediamine in the presence of H$_2$O$_2$, indicating its peroxidase-like activity as natural Horseradish peroxidase (HRP). The catalytic performance of the nanozyme was further investigated through the typical Michaelis–Menten kinetics. The results showed that the proposed sensor exhibited improved catalytic properties with a wide linear relationship (0.4–50 μM) and a low detection limit of 3.68 μM for HQ detection in aqueous medium. Meanwhile, the mechanism of HQ sensing in the presence of CuS–MoS$_2$ nanozyme was systematically investigated. Moreover, the CuS–MoS$_2$ nanozyme possessed significant photocatalytic activity and 83% HQ decomposition was achieved within 240 min under irradiation of natural sunlight. The mechanism of enhanced photocatalytic degradation of HQ through the formation of *OH radicals as reactive species was evidenced by analyzing the formation of fluorescent active molecules on the addition of terephthalic acid and by high-resolution mass spectrometry. Thus CuS–MoS$_2$ represents a new and promising HQ sensing material in a highly sensitive and fast manner as well as an efficient photocatalyst for the degradation of HQ to its non-toxic products under natural sunlight irradiation.

1 Introduction

The recent advancement in nanotechnology has offered enormous opportunities for developing nanozyme materials with extraordinary characteristics and remarkable catalytic efficiency in different potential applications including environmental protection, biosensing, disease treatments, etc. Recently, nanozymes have gained significant attention due to their potential in replacing natural enzymes with high stability, superior catalytic activity and lower cost of synthesis. The adjustable size and morphologies, and tunable physical and chemical properties make enzymes foremost catalysts in different applications such as radiotherapy, cancer treatment, sensing, catalysis, etc. Copper sulphide (CuS), a typical p-type semiconductor material, possesses a narrow band gap (2.1 eV) in which an empty 3p-orbital of sulphur behaves as an electron acceptor and exhibits excellent physical and chemical properties. To date, different researchers have established the peroxidase-like catalytic activity and photocatalytic activity of CuS NPs. But, there are some drawbacks including a complicated modification technique and easy aggregation, which are associated with the nanomaterial based catalysts which lead to obstructing their widespread application. In order to improve the catalytic performance, nanoparticles are fabricated on the surface of different support materials which lead to the formation of new heterostructure materials with superior physical and chemical characteristics and superior catalytic activity.

Since the revolutionary discovery of monolayer graphene in 2004, other two-dimensional (2D) layered materials particularly...
layered transition metal dichalcogenides (LTMDs) have attracted intensive attention from researchers in a variety of applications. Among the different TMDs, naturally occurring mono and few-layer molybdenum disulfide (MoS2) exhibits tunable band gaps (1.2–1.8 eV), high thermal stability and has received significant attention from researchers of different fields in recent years. Bulk MoS2 is made up of three atomic layers of S-Mo-S sandwiched-like structures, bound by weak van der Waals forces and easily exfoliated to a single- or few-layered structure by different chemical or physical approaches.

Because of the large specific surface area and rich active edges, graphene-like MoS2 is considered as a favorable support material for the decoration of nanomaterials with extending functionalities for potential catalytic performance. To date many metal sulfide nanoparticles have been successfully decorated on MoS2 sheets, which possess novel properties and functionalities for utilization in different potential fields. Based on previous reports, it is found that MoS2 behaves as a nanozyme with the capability to decompose H2O2 to hydroxyl radicals (·OH) which can oxidize chromogenic substrates to produce the corresponding oxidized colored products. Cai’s group designed a colorimetric probe based on the peroxidase-mimic activity of MoS2-Pt3Au1 nanocomposites for the detection of phenolic compounds in aqueous medium. Combination of CuS nanoparticles with MoS2 sheets leads to the formation of a nanocomposite with a modified electronic structure and exhibiting strong electron capture at low initial reduction potential and the fast current transfer reaction.

Hydroquinone (HQ), one type of phenolic compound, is commonly used as a dynamic organic raw material in textile, cosmetic, dyestuff, pharmaceutical, plastic, rubber and pesticide industries. Owing to the low degradability in the ecological circumstances and high toxicity, excessive release of HQ during its production and application processes has become harmful to humans and the environment. Continual exposure to HQ can cause headache, vomiting, nausea, abdominal cramps, dizziness, and muscle twitching, and affect kidneys and liver. Therefore detection of HQ in the natural environment and its removal have attracted enormous importance. Different analytical techniques including liquid chromatography, spectrophotometry, photoluminescence and electrochemical techniques have been used for the detection of HQ in recent years. Compared to these conventional methods, the colorimetric detection technique is considered a more efficient technique because of its simplicity, high sensitivity and selectivity, low cost, and visualization by the naked eye without sophisticated and expensive instruments.

Wang et al. utilized 3D porous ZnO/ZnFe2O4/graphene foam (3D ZZFO/GF) for colorimetric detection of hydroquinone based on its peroxidase-like activity. They reported the lower detection limit for hydroquinone up to 3.75 μM using this colorimetric probe. Song and co-workers detected hydroquinone up to a concentration of 2.7 μM using NiCo2O4 microspheres based on its oxidase-like activity towards the oxidation of TMB.

Similarly, due to the cost-effectiveness, eco-friendly nature, simple operation technique, and production of non-toxic degraded products, the photodegradation technique is considered as a highly efficient and widely used method for environmental remediation purposes in comparison to different traditional techniques. A photocatalyst consisting of nanoparticles with unique physical and chemical properties exhibits extraordinary catalytic efficiency and is widely used for photo induced degradation of different organic pollutant molecules. Visible light active CuS nanoparticle decorated MoS2 sheets possesses a high surface to volume ratio, excellent electrical and optical properties and a high rate of generation of charged species due to the faster electron migration between the valence band (VB) and the conduction band (CB) which makes the heterostructure CuS-MoS2 nanocomposite an excellent photocatalyst for HQ degradation in an aqueous medium. Many research groups reported that MoS2 nanosheets and MoS2 derived nanocomposite materials exhibited excellent photocatalytic activity and long-term stability towards the H2 evolution reaction. Li et al. developed a nano CuS/MoS2 composite by dealloying amorphous Ti0xCu1−xO y (x = 1, 2, 3 at%) ribbons in acid solution. The nanocomposite with large surface area and excellent stability successfully was utilized for the degradation of toxic organic dyes under irradiation of visible light.

Zhao’s group reported the photodegradation of hydroquinone catalyzed by Au/TiO2/RGO nanocomposites under irradiation of visible light and reported ~90% photodegradation efficiency of the photocatalyst towards HQ after 1 h. Gong et al. investigated the decomposition of aqueous hydroquinone utilizing nanosized titanium dioxide (anatase) fabricated on activated carbon powder (TiO2/AC) under UV irradiation and observed 80% degradation efficiency. Photocatalytic degradation of HQ in the presence of Fe loaded polystyrene–divinyl benzene polymeric hybrid ion exchange (HIX) resin was studied by Emara and his group. However, the above studies are mainly focused on the degradation of HQ utilizing a metal oxide based photocatalyst. To the best of our knowledge, there are few reports on the decomposition of HQ in the presence of transition metal sulphide based photocatalysts under natural sunlight irradiation.

The present study includes the decoration of CuS nanoparticles on MoS2 sheets by a hydrothermal method and characterization by different analytical tools. The synthesized CuS-MoS2 nanocomposite is successfully utilized in the detection of HQ molecules based on its peroxidase-mimic activity towards the catalytic oxidation of colorless chromogenic substrate TMB to blue colored oxTMB. Moreover, the synthesized CuS-MoS2 nanocomposite is successfully used for sunlight induced photocatalytic degradation of HQ molecules present in an aqueous medium that is not studied yet. A possible mechanism involving chromogenic detection and photocatalytic degradation is also proposed. The current study demonstrates that CuS-MoS2 exhibits high stability, good recyclability, and high catalytic activity in aqueous medium.

2 Experimental section
2.1 Materials
(NH4)2MoS4 (Qualigens, India), thiourea (Sigma Aldrich, Germany), copper sulphate pentahydrate (Sigma Aldrich, Germany),...
3,3',5,5'-tetramethylbenzidine (TMB, Sigma Aldrich, USA), 2,2'-azino-bis(3-ethylbenzo-thiazoline-6-sulfonic acid)diammonium salt (ABTS, C18H24N6O6S4, Sigma Aldrich, Germany), o-phenylenediamine (OPD, Sigma Aldrich, Germany), H2O2 (30%, Qualigens, India), hydroquinone (Sigma Aldrich, Germany), phenol (Alfa Aesar), resorcinol (Himedia, India), catechol (Himedia, India), NaCl (E Merck, India), MgCl2 (E Merck, India), and Na2SO4 (E Merck, India) were used.

2.2 Synthesis and characterization of the CuS–MoS2 nanocomposite

The detailed synthesis and characterization of the base material MoS2 sheets were discussed in our previous publication.41 Typically for the synthesis of MoS2 sheets, ammonium tetrathiomolybdate (NH4)2MoS4 was kept at 400 °C for 2 h in a dynamic vacuum (residual pressure 0.1 Torr). The as-obtained black solid was dispersed in deionized water (5 mg mL⁻¹) and the dispersion was filtered through a Whatman anodisc filter membrane (pore size 0.02 mm) and dried in air.

For the synthesis of CuS–MoS2 nanocomposite, 2 mmol of CuSO4.5H2O and 2 mmol of thiourea were added to 1 mg mL⁻¹ of MoS2 suspension and stirred for 60 min at room temperature. After that the mixture was transferred into a Teflon lined autoclave and kept at 180 °C for 6 h. The product was separated by simple filtration and washed with water and ethanol and dried at 60 °C for 4 h. The detailed synthesis of MoS2 sheets and CuS–MoS2 nanocomposite is presented in Scheme 1.

The detailed characterization of the CuS–MoS2 nanocomposite is discussed in the ESI.†

2.3 Peroxidase like enzyme activity of CuS–MoS2 nanocomposite

The catalytic activity of the nanozyme was explored by carrying out the oxidation of 0.5 mM of 3,3',5,5'-tetramethylbenzidine (TMB), 2,2'-azino-bis(3-ethylbenzo-thiazoline-6-sulfonic acid)diammonium salt (ABTS) and o-phenylenediamine (OPD) separately in sodium acetate buffer (0.1 M, pH 4) containing 6 mg L⁻¹ CuS–MoS2 nanozyme and 50 μL H2O2. After reaction for 10 min (25 °C), TMB converted to a blue colored intermediate of the oxidized product (oxTMB). The resultant mixture was quantitatively analyzed by UV-vis spectrophotometry within the wavelength range of 400–800 nm. Similarly, ABTS and OPD were also oxidized to their corresponding colored products which were also analyzed with the help of a UV-vis spectrophotometer.

To optimize the analytical conditions for the proposed nanozyme, the peroxidase-like efficiency was investigated with the variation of pH from 2 to 10, catalyst concentration from 2 mg L⁻¹ to 7 mg L⁻¹ and temperature from 25 °C to 50 °C.

The catalytic affinity of CuS–MoS2 towards the peroxidase substrate was investigated by the steady state kinetic parameters such as Michaelis Menten constant (Km) and maximum velocity (Vmax), evaluated by using the Lineweaver–Burk reciprocal equation (eqn (1)) obtained by varying the concentration within a certain range.

\[
\frac{1}{V} = \frac{K_m}{V_m[S]} + \frac{1}{V_m}
\]  

(1)

2.4 Potential application in the detection of hydroquinone (HQ)

In the view of the reducibility of the peroxidase oxidation of TMB on the addition of HQ, the concentration of HQ in an aqueous solution was determined. When different concentrations of HQ were added to the reaction mixture, the blue color of oxTMB was got faded. The concentration of HQ was evaluated by analyzing the UV-vis absorbance at 650 nm wavelength.

2.5 Photocatalytic degradation of HQ in the presence of CuS–MoS2 photocatalyst

The photocatalytic efficiency of the synthesized nanocomposite was assessed by carrying out the degradation of HQ under natural sunlight irradiation in the month of June and July and in between 10 am and 3 pm in Jorhat City, Assam, India, and the average intensity of sunlight was found to be ~780 W m⁻² measured by using a Solar Power Meter, KM-SPM-11. In a typical process, 500 mg L⁻¹ of the photocatalyst was added into a 50 mL aqueous solution of HQ (0.01 M), followed by stirring the suspension in the dark for 60 min to establish an adsorption–desorption equilibrium. The mixture was stirred.
for 240 min under natural sunlight irradiation. At a given time interval of the irradiation, 3.0 mL of the mixture was collected and the photocatalyst was separated by centrifugation at 8000 rpm for 10 min. HQ concentration was determined with the help of a UV-vis spectrophotometer (MS-11-UV-1800, Shimadzu, Japan) at a wavelength of 289 nm.

2.6 Analysis of the formation of reactive species

An *in situ* scavenging experiment was carried out to detect the reactive species that played a main role in the HQ degradation process catalyzed by a photocatalyst. 0.1 mM of 2-propanol (Merck, India) and EDTA-2Na (Nice Chem. Pvt. Ltd, Cochin) were used as scavengers for hydroxyl radicals (\(^{1}\)OH) and holes (h\(^{+}\)), respectively. The degradation of HQ in presence of 2-propanol and EDTA-2Na was examined to investigate the contribution of the reactive species in photodegradation reaction.

2.7 Reusability of the photocatalyst

To investigate the stability of the synthesized nanocomposite, we carried out the recyclability of the photocatalyst up to five repeated cycles under the same experimental conditions adopted for the degradation of HQ. To execute the reusability study, 50 mL of a mixture containing 500 mg L\(^{-1}\) catalyst and 0.01 M of HQ was stirred for 240 min, then the catalyst was separated by centrifugation for 10 min and the supernatant was analysed by UV-vis spectrophotometry at 289 nm. The sediment was washed many times with deionized water, dried and reused for the next cycle.

3 Results and discussion

3.1 Characterization of CuS–MoS\(_2\) nanocomposite

The crystal nature of the as-prepared nanocomposite was examined by PXRD analysis to investigate the structural characteristics. As shown in Fig. 1a, the distinctive peaks of CuS NPs are located at 2\(\theta\) values of 27.52°, 29.12°, 31.60°, 32.56°, 52.64° and 59.22° corresponding to the crystalline planes (101), (102), (103), (006), (110), (114) and (116) with \(d\)-spacings values of 3.23, 3.06, 2.82, 2.74, 1.90, 1.73, and 1.55 Å (JCPDS Card No.: 00-001-1281), respectively. The peaks at around 14.20°, 39.38°, 74.10° and 78.64° are ascribed to the characteristic peak of MoS\(_2\) sheets as discussed in our previous publication.\(^{10}\)

The BET surface area of CuS–MoS\(_2\) nanocomposite was found to be 18.264 m\(^2\) g\(^{-1}\) with a pore volume of 0.076 cm\(^3\) g\(^{-1}\) and a pore radius of 43.26 Å calculated from the Barrett-Joyner-Halenda (BJH) plot. The typical N\(_2\) adsorption–desorption isotherm with the corresponding pore size distribution of CuS–MoS\(_2\) nanocomposite is presented in Fig. 1b. A comparative table for BET surface area, pore volume and pore radius of CuS–MoS\(_2\) nanocomposite with bare MoS\(_2\) and CuS nanoparticles is presented in the ESI\(^{†}\) (Table S1).

The TEM images (Fig. 2a–c) of the synthesized CuS–MoS\(_2\) nanocomposite show the distribution of spherical CuS nanoparticles with a particle size of 4.63 ± 0.24 nm calculated from particle size analysis (Fig. 2e) on MoS\(_2\) sheets. The HRTEM image (Fig. 2d) represents the crystalline behavior of CuS nanoparticles depicting a lattice fringe of 0.19 nm related to the (110) crystalline plane. The SAED pattern (Fig. 2f) also consists of (102), (110) and (114) crystal planes of CuS nanoparticles. TEM images of MoS\(_2\) sheets and CuS nanoparticles are shown in Fig. S1 (ESI\(^{†}\)).

The chemical composition and oxidation state of the CuS–MoS\(_2\) nanocomposite was investigated by X-ray photoelectron spectroscopy (XPS) analysis (Fig. 3). The XPS survey spectrum of the CuS–MoS\(_2\) nanocomposite (Fig. 3a) shows the characteristic peaks of C1s and O1s located at 285.8 and 531.2 eV, respectively, in addition to the peaks corresponding to Mo3d, S2p and Cu2p.\(^{72,73}\) The high-resolution Cu2p spectrum shows the peaks at binding energies of 932.3 and 952.1 eV corresponding to the spin–orbit splitting of Cu2p\(_{3/2}\) and Cu2p\(_{1/2}\) peaks, respectively (Fig. 3b).\(^{74}\) In addition to these, two “shakeup” satellite peaks at around 944.4 eV and 963.3 eV demonstrate the presence of...
paramagnetic Cu$^{2+}$ ions.\textsuperscript{75} The two characteristic peaks obtained at 228.2 eV and 232.4 eV in the deconvoluted high-resolution spectrum of Mo3d are attributed to the spin–orbit splitting of Mo 3d$^{5/2}$ and 3d$^{3/2}$ for Mo(IV) (Fig. 3c). Two other peaks appear at 226 eV and 235.1 eV related to the 2s orbital of sulfur atoms and the 3d orbital of Mo(VI), which may be due to the air exposure of the sample.\textsuperscript{76} The characteristic peaks for the S2p$^{3/2}$ and S2p$^{1/2}$ orbitals of S$^{2–}$ are observed at 161.3 and 162.5 eV, respectively (Fig. 3d).\textsuperscript{73,77}

### 3.2 Peroxidase like activity of CuS–MoS$_2$

The CuS–MoS$_2$ nanocomposite shows peroxidase-like catalytic activity for the oxidation of chromogenic substrate TMB in acidic medium. Addition of CuS–MoS$_2$ to a mixture of H$_2$O$_2$ and TMB results in the formation of a blue colored oxidized product exhibiting a remarkable absorption peak at 650 nm. As shown in Fig. S2a (ESI\textsuperscript{†}), no absorption was observed at 650 nm in the case of the TMB + CuS–MoS$_2$ system while a negligible color change was observed in case of H$_2$O$_2$ + TMB system under the same experimental conditions. Meanwhile, the CuS–MoS$_2$ + H$_2$O$_2$ + TMB system produces a strong absorption peak at 650 nm in comparison to MoS$_2$ + H$_2$O$_2$ + TMB and CuS + H$_2$O$_2$ + TMB systems which indicates better catalytic properties of the heterostructure material because of its synergistic coupling effect occurred at the interface of MoS$_2$ sheets and CuS nanoparticles. Besides TMB, the CuS–MoS$_2$ nanocomposite can catalyze the oxidation of other peroxidase substrates like ABTS and OPD in presence of H$_2$O$_2$ (Fig. S2b, ESI\textsuperscript{†}). The inset shows the color variation in different reaction systems. These results prove that CuS–MoS$_2$ behaves as a peroxidase enzyme towards peroxidase substrates.

#### 3.2.1 Optimization of experimental conditions.

Similar to natural enzymes, the peroxidase activity of the synthesized CuS–MoS$_2$ nanozyme is affected by several parameters including the incubation time, pH, catalyst concentration \textit{etc.} The reaction conditions were optimized to get a better performance of the nanozyme. Fig. S2d (ESI\textsuperscript{†}) shows that the catalytic activity of the artificial nanozyme is enhanced with increasing catalyst dosage. The influence of pH and temperature on the catalytic activity of the CuS–MoS$_2$ nanozyme was studied by varying the pH from 2 to 10 and temperature from 25°C to 50°C. Fig. S2e and Fig. S2f (ESI\textsuperscript{†}) show that, for maximum absorption, the optimal pH was found to be 4 and temperature was found to be 35°C. By considering the convenience and economy of the process, the catalytic oxidation was executed at room temperature (25°C).

#### 3.2.2 Determination of kinetic parameters for the peroxidase oxidation reaction.

The kinetic parameters of the reaction catalyzed by the CuS–MoS$_2$ nanocomposite were determined by using the initial rate method with H$_2$O$_2$ and TMB as a substrate. The value of the rate of the reaction was calculated from the absorbance data (A) using the standard equation

$$A = \varepsilon \times c \times l \quad (2)$$

where \(\varepsilon = 39,000 \text{ M}^{-1} \text{ cm}^{-1}\) for oxTMB.\textsuperscript{78} The catalytic parameters (\(K_m\) and \(V_m\)) were determined from the Lineweaver–Burk reciprocal plot (Fig. S3, ESI\textsuperscript{†}) and are presented in Table 1. The Michaelis–Menten constant (\(K_m\)) with TMB for CuS–MoS$_2$ (0.244 mM) is lower than that of HRP (0.434 mM) suggesting a greater affinity towards TMB in comparison to natural HRP. The \(K_m\) value with H$_2$O$_2$ was found to be 0.033 mM which is also lower than that of HRP (3.7 mM).\textsuperscript{79} These results signify that, to
achieve the maximum peroxidase-like activity, lower H$_2$O$_2$ and TMB concentrations are required in the presence of our synthesized nanozyme as compared to that of HRP. The data of Table 1 also reveal that the proposed peroxidase enzyme has much more affinity to the substrates than other reported peroxidase mimics.

### 3.2.3 Detection of HQ using the CuS–MoS$_2$ nanozyme.
Based on the inherent peroxidase mimetic properties of CuS–MoS$_2$, we developed an easy and simple colorimetric tool to detect toxic HQ in an aqueous medium. The presence of CuS–MoS$_2$ nanocomposite promotes the electron transfer between TMB and H$_2$O$_2$ molecules and thus accelerates the oxidation process of colorless TMB to blue colored oxidized TMB. HQ molecules could easily combine with sulfydryl functional groups of MoS$_2$ nanosheets, and thus adsorb onto the CuS–MoS$_2$ surface. The free electrons present on the CuS–MoS$_2$ surface then transfer to HQ molecules that can transfer these electrons to oxTMB. Accepting electrons from HQ causes the reduction of the blue colored oxTMB product to colorless TMB and simultaneously HQ converts to p-benzoquinone as shown in Scheme 2. Fig. 4a shows that the addition of HQ causes rapid fading in blue color and with an increase in HQ concentration, the absorbance at 650 nm wavelength is gradually decreased. Applying this strategy, HQ was detected up to a lower limit of 3.68 μM with the linear range of 0.4–50 μM. The comparison of the performance of the synthesized colorimetric probe in the potential application of HQ detection with other colorimetric probe is presented in Table S2 (ESI†).

It is seen from the data of Table S2 (ESI†) that our proposed colorimetric probe has comparable efficiency towards HQ detection to that of the reported sensing probe.

In order to investigate the selectivity of the proposed colorimetric assay, the absorbance of oxTMB was monitored in the presence of different interference substances including other phenolic compounds and different metal ions. It is seen from Fig. 4c that, the presence of 30 μM of different metal ions

### Table 1 Kinetic parameters of different peroxidase nanozymes

<table>
<thead>
<tr>
<th>Nanozymes</th>
<th>Substrates</th>
<th>$K_m$ (mM)</th>
<th>$V_m$ ($10^{-8}$ M s$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HRP</td>
<td>H$_2$O$_2$</td>
<td>3.7</td>
<td>8.71</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>TMB</td>
<td>0.434</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>MoS$_2}$/PPy</td>
<td>H$_2$O$_2$</td>
<td>12.8</td>
<td>15.1</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>TMB</td>
<td>0.41</td>
<td>47.4</td>
<td></td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>H$_2$O$_2$</td>
<td>0.116</td>
<td>2.42</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>TMB</td>
<td>0.387</td>
<td>7.23</td>
<td></td>
</tr>
<tr>
<td>CuS–MoS$_2$</td>
<td>H$_2$O$_2$</td>
<td>0.033</td>
<td>15.15</td>
<td>Present study</td>
</tr>
<tr>
<td></td>
<td>TMB</td>
<td>0.244</td>
<td>9.12</td>
<td></td>
</tr>
</tbody>
</table>
(Ca$^{2+}$, Na$^+$, and Mg$^{2+}$) and phenolic compounds like phenol, catechol and resorcinol did not cause any significant change in the absorbance value of oxTMB at 650 nm. The presence of Cu$^{2+}$ ions increases the absorbance intensity of oxTMB due to the

Scheme 2  Representation of peroxidase mimic activity of CuS–MoS$_2$ nanocomposite towards HQ detection.

Fig. 4  (a) Variation of the UV-vis spectra of oxTMB in the presence and absence of HQ, (b) linear calibration plot for the detection of HQ (catalyst dosage: 6 mg L$^{-1}$; pH: 4; temp.: 25 °C; TMB: 0.5 mM; incubation time: 10 min), and (c) absorbance of oxTMB (650 nm) in the presence of 30 μM different interfering agent.

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catalytic decomposition of H₂O₂ to *OH radicals by Cu²⁺ ions via the Fenton type reaction and thus accelerates the oxidation process of TMB. These results signify that the proposed colorimetric probe exhibits an outstanding anti-interference ability.

3.2.4 Detection of HQ in real samples. To assess the practical applicability of the proposed colorimetric probe, CuS–MoS₂ was used to determine HQ in real environmental samples (local river, pond, tap and tube well water) spiking with different concentrations of HQ solution under the optimum reaction conditions. The recovery of HQ was determined using the standard equation (recovery (%) = HQ addded − HQ found/ HQ added × 100) and is presented in Table 2. The result suggests that the proposed colorimetric probe showed a feasible and accurate method to detect HQ in environmental samples.

3.3 Photocatalytic degradation HQ in the presence of CuS–MoS₂ under natural sunlight irradiation

The photocatalytic properties of the synthesized CuS–MoS₂ nanocomposite was examined by studying the decomposition reaction of HQ under natural sunlight irradiation. As displayed in Fig. S4a (ESI†), the HQ is very much stable and only 9% decomposition of HQ was achieved within 240 min. In the presence of the CuS–MoS₂ nanocomposite, 17% removal of HQ occurred due to adsorption on the catalyst surface. The CuS–MoS₂ nanocomposite exhibits good photocatalytic activity under sunlight irradiation and 83% of HQ was decomposed within 240 min under sunlight irradiation. The superior catalytic activity of CuS–MoS₂ nanocomposite was due to the formation of a heterostructure, which enhanced the separation of photoinduced electron–hole pairs and production of larger amounts of reactive species which are involved in the decomposition of the organic pollutants. Fig. S4b (ESI†) shows that with an increase in catalyst dosage the photocatalytic efficiency of CuS–MoS₂ was increased due to the enhancement of HQ adsorption on the catalyst surface which results in an increase in the degradation of HQ under sunlight irradiation. Moreover, with increasing photocatalyst dosage, a larger number of photons can be absorbed and thus a large number of O₂* and *OH radicals are formed on its surface which accelerates the progress of the photocatalysis process. With an increase in HQ concentration, the photocatalytic efficiency was decreased due to the blockage of the active sites of the catalyst surface (Fig. S4c, ESI†).

The initial pH of the reaction system has an important role in the photocatalytic decomposition process. It is observed from Fig. 5c that HQ degradation was low under alkaline conditions and maximum degradation was achieved under acidic conditions. The influence of solution pH on HQ degradation was explained by studying the effect of an electrical double layer on the adsorption–desorption process. Fig. 5a shows that under acidic conditions, the nanocomposite surface becomes positive due to the accumulation of H⁺ ions surrounding the catalyst surface whereas in an alkaline medium, the catalyst surface becomes negatively charged. The hydroxyl groups of HQ molecules play a key role in the adsorption on the photocatalyst surface. HQ shows an amphoteric character and it exists in different forms at different pH. In an acidic medium, the –OH groups get protonated and more interactions between HQH⁺ and the negatively charged catalyst take place. This results in more adsorption of HQ on the catalyst surface as well as more degradation of HQ molecules under the acidic conditions. In an alkaline medium, the impingement of HQ towards the catalyst surface becomes difficult which lowers the adsorption and degradation of HQ molecules.

It is found that the presence of 0.01 M different electrolytes like (NaCl, MgCl₂ and Na₂SO₄) remarkably changes the zeta potential of the CuS–MoS₂ photocatalyst surface. The presence of electrolytes can form an electrical double layer around the negatively charged photocatalyst surface due to the preferential electrostatic adsorption of the cations and thus the surface charge of the photocatalyst tends towards a positive value. But the counter ions with different polarizability can influence the cation’s adsorption. Thus the surface charge (zeta potential) of CuS–MoS₂ nanocomposite was found to be more negative in the presence of Na₂SO₄ (−16.04 mV) in comparison to NaCl (−7.20 mV) due to the more adsorption of highly polarizable SO₄²⁻ ions. Divalent cations are more strongly adsorbed on the negatively charged CuS–MoS₂ nanocomposite surface and hence the surface charge (zeta potential) value was found to be more positive in the presence of MgCl₂ (−5.45 mV) (Fig. 5b). The presence of electrolytes can also affect the photodegradation efficiency of CuS–MoS₂ photocatalyst towards HQ degradation. At pH 5, HQ exists as HQH⁺ and the adsorption of the positively charged species on the photocatalyst surface faces difficulty when the zeta potential value approaches towards a positive value. Moreover, the presence of anions like Cl⁻ and SO₄²⁻ can inhibit the photocatalytic efficiency by forming weaker species radicals (Cl²⁻, Cl₂− and SO₄²⁻) through the reaction with *OH radicals. The photocatalytic efficacy of CuS–MoS₂ photocatalyst towards HQ degradation in the presence of different electrolytes is shown in Fig. 5d. The higher inhibition degree in the presence of Cl⁻ is due to the generation of reactive chlorine radicals with much lower redox potential than SO₄²⁻ and *OH radicals. The comparative photocatalytic efficiency of CuS–MoS₂ nanocomposite towards HQ degradation with other photocatalyst systems is presented in Table S3 (ESI†).

<table>
<thead>
<tr>
<th>Environmental samples</th>
<th>HQ added (μM)</th>
<th>HQ found (μM)</th>
<th>Recovery (%)</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pond water</td>
<td>30</td>
<td>29.3</td>
<td>97.66</td>
<td>0.52</td>
</tr>
<tr>
<td>Tap water</td>
<td>30</td>
<td>29.1</td>
<td>90.3</td>
<td>0.98</td>
</tr>
<tr>
<td>River well water</td>
<td>30</td>
<td>28.8</td>
<td>95.6</td>
<td>0.42</td>
</tr>
</tbody>
</table>

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3.4 Kinetics of photoinduced HQ degradation

To depict the heterogeneous photocatalytic decomposition of HQ in the presence of CuS–MoS₂ photocatalyst, the Langmuir–Hinshelwood first-order kinetics model was used. HQ molecules were effectively adsorbed on the CuS–MoS₂ surface and oxidized by reaction with the photogenerated electron–hole pair. The pseudo-first-order reaction kinetics for HQ degradation was determined by plotting reaction time \( t \) versus \( \ln \left( \frac{C_0}{C_t} \right) \) according to the following equation (Fig. 6):

\[
\ln \left( \frac{C_0}{C_t} \right) = kt
\]

where \( C_0 \) and \( C_t \) are the concentrations of the substrate at \( t = 0 \) and \( t = t \) min respectively. \( K \) is the first-order rate constant. The kinetic study was carried out at a HQ concentration of 0.01 M, a catalyst concentration of 500 mg L\(^{-1}\) and at a pH of 3 to 11. The rate constants for the photodegradation of HQ at different pH are presented in Table 3.

The oxidation of HQ molecules to CO\(_2\) and H\(_2\)O in the presence of CuS–MoS₂ photocatalyst was investigated by analysing the chemical oxygen demand (COD) before and after the photodegradation process utilizing a COD apparatus spectroquant Pharo 300 (Merck, USA). The photocatalytic reaction of HQ for COD measurement was carried out at pH 5 with a catalyst concentration of 500 mg L\(^{-1}\) and a HQ concentration of 0.01 M. The photodegradation efficiency from COD data was determined using the following equation:

\[
\text{Photodegradation efficiency} \% = \frac{\text{COD}_{\text{Initial}} - \text{COD}_{\text{Final}}}{\text{COD}_{\text{Initial}}} \times 100
\]

Fig. 5 (a) Zeta potential of CuS–MoS₂ nanocomposite at different pH, (b) zeta potential of CuS–MoS₂ nanocomposite in the presence of different electrolytes, and effect of (c) pH and (d) 0.01 M different electrolytes on the photodegradation of HQ (catalyst conc: 500 mg L\(^{-1}\); HQ conc.: 0.01 M; pH 5; time: 240 min).

Fig. 6 Kinetics of the photocatalytic degradation of HQ in the presence of CuS–MoS₂ photocatalyst.
Combining with dissolved O$_2$. These O$_2$ species. The holes can react with H$_2$O molecules and produce H$_2$O molecules and results in the formation of hydroxyl radicals (OH). These active oxidizing species can carry out the decomposition of HQ molecules to non-toxic products like CO$_2$ and H$_2$O. A schematic representation of the photocatalytic degradation of HQ in the presence of CuS–MoS$_2$ nanocomposite is shown in Scheme 3.

The formation of intermediates and final products during the photocatalytic degradation of HQ in presence of CuS–MoS$_2$ photocatalyst was confirmed by High-Resolution Mass Spectrometer (HRMS) analysis recorded by electrospray ionization with Xevo XS QT of a mass spectrometer. As shown in Fig. S6a (ESI†), in the case of initial HQ solution the mass peaks at m/z values of 110 and 84 are attributed to HQ and phenol, obtained from the aerobic oxidation of HQ. After 120 min sunlight irradiation, the intensity of the mass peak at m/z 110 was decreased and a new peak appears at m/z 126 corresponding to 1,2,4-benzenetriol, the intermediate product (Fig. S6b, ESI†). In Fig. S6c (ESI†), the peaks appearing at m/z values of 104 and 145 are attributed to malonic and adipic acid, respectively. The peaks corresponding to the intermediate acetic acid were not detected by HRMS analysis (Scheme 2). The malonic acid and adipic acid are finally converted to the final products like CO$_2$ and H$_2$O.

The evolution of the COD versus time is illustrated in Fig. S5 (ESI†). In the presence of CuS–MoS$_2$ photocatalyst, 47.26% photodegradation efficiency was observed after 240 min.

### 3.5 Mechanism of the photocatalytic decomposition of HQ

The semiconductor-based CuS nanoparticles with a band gap of 2.5 eV can generate electron–hole pairs under sunlight irradiation. The band edges of CuS for the conduction band (CB) and valence band (VB) are −0.36 eV and 1.89 eV, respectively. Moreover, CuS has a stronger tendency to capture electrons due to the presence of abundant electron holes in its empty 3p orbital of sulfur. It is known that both Mo and S possess the capacity to accept electrons and protons. MoS$_2$ sheets have 0.36 eV band edges /C0 and 1.89 eV, respectively. Moreover, CuS has a stronger tendency to capture electrons due to the presence of abundant electron holes in its empty 3p orbital of sulfur. It is known that both Mo and S possess the capacity to accept electrons and protons. MoS$_2$ sheets have −0.51 eV band edges for the conduction band and 1.07 eV for the valence band. In CuS–MoS$_2$, a heterostructure of two semiconducting materials enhances the scope of solar light absorption in the visible region, and spatial separation and transportation of photoinduced electron–hole pairs. When a photon strikes, the electrons of the VB are excited to the CB in CuS nanoparticles. Moreover, the photogenerated electrons can migrate to the CB of CuS from the VB of MoS$_2$ due to the more negative position of the CB in MoS$_2$ than in CuS. This leads to the separation of charged species and increases the lifetime of the photogenerated electron/hole pair. These electrons can produce superoxide anions (O$_2^-$) by combining with dissolved O$_2$. These O$_2^-$ radicals react with H$_2$O molecules and results in the formation of OH reactive species. The holes can react with H$_2$O molecules and produce hydroxyl radicals (OH). These active oxidizing species can carry out the decomposition of HQ molecules to non-toxic products like CO$_2$ and H$_2$O. A schematic representation of the photocatalytic degradation of HQ in the presence of CuS–MoS$_2$ nanocomposite is shown in Scheme 3.

The influence of different electrolytes on the formation of OH species was also examined by monitoring the fluorescence intensity of the OHTA complex in presence of 0.01 M NaCl, MgCl$_2$ and Na$_2$SO$_4$. Fig. 7b shows that the fluorescence intensity in the presence of electrolytes decreased in the order as Na$_2$SO$_4$ > NaCl > MgCl$_2$ due to the scavenging of the OH species as discussed in Section 3.3.

The generation of reactive species (OH and h$^+$) in the photocatalytic process was also studied by scavenging...
experiment in the presence of isopropanol and EDTA-2Na as scavengers for \( {^*}{\text{OH}} \) and \( h^+ \) species, respectively. Fig. 7c shows that the photodegradation efficiency was greatly inhibited in the presence of isopropanol as compared to EDTA-2Na. This observation confirmed that \( {^*}{\text{OH}} \) radicals were the main reactive species to carry out the decomposition of HQ in the presence of CuS–MoS\(_2\) nanocomposite under natural sunlight irradiation.

### 3.6 Reusability test

To monitor the stability of the CuS–MoS\(_2\) photocatalytic system, recyclability test was performed up to seven consecutive cycles without any physical and chemical modifications. After each cycle, the catalyst was washed and dried at 60 °C for 4 h and used for the next time. Fig. S7 (ESI†) shows that the degradation efficiency gradually decreased with an increase in reused times. The cause of the gradual decrease in the catalytic efficiency is the gradual decrease of catalytic active sites by the adsorption of HQ and its intermediates on the catalyst surface after each cycle. Repeated use of nanocomposites also weakens the van der Waals interactions between the nanoparticle clusters, which causes the agglomeration of nanoparticles and reduces the catalytic efficiency of the nanocomposite after each cycle. Moreover, with successive washing and drying, the active sites on the catalytic surface get fatigued.\(^{85,86}\)

Moreover, the structural stability of the photocatalyst was analyzed after 5 consecutive cycles and it was found that the photocatalyst underwent agglomeration due to the van der Waals interactions among the CuS NPs after use in photocatalysis as shown in TEM images (Fig. S8a and b, ESI†). The XRD pattern (Fig. S8c, ESI†) presents the crystallinity of the synthesized CuS–MoS\(_2\) photocatalyst after being used in the photocatalytic process. The XRD peaks appear at 2\( \theta \) values of 27.82°, 29.28°, 31.78°, 32.82°, 47.92°, 52.68° and 59.28° corresponding to planes (101), (102), (103), (006), (110), (114) and (116), respectively (JCPDS Card No: 00-001-1281), which matched with those of a fresh catalyst. Two other peaks at 14.32° and 46.30° are the characteristic peaks of MoS\(_2\) sheets and Cu\(_2\)S NPs, respectively.

The oxidation states of the CuS–MoS\(_2\) nanocomposite after photocatalytic reactions were examined by XPS measurements (Fig. 8). The high-resolution Cu 2p spectrum was obtained with two main peaks at 932.3 eV and 952 eV for Cu 2p\(_{3/2}\) and Cu 2p\(_{1/2}\), respectively (Fig. 8a). In addition, two “shakeup” satellite peaks at around 944.4 eV and 963.3 eV indicate the presence of Cu\(_{2+}\)
ions. Similarly, the high-resolution deconvoluted spectrum of Mo 3d shows two characteristic peaks at 228.1 eV and 232.2 eV attributed to the spin–orbit splitting of Mo 3d<sub>5/2</sub> and 3d<sub>3/2</sub> for Mo(IV) (Fig. 8b). Two other peaks appear at 226 eV and 235.1 eV corresponding to the 2s orbital of sulfur atoms and the 3d orbital of Mo(VI). Thus, the XPS measurement results of the reused CuS–MoS<sub>2</sub> nanocomposite are similar to those of the freshly prepared CuS–MoS<sub>2</sub>, indicating that the photocatalyst is able to retain its characteristics during the photocatalytic degradation of HQ.

4. Conclusions

In summary, CuS–MoS<sub>2</sub> nanocomposite was synthesized via a simple hydrothermal method and using low-cost starting materials. The dual responsive CuS–MoS<sub>2</sub> nanocomposite was successfully utilized for the sensitive and selective detection and photocatalytic decomposition of organic pollutant molecule, hydroquinone (HQ). The nanocomposite exhibited intrinsic peroxidase-like activity and catalyzed the oxidation reaction of chromogenic substrates in presence of H<sub>2</sub>O<sub>2</sub> to produce their corresponding oxidized colored product. Based on this peroxidase mimetic, CuS–MoS<sub>2</sub> was used as an artificial nanozyme for the colorimetric detection of toxic phenolic derivative, HQ and was found to have efficient sensitivity up to the lower limit of 3.68 μM HQ concentration. This selective and sensitive colorimetric probe was used for the detection of HQ in environmental water systems and effectively recovered the HQ amount spiked with the water samples. The synthesized nanocomposite possessed excellent photocatalytic efficiency and 83% HQ decomposition was achieved in the presence of this photocatalyst under natural sunlight irradiation. The mechanism of colorimetric detection and photocatalytic decomposition of HQ was also discussed in the current study. This work leads a new path for the utilization of semiconductor-based heterogeneous systems in the potential application of the environmental remediation process.

Conflicts of interest

There are no conflicts to declare.

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