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A nanoporous Ni(OH)₂ interlinked Co₃O₄ heterojunction: a novel approach to chromium(vi) detection

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The present study broadly explores the synthesis, structural characteristics, and electrochemical performance of a nanoporous Ni(OH)₂/Co₃O₄ heterojunction engineered for efficient enzymatic sensing of hexavalent chromium Cr(vi). The synthesized heterostructure consists of a porous Ni(OH)₂/Co₃O₄ matrix (nanopores, with dimensions approximately ranging from 6 to 10 nm) intimately coupled with evenly dispersed Co₃O₄ nanocrystals, forming a well-integrated interface that enables strong synergistic redox coupling and rapid electron transport across the junction. The nanoporous framework significantly increases the electrochemically active surface area offering abundant catalytically active sites and facilitates improved transport of electrolytes. Simultaneously, the heterojunction ensures continuous conductive pathways, thereby minimizing charge-transfer resistance and enhancing overall electron mobility. The combined structural and electronic advantages translate into markedly improved sensitivity, catalytic activity, and operational stability for enzymatic Cr(vi) detection with a limit of detection (LOD) of 39 nM. Overall, the results underscore the significant role of heterojunction engineering in enhancing the performance of metal hydroxide–oxide materials for advanced environmental sensing applications.

1. Introduction

Hexavalent chromium (Cr(vi)) is a highly toxic and carcinogenic pollutant prevalent in industrial effluents, posing significant environmental and health risks. Its reduction to the less toxic trivalent chromium (Cr(III)) and accurate sensing are crucial for environmental remediation and monitoring. The reduction of Cr(vi) to the less harmful Cr(III) is a critical process in detoxifying contaminated water. Chronic exposure to Cr(vi) causes bronchitis and liver, kidney, and nerve tissue damage, and it has been shown to have carcinogenic, mutagenic, and genotoxic effects.^{1,2} While the U.S. Environmental Protection Agency (EPA) says that 0.1 mg L⁻¹ is the permissible quantity, the World Health Organization (WHO) recommends a tolerable value of 0.050 mg L⁻¹ for Cr in drinking water.^{3–5} Thus, rapid and effective Cr(vi) detection technology is essential for ensuring the safety of drinking water sources and food products. When it comes to sensing, common detection techniques include X-ray fluorescence, voltammetry, spectrofluorometry, spectrophotometry (colorimetric), inductively coupled plasma atomic emission spectrometry or mass spectrometry, and graphite furnace atomic absorption spectrometry.⁶ Despite their extremely high sensitivity, optical atomic spectrometry and mass spectrometry are incompatible with on-site detection and necessitate highly skilled individuals and expensive, complicated equipment to perform. Analyte detection *via* colorimetric techniques is one of the most popular approaches due to its ease of use, particularly when it involves a color shift that is visible to the unaided eye. Nanozymes are a class of nanomaterials that, because of their inherent characteristics, such as size, structure, surface charge, *etc.*, can effectively mimic normal enzymes by catalyzing H₂O₂-mediated reactions.^{7,8} For instance, Cr(vi) was detected and quantified utilizing gold amalgam nanocomposites with oxidase capabilities and 3,3',5,5'-tetramethylbenzidine (TMB) as a substrate.⁵ Using polyethylenimine-stabilized Ag nanoclusters, oxidation of TMB by Cr(vi) was employed in a different investigation to detect the same with a broader linearity range of 0.25–5.2 mg L⁻¹ and

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a LOD and LOQ of 0.0572 and 0.1924 mg L⁻¹, respectively.⁹ Similarly, in the presence of TMB and H₂O₂, polyethylene glycol-functionalized poly(*N*-phenyl glycine) (PNPG-PEG) nanoparticles were employed to improve the signal for the detection of Cr(VI).¹⁰ Good linearity (0.01–0.1 μM) and LOD (0.012 μM) were attained using the approach. Because of its potent anti-interference properties, non-toxicity, and excellent stability, TMB has been used as a chromogenic chemical in a number of other investigations.^{11,12}

The detection of Cr(VI) has significantly advanced with recent developments in nanozyme-based sensing platforms that include use of defect-engineered single-atom catalysts, MOF-based oxidoreductase mimics, and fluorescent carbon nanodots.^{13–16} Despite their high sensitivity, many systems suffer from poor structural stability in acidic environments, high substrate affinity, aggregation-induced deactivation, and restricted electron-transfer efficiency.¹⁷ Furthermore, there is still a lack of research on rationally engineered nanoporous heterojunctions that optimize accessibility to catalytic sites and interfacial redox coupling. Therefore, by improving charge transfer, enhancing active site density, and boosting catalytic kinetics for effective Cr(VI) detection, the development of a structurally integrated Ni(OH)₂/Co₃O₄ nanoporous heterojunction offers a promising strategy to overcome these limitations.

Bimetallic metal oxides play a crucial role in the sensing and reduction of Cr(VI) due to their enhanced catalytic, electrochemical, and adsorption properties.¹⁸ The incorporation of two different metals into the metal oxide framework often results in synergistic effects that improve performance in environmental applications, particularly in the detection and detoxification of Cr(VI).¹⁹

The presence of two metals in a metal oxide matrix can create more active sites and enhance electron transfer processes, which are essential for the reduction of Cr(VI).²⁰ Furthermore, the combination of two metals increases the adsorption capacity for Cr(VI), attributed to the varied oxidation states and coordination environments that bimetallic oxides offer.²¹ This enhancement in adsorption is crucial for capturing Cr(VI) ions from contaminated water. Nanoporous heterojunctions based on bimetallic oxides have emerged as promising candidates for Cr(VI) sensing and reduction due to their unique structural and electronic properties.²² The heterojunction formation facilitates efficient electron transfer, essential for the reduction process. Moreover, the stability and durability of bimetallic oxides under harsh conditions are crucial for practical applications in water treatment and environmental remediation.²²

In addition to conventional catalytic and nanozyme-based sensing techniques, semiconductor photocatalysis has become a successful method for monitoring pollutants and environmental remediation. Cr(VI) can be degraded more easily with the help of photocatalytic materials, which produce reactive oxygen species owing to photoinduced charge separation.^{20,22} Recent developments in plasmonic and hot electron photocatalysis have additionally expanded the potential of catalytic nanomaterials *via* enabling effective utilization of light energy through localized surface plasmon resonance (SPR) and

energetic charge carriers.²³ Hot-electron-mediated processes can greatly improve interfacial redox reactions by enhancing charge injection and suppressing recombination losses.^{23,24} These new concepts emphasize the effectiveness of electron-transfer routes and interfacial charge transport in catalytic nanostructures.^{25,26}

While our present work is focused on colorimetric sensing using nanozymes rather than photocatalysis, the design of nanoporous Ni(OH)₂/Co₃O₄ heterojunctions is fundamentally similar to photocatalytic systems in terms of heterointerface-driven charge separation and improved catalytic activity. By optimizing the interface between Ni(OH)₂ and Co₃O₄, we enable efficient electron transfer pathways that are vital for both nanozymatic oxidation of TMB and the potential photocatalytic detoxification of industrial effluents.

Highlighting the critical role of nanoporous materials, this article explores the synthesis, characterization, and catalytic capabilities of the nanoporous Ni(OH)₂/Co₃O₄ heterojunction in Cr(VI) sensing. Employing a multidisciplinary approach spanning chemistry, materials science, and environmental engineering, this research aims to advance the development of efficient, sustainable strategies for mitigating hazardous pollutants and safeguarding environmental integrity. The novelty of the present work lies in the rational design of a nanoporous Ni(OH)₂/Co₃O₄ heterojunction that integrates interfacial redox coupling with a high-surface-area nano-architecture to enhance peroxidase-like catalytic performance. In contrast to previously documented mono-metallic or randomly built bimetallic nanozymes, the developed interface enables faster electron transfer between Ni²⁺ and Co²⁺/Co³⁺ centres that contributes to improving the formation of reactive oxygen species, which helps in the detection of Cr(VI). Heterojunction-mediated charge transport in combination with nanoporous morphology offers an effective catalytic enhancement method for stable and sensitive Cr(VI) colorimetric detection.

2. Materials and methods

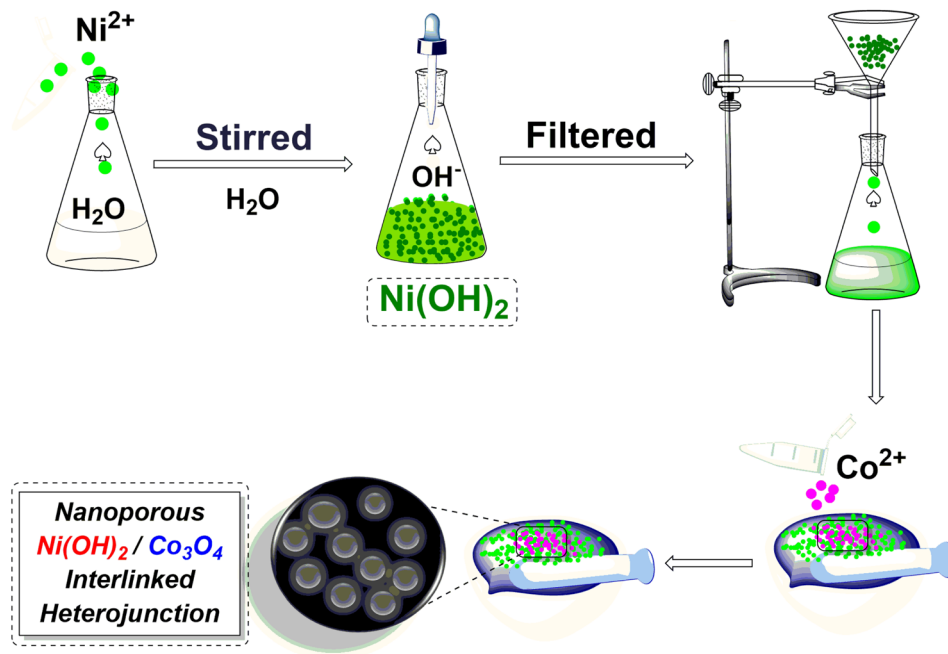
2.1. Materials

Cobalt chloride (CoCl₂) and nickel chloride (NiCl₂·6H₂O) were purchased from E-Merck, India. Sodium hydroxide (NaOH) was brought from E-Merck. 4-Nitrophenol and sodium borohydride (NaBH₄) were received from Sigma-Aldrich, Germany. K₂Cr₂O₇ was purchased from E-Merck, India. 3,3',5,5'-Tetramethylbenzidine (TMB) was purchased from Sigma-Aldrich, USA. All the chemicals were used as received and without any further purification.

2.2. Instrumental techniques

The Fourier-transform Infrared Spectroscopy (FT-IR) spectrum was recorded in the mid-IR range of 450–4000 cm⁻¹ using a Frontier-MIR-FIR from PerkinElmer. The FT-IR spectra of solid samples were recorded in DRIFT mode by grinding the samples with KBr. Powder X-ray diffraction (PXRD) measurements were recorded using a BRUKER AXS D8 FOCUS





Scheme 1 A schematic illustration for the synthesis of Ni(OH)₂/Co₃O₄.

instrument in low angle mode at 2θ values ranging between 10–80°. Raman analyses were done on a Horiba LabRAM HR spectrophotometer equipped with a He–Ne laser with an excitation wavelength of 514.5 nm. The electronic absorption spectrum was recorded using a SHIMADZU UV-2600i spectrophotometer. The XPS analysis was carried out on an ESCALAB Xi+ (Thermo Fisher Scientific Pvt. Ltd, UK). A UV/visible spectrophotometer (SPECORD-200, Analytik Jena, Germany) was used to measure the produced nanocomposite's peroxidase activity toward Cr(vi) detection.

2.3. Synthesis of the bimetallic nanocatalyst, Ni(OH)₂/Co₃O₄

To synthesize the nanocatalyst, 14.4 mg of nickel chloride (NiCl₂·2H₂O) is dissolved in 100 mL of water. A concentrated solution of sodium hydroxide (NaOH) is then added until complete precipitation of nickel hydroxide, Ni(OH)₂, occurs. The resulting precipitate is washed several times with hot water and subsequently dried in an oven. Next, the dried Ni(OH)₂ precipitate is meticulously mixed with 7.5 mg of cobalt chloride (CoCl₂) in a mortar and pestle for 8 h. The resulting mixture is washed repeatedly with hot water to eliminate any impurities present, followed by drying in an oven at 100 °C to obtain the final bimetallic Ni(OH)₂/Co₃O₄ nanocatalyst (Scheme 1).

2.4. Investigation of Ni(OH)₂/Co₃O₄ peroxidase-like properties

Chromogenic TMB molecules are effectively oxidized by Ni(OH)₂/Co₃O₄ to produce an oxidized blue-colored TMB product (Ox-TMB). The standard procedure involved adding 100 μL of Ni(OH)₂/Co₃O₄ (50 mg L⁻¹) to a 0.5 mM TMB solution in an acetate buffer of pH 4. After adjusting the reaction mixture's volume to 3 mL and adding 50 μL of H₂O₂ (30%) solution, the

mixture was incubated for 20 min at 25 °C in a water bath shaker. The Ox-TMB product was monitored using a UV-visible spectrophotometer at a λ_{\max} value of 652 nm. Different parameters such as the concentration of Ni(OH)₂/Co₃O₄, the pH of the reaction mixture and temperature were investigated. Next, the temperature and initial pH of the reaction mixture were changed in order to examine the TMB oxidation processes.

By adjusting TMB and H₂O₂ within a specific concentration range, typical Michaelis–Menten curves for the Ni(OH)₂/Co₃O₄ nanocomposite were produced. The Michaelis–Menten constant (K_m) and the Lineweaver–Burk double reciprocal plot were used to calculate the enzyme's affinity for the substrate. The Lineweaver–Burk plot uses the following equation:

$$\frac{1}{v} = \left(\frac{K_m}{V_m}\right) \left(\frac{1}{[S]}\right) + \left(\frac{1}{V_m}\right) \quad (1)$$

where v = initial velocity; V_m = maximal reaction velocity; and $[S]$ = substrate concentration.

2.5. Colorimetric detection of Cr(vi) in aqueous solution

The detection of Cr(vi) in aqueous media was used to investigate the nanozymatic detection activity of the Ni(OH)₂/Co₃O₄ nanocomposite. Separate additions of Cr(vi) (50–500 nM concentrations) were made to the reaction mixture, which contained 50 μL H₂O₂ (30%) in a buffer solution of pH 3, 0.5 mM TMB, and 100 μL Ni(OH)₂/Co₃O₄ nanocomposite. Following this, Cr(vi) detection was performed using changes in UV-vis absorbance intensities at 652 nm for the Ox-TMB product. In order to investigate the selectivity of the Ni(OH)₂/Co₃O₄ nanocomposite, 200 nM of various interfering ions, namely Pb(II), Na(I), Cu(II), Hg(II), As(III), K(I), Cd(II), and Co(II), were added to the reaction mixture in a manner as described above.



3. Results and discussion

3.1. Characterization of the Ni(OH)₂/Co₃O₄ heterojunction

Transmission electron microscopy (TEM) was employed to assess the crystallinity and confirm the morphology of the synthesized Ni(OH)₂/Co₃O₄ heterojunctions. The TEM images presented in Fig. 1 illustrates the nanoporous morphology of the Ni(OH)₂/Co₃O₄ nanocomposite, with Ni(OH)₂ interlinked with Co₃O₄ nanocrystals. Fig. 1a–c demonstrate a homogenous formation of nanopores, with dimensions approximately ranging from 6 to 10 nm, clearly showcasing the heterojunction structures. High-resolution TEM (HRTEM) analysis (Fig. 1d) reveals an interplanar spacing of about 0.24 nm, which corresponds to the spacing between the (311) crystal planes of the Ni(OH)₂/Co₃O₄ nanocomposite.²⁷ This interplanar spacing is indicative of the crystalline nature and confirms the successful synthesis of the heterojunction material, which is also

supported by the SAED pattern of the synthesised material (inset of Fig. 1d). We have calculated the average crystallite size of the nanoporous Ni(OH)₂ interlinked Co₃O₄ heterojunction using the Scherrer equation based on the XRD data provided.^{28,29}

This calculated value is in excellent agreement with the TEM analysis, which shows a homogenous formation of nanocrystals and nanopores with dimensions ranging from 6 to 10 nm. The calculated size supports the HRTEM observation of an interplanar spacing of 0.24 nm for the (311) crystal planes, confirming high crystallinity within these small domains.

These findings are significant as they underscore the nanoporous architecture of the synthesized material, which is crucial for enhancing the catalytic activities.

In the XRD spectra, the peaks at 31, 39.3, 43.8 and 56.1 correspond to Co₃O₄ and peaks correspond to Ni(OH)₂ were observed at 2θ values of 37.5, 46, and 61, as shown in Fig. 2a.^{27,30}

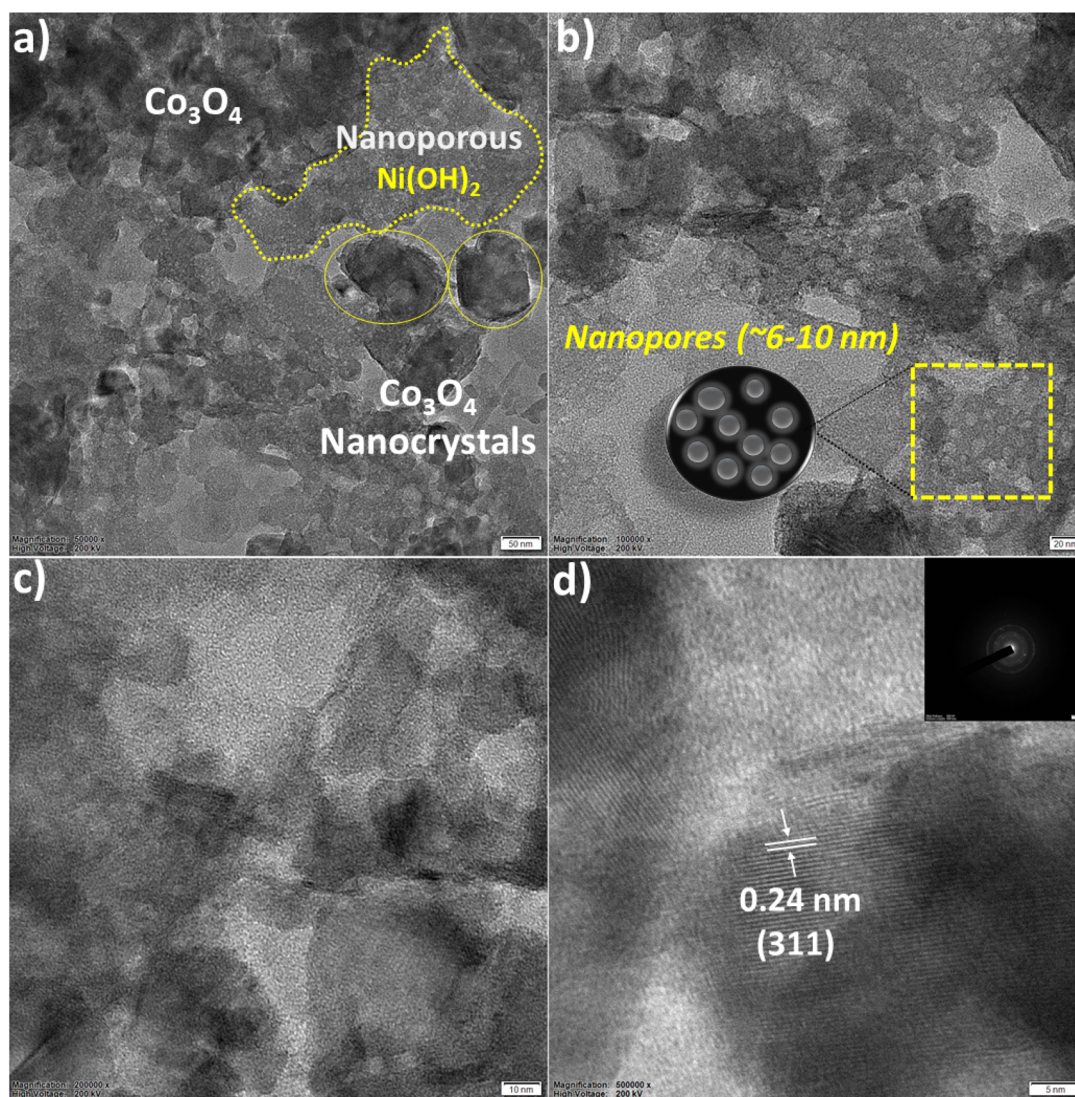


Fig. 1 TEM images of the synthesized Ni(OH)₂/Co₃O₄ heterojunctions. (a–c) Formation of nanopores in the dimension range of ~6–10 nm, illustrating the interconnected structure. (d) HRTEM image showing an interplanar spacing of about 0.24 nm (inset of (d) shows the selected area electron diffraction, SAED pattern).



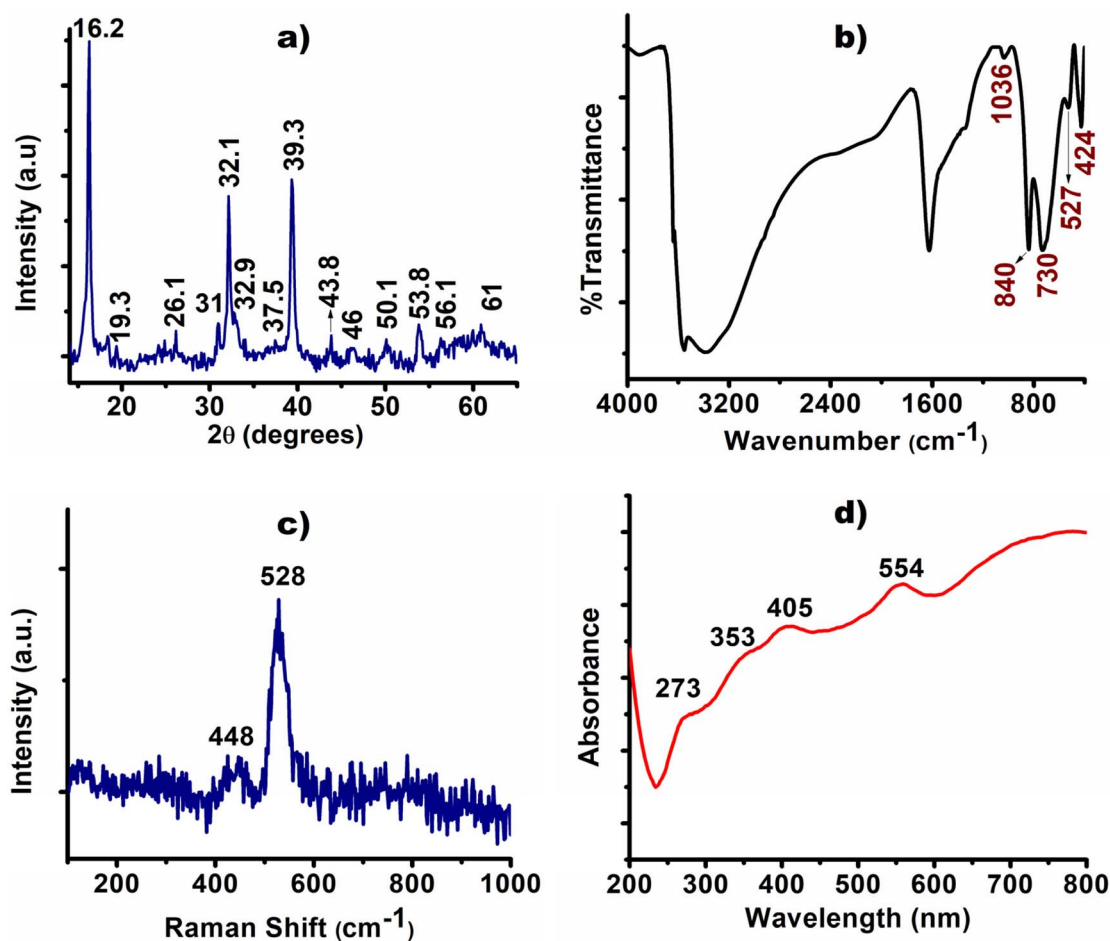


Fig. 2 (a) XRD, (b) FT-IR, (c) Raman and (d) UV-DRS analysis of the Ni(OH)₂/Co₃O₄ nanocomposite.

In the FT-IR spectra, the peak at 418 cm⁻¹ is assigned to the Ni–O stretching band of Ni(OH)₂. Additionally, the spinel structure of the material exhibits characteristic vibrational bands at 530 cm⁻¹ and 730 cm⁻¹, which correspond to the Co²⁺–O vibrations in the tetrahedral sites and the Co³⁺–O vibrations in the octahedral sites of the Co₃O₄ unit, respectively (Fig. 2b).^{27,31} The Raman spectra of the synthesized Ni(OH)₂/Co₃O₄ clearly display peaks at 448 and 528 cm⁻¹, which evidently demonstrate the presence of both Ni–O and Co₃O₄ units in the Ni(OH)₂/Co₃O₄ composite (Fig. 2c).²⁷ From the UV-DRS spectra, the absorption peak at 273 nm corresponds to O²⁻ → Co²⁺ and that at 554 nm corresponds to the O²⁻ → Co³⁺ charge transfer transition of the Co₃O₄ unit.^{32,33} The peaks observed at 353 and 405 nm could be attributed to the Ni–O transition in Ni(OH)₂ NPs, Fig. 2d.³⁴

The crystalline nature and phase purity of the nanoporous Ni(OH)₂/Co₃O₄ heterojunction were evaluated using PXRD and TEM-SAED analysis. The average crystallite size was calculated to be approximately ~9.5 nm using the Scherrer equation and the detailed calculation is provided in the SI.³⁵ This is in excellent agreement with the TEM observations, which reveal interlinked nanocrystals and nanopores within the 6–10 nm range. The calculated size supports the HRTEM observation of

an interplanar spacing of 0.24 nm for the (311) crystal planes, confirming high crystallinity within these small domains.^{36,37}

Based on X-ray Photoelectron Spectroscopy (XPS) spectra, the presence of Co and Ni was confirmed based on distinctive peaks and binding energies. Binding energy values found at 856.3 eV for 2p_{3/2} and 873.9 eV for 2p_{1/2} correspond to Ni²⁺ in Ni(OH)₂.³⁸ The satellite peaks at 862.1 eV and 880.6 eV further support the presence of NiO (Fig. 3a).³⁹ Binding energy values observed at 781.6 eV and 798.1 eV for 2p_{3/2} and 2p_{1/2}, respectively, indicate the presence of Co²⁺. After deconvolution, the peak at 796.5 eV confirms the presence of Co³⁺ in the synthesized material.⁴⁰ The satellite peaks observed at 786.1 eV and 803.2 eV were characteristic of the spinel structure of the synthesized material, also confirmed by FTIR analysis (Fig. 3b).⁴⁰ These findings confirm the formation of Co₃O₄ and Ni(OH)₂ in the analysed sample, providing valuable insight into its chemical composition and structure. Zhao *et al.* also observed similar binding energy values in the spinel structure of the synthesized Co₃O₄ nanostructures.⁴¹ In the oxygen (O) spectra of the synthesized material, two peaks appeared after deconvolution at 530.7 eV and 531.5 eV, indicative of different O binding sites (Fig. 3c).⁴² The peak found at 530.7 eV is attributed to metal oxide formation and that at 531.5 eV is attributed to oxygen vacancies.⁴²



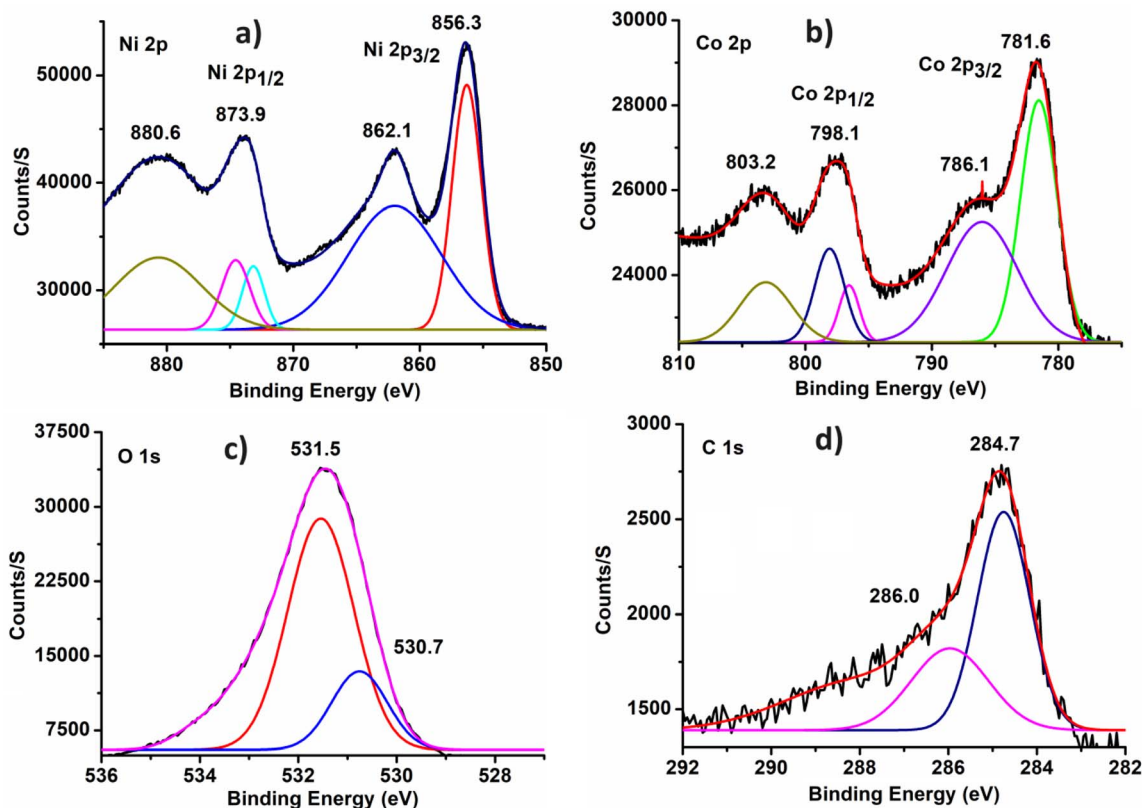


Fig. 3 XPS spectra of (a) Ni 2p, (b) Co 2p, (c) O 1s, and (d) C 1s of the synthesized Ni(OH)₂/Co₃O₄ nanocomposite.

Carbon (C) spectra of the material revealed two peaks at binding energy values of 284.7 eV for C–C bonds and 286.0 eV for the presence of O–C=O groups, respectively, Fig. 3d.⁴⁰

3.2. Ni(OH)₂/Co₃O₄ nanocomposite's intrinsic peroxidase-like activity and reaction condition optimization

The oxidation reaction of TMB in the presence of H₂O₂ was used to investigate the peroxidase-like activity of the Ni(OH)₂/Co₃O₄ nanocomposite. The resulting blue colored oxidized product of TMB showed absorbance maxima at 652 nm due to the formation of 3,3',5,5'-tetramethylbenzidine diimine (TMBDI).⁴³

To illustrate the Ni(OH)₂/Co₃O₄ nanocomposite's peroxidase-like catalytic activity, the oxidation of TMB was investigated under various conditions. Ni(OH)₂/Co₃O₄ nanocomposite-catalyzed TMB oxidation was carried out as a control without H₂O₂. Since there was no color change, it can be concluded that TMB oxidation requires both H₂O₂ and the Ni(OH)₂/Co₃O₄ nanocomposite. The peroxidase-like catalytic activity towards TMB oxidation was found to be significantly higher when the reaction was conducted in the presence of the catalyst as well as H₂O₂. The changes observed due to the oxidation of TMB are depicted in Fig. 4.

It was possible to determine the ideal analytical conditions by examining how the pH, temperature, and catalyst quantity affected the peroxidase-like activity of the Ni(OH)₂/Co₃O₄ catalyst. Fig. 5A shows how pH affects the activity of the Ni(OH)₂/Co₃O₄ catalyst. The catalytic activity of Ni(OH)₂/Co₃O₄ quickly declines beyond pH 3, which is also the pH at which maximum

absorbance is seen. At a concentration of 100 mg L⁻¹ of Ni(OH)₂/Co₃O₄ nanocomposite, the maximum catalytic activity was observed at 25 °C (Fig. 5B, C). Thus, the following

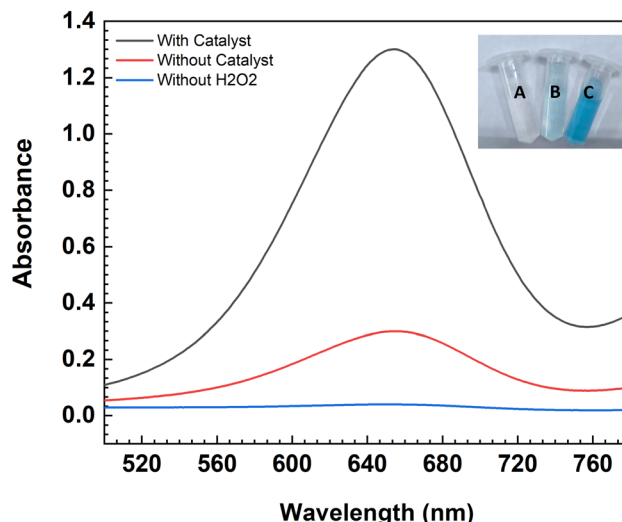


Fig. 4 UV-visible spectrum of 0.5 mM TMB without H₂O₂, without the Ni(OH)₂/Co₃O₄ nanocomposite and in the presence of both H₂O₂ and the Ni(OH)₂/Co₃O₄ nanocomposite. The inset shows the corresponding photographs (A = without H₂O₂; B = without the Ni(OH)₂/Co₃O₄ nanocomposite but in the presence of H₂O₂; C = presence of both the Ni(OH)₂/Co₃O₄ nanocomposite and H₂O₂).



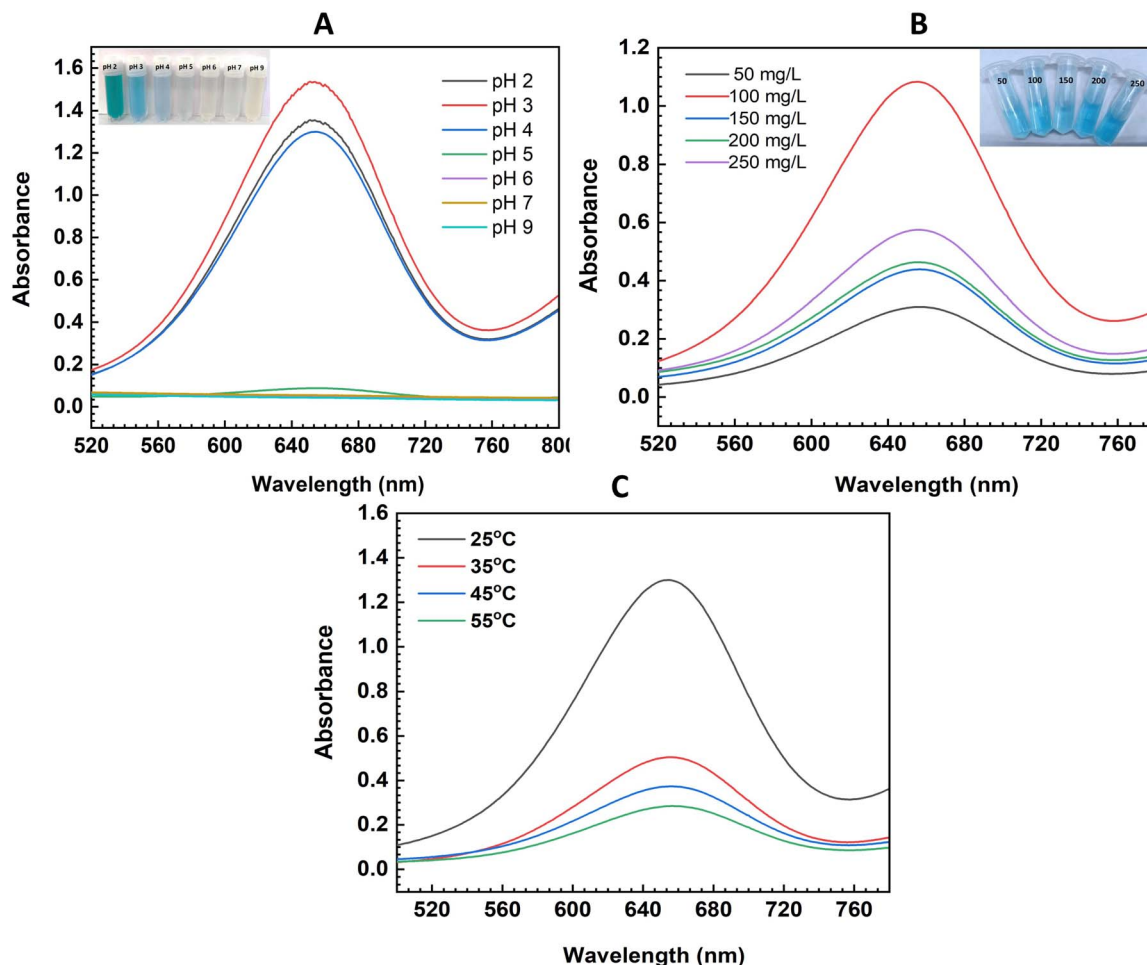


Fig. 5 UV-visible absorption spectra for oxidation of TMB using the Ni(OH)₂/Co₃O₄ nanocomposite at different (A) pH values, (B) catalyst concentrations and (C) temperatures.

circumstances result in the highest catalytic activity: 100 mgL⁻¹ of Ni(OH)₂/Co₃O₄ nanocomposite at pH 3 and 25 °C.

3.3. Kinetic evaluation of the Ni(OH)₂/Co₃O₄ nanocomposite as a peroxidase mimic and determination of the Michaelis constant

Utilizing steady state kinetics and the initial rate approach, the intrinsic peroxidase-like catalytic activity of the Ni(OH)₂/Co₃O₄ nanocomposite was examined utilizing TMB and H₂O₂ as substrates. While maintaining a constant concentration of the other reagents, kinetic analysis was carried out by varying the concentration of the substrates (TMB and H₂O₂). Beer–Lambert law was used to convert the absorbance readings to their respective concentrations:

$$A = \epsilon_{\text{TMBDI}} \times c \times L \quad (2)$$

where $\epsilon_{\text{TMBDI}} = 39\,000 \text{ M}^{-1} \text{ cm}^{-1}$ at 652 nm for TMBDI, c = concentration of the sample and L refers to the path length.⁴⁴

Typical Michaelis Menten curves for TMB and H₂O₂ (shown in Fig. 6A and B, respectively), as substrates in a certain concentration range, were produced by converting the

appropriate concentration terms to velocity terms. Lineweaver–Burk double reciprocal plots were then used to determine the catalytic parameters K_m (Michaelis constant) and V_m (maximal velocity) of the enzyme mimics Ni(OH)₂/Co₃O₄. The slope of the Lineweaver–Burk double reciprocal plots (as shown in the insets of Fig. 6A and B) yields the value of K_m , while their intercept yields the value of V_m . The K_m value of Ni(OH)₂/Co₃O₄ for TMB as a substrate was found to be 0.53 mM whereas that for H₂O₂ was found to be 2.42 mM. The corresponding V_m values for TMB and H₂O₂ as substrates were found to be $4.77 \times 10^{-8} \text{ M s}^{-1}$ and $2.80 \times 10^{-8} \text{ M s}^{-1}$, respectively.

The low K_m value (0.53 mM for TMB) for Ni(OH)₂/Co₃O₄ suggests that it has a higher substrate affinity for TMB. Additionally, compared to many other enzyme mimics as shown in Table S1, the K_m value reported for Ni(OH)₂/Co₃O₄ with H₂O₂ is significantly lower, indicating that a lower H₂O₂ concentration is needed for TMB oxidation.

3.4. Plausible mechanism of the peroxidase-like activity

The pertinent reactive species in the catalytic system were observed in order to examine the catalytic mechanism of the



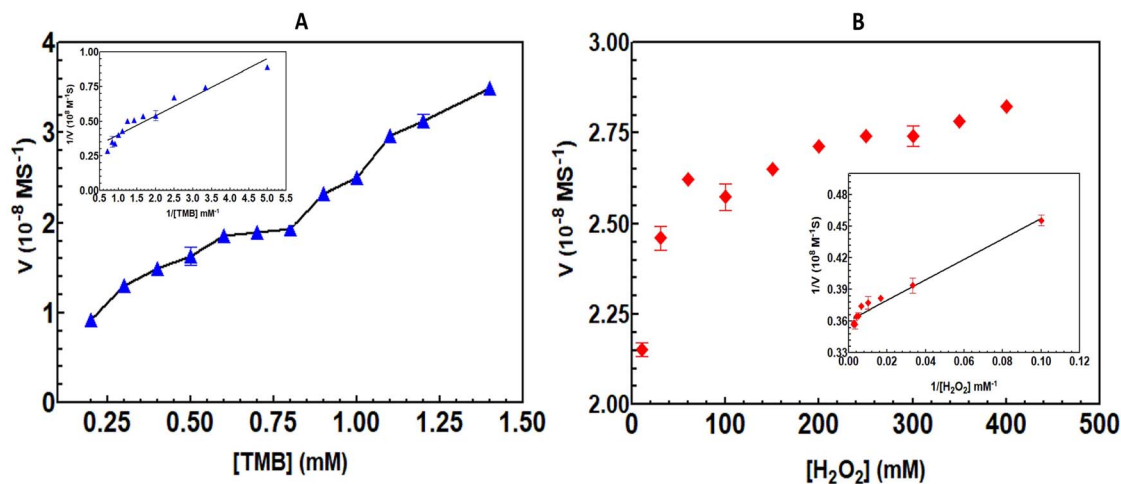
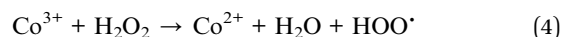


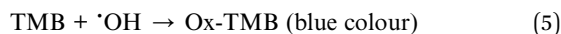
Fig. 6 Ni(OH)₂/Co₃O₄ nanocomposites' catalytic mechanism and steady-state kinetic assay. (A) TMB concentration variation at a fixed H₂O₂ concentration (50 mM). (B) H₂O₂ concentration variation at a fixed TMB concentration (0.5 mM). The inset displays the matching Lineweaver-Burk plots of the double reciprocal of the Michaelis-Menten equation.

peroxidase-like activity of the Ni(OH)₂/Co₃O₄ nanocomposites. The peroxidase-like activities of nanozymes catalyse the generation of hydroxyl radicals ([•]OH) from hydrogen peroxide (H₂O₂), which in turn oxidizes the chromogenic substrate to produce the blue colour. Ni(OH)₂/Co₃O₄ nanocomposites exhibit strong peroxidase-mimicking activity as a result of their Fenton-like behavior in the presence of H₂O₂. TMB molecules are adsorbed onto the surface of the Ni(OH)₂/Co₃O₄ nanocomposites. The adsorption of TMB molecules onto the surface of the Ni(OH)₂/Co₃O₄ nanocomposite surface occurs through π-π interactions between their functional groups. Ni(OH)₂/Co₃O₄ facilitates Fenton reactions that generate [•]OH radicals from H₂O₂. The reactions involved in the Fenton process are shown in the equations below (eqn (3)–(5)).^{45,46}

Co₃O₄ has mixed valence states (Co²⁺ and Co³⁺) that accelerate Fenton-like reactions to break down H₂O₂.



The [•]OH radical, being a powerful oxidizing species, converts TMB into blue-colored Ox-TMB, which exists in equilibrium with the cation free radical TMB^{•+}.



Although we could not quantify the decomposition of H₂O₂ (as it was used in a significantly lower amount, 50 μL), its role in generation of [•]OH can be evaluated using a fluorescent method using terephthalic acid (TA) as a probe molecule. TA reacts selectively with [•]OH to form 2-hydroxyterephthalic acid (TAOH) that shows a characteristic fluorescence emission at 410 nm. The excitation and emission wavelengths are at 315 nm and 410 nm, respectively. The fluorescence signal of TAOH confirms the formation of [•]OH in the reaction system. In a typical experiment, an optimized amount of the catalysts (100 mg L⁻¹)

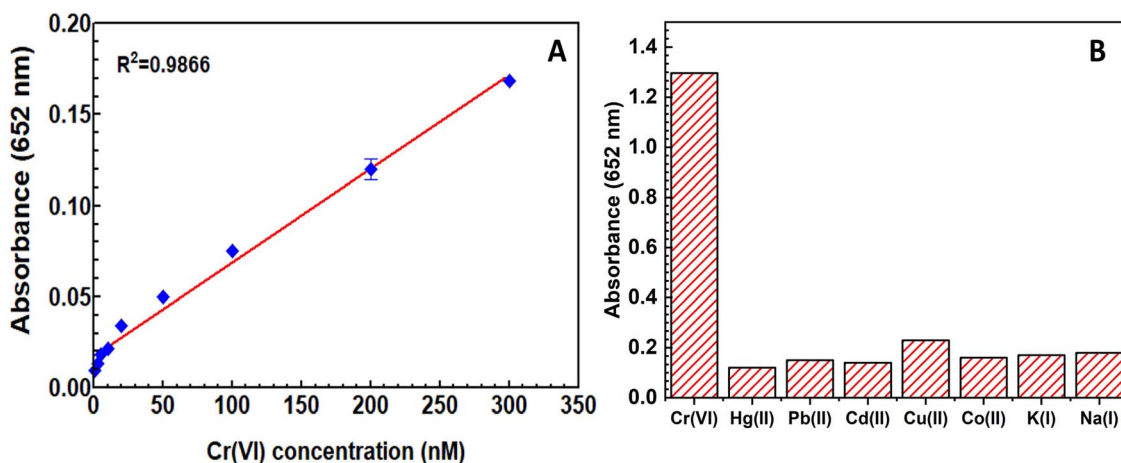


Fig. 7 (A) Standard Cr(vi) concentration response curve under optimum conditions using the Ni(OH)₂/Co₃O₄ nanocomposite and (B) selectivity study of Ox-TMB absorbance following the sensing process in the presence of various inorganic ions.



Table 1 Evaluation of the activity of Ni(OH)₂/Co₃O₄ towards colorimetric Cr(vi) detection activity in comparison to previously published materials

Sl. no.	Material	Linear range	Limit of detection	Reference
1	N- and S-doped carbon dots	1–40 μM	0.52 μM	50
2	Ag–Ag nanocluster	0.6–10 μM	0.3 μM	51
3	Graphene QDs	1–500 μM	190 nM	52
4	CuS/Fe ₃ O ₄	0–1500 μM	60 nM	53
5	Fe ₃ O ₄ @MQDs	0–60 μM	0.26 nM	54
6	Cu–PyC MOF	0.5–50 μM	0.051 μM	55
7	PNPG-PEG	0.05–12.5 μM	520 nM	10
8	CoFe ₂ O ₄ /H ₂ PPOP	0.6–100 μM	0.026 μM	56
8	Ni(OH) ₂ /Co ₃ O ₄	10–300 nM	39 nM	This work

was dispersed in an aqueous TA/NaOH solution (1 : 2 molar ratio) containing 50 μL H₂O₂. The fluorescence spectra were recorded at 5 min and 20 min (as shown in Fig. S1, in SI). The enhanced PL intensity at 20 min indicates a more efficient generation of [•]OH compared to that at 5 min. Since fluorescence intensity at 410 nm is directly proportional to [•]OH production, the stronger emission confirms higher [•]OH generation, leading to faster and more efficient TMB oxidation.

3.5. Detection of Cr(vi) using Ni(OH)₂/Co₃O₄ nanocomposites and selectivity study

The nanozymatic detection technique has garnered significant attention in the last years because of its simplicity, convenience of use without a sophisticated instrument, and visibility to the unaided eye.⁴⁷ Accordingly, the Ni(OH)₂/Co₃O₄ nanocomposite was also effectively used for the colorimetric detection of Cr(vi) due to its superior peroxidase-like activity, as was previously mentioned.

Typically, in an acetate buffer of pH 3, Ni(OH)₂/Co₃O₄ nanocomposites, H₂O₂ (30%) and TMB under their optimum conditions were allowed to mix with varying quantities of freshly prepared Cr(vi) solutions (1–300 nM) and allowed to react with the reaction mixture at 25 °C. At a wavelength of 652 nm, the Ox-TMB product's UV-Vis absorbance variations were observed for these various Cr(vi) concentrations. As the concentration of Cr(vi) rose, the absorbance intensity for the Ox-TMB product increased progressively. In acidic media, Cr(vi) can break down H₂O₂ into O₂ and H₂O. Fenton reactions allow both O₂ and H₂O to combine with electrons on the surface of

Ni(OH)₂/Co₃O₄ to form [•]OH. As a result, when Cr(vi) is present in the reaction mixture, TMB oxidation rises.⁴⁸ The absorbance at 652 nm vs. concentration of Cr(vi) was plotted to create a calibration curve based on the variations in absorbance intensity, as shown in Fig. 7A. In the linear range of 10–300 nM, the LOD for Cr(vi) detection was found to be 39 nM. Comparing Ni(OH)₂/Co₃O₄ activity to that of the majority of other previously published nanomaterials (Table 1) for colorimetric detection of Cr(vi), the LOD is noticeably lower.

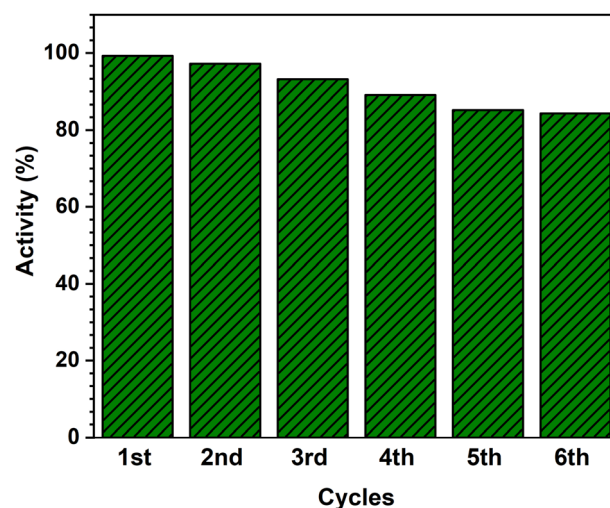
In the presence of 200 nM of various interfering ions, including Hg(II), Pb(II), Cd(II), Cu(II), Co(II), K(I), and Na(I), the selectivity of Ni(OH)₂/Co₃O₄ was also examined in the colorimetric detection of Cr(vi), as shown in Fig. 7B. The presence of Cr(vi) significantly boosts the TMB oxidation efficiency, most likely as a result of the ions' strong catalytic sites and adsorption at the Ni(OH)₂/Co₃O₄ surface. Although not as strongly as with Cr(vi), other metal ions also interact with the surface of Ni(OH)₂/Co₃O₄.⁴⁹ When Cr(vi) was present, there was a noticeable rise in the Ox-TMB absorption intensity.

3.6. Detection of Cr(vi) ions in environmental samples

The synthesized materials' practical sensor application for the detection of the Cr(vi) ion in various environmental samples was

Table 2 Measurement of Cr(vi) in real-world samples

Sample	Cr(vi) added (nM)	Cr(vi) detected (nM)	Recovery (%)
Tap water	10	9.94	99.40
	50	49.72	99.44
	100	99.50	99.50
Pond water	10	10.1	101.00
	50	49.20	98.40
	100	98.47	98.47
Well water	10	9.61	96.10
	50	48.80	97.60
	100	97.52	97.52

**Fig. 8** Reusability study of the Ni(OH)₂/Co₃O₄ nanocomposite for the TMB oxidation reaction.

examined. Table 2 shows the relative standard deviation and recovery % for the various environmental samples. In several environmental samples, the suggested approach demonstrated a good recovery % for Cr(vi). The findings imply that the suggested sensor can be utilized to detect Cr(vi) in actual samples with good recovery values.

3.7. Reusability study of the Ni(OH)₂/Co₃O₄ nanocomposite

By performing the reaction six times, the reusability of the Ni(OH)₂/Co₃O₄ nanocomposite as an enzyme mimic for TMB oxidation was examined. After six catalytic cycles, the relative activity was 84.32% of the initial activity, as illustrated in Fig. 8. According to the results, the Ni(OH)₂/Co₃O₄ nanocomposite is a nano-enzyme with superior stability and catalytic activity.

We have performed a PXRD analysis on the catalyst recovered after five consecutive cycles. The post-catalysis PXRD pattern (now included as Fig. S2 in the SI) shows no significant shift in peak positions or emergence of new phases. This indicates that the heterojunction maintains its structural integrity and phase stability during the sensing of chromium(vi), justifying its excellent reusability. Sensors often face surface poisoning or phase transformation. By showing that the Co₃O₄ and Ni(OH)₂ peaks remain unchanged after use, we demonstrate that the detection mechanism is likely surface-redox driven rather than a destructive chemical reaction, confirming the robustness of the material as claimed in the Abstract.

4. Conclusion

In conclusion, we have successfully designed and synthesized a nanoporous Ni(OH)₂/Co₃O₄ heterojunction and demonstrated its enhanced peroxidase-like activity for sensitive colorimetric detection of Cr(vi). Integrating engineered heterointerfaces into nanoporous structures has effectively enhanced both catalytic and sensing efficiency. The development of a distinct heterojunction was confirmed by structural analysis, whereas kinetic studies established improved substrate affinity and effective H₂O₂ activation due to synergistic Ni²⁺-Co²⁺/Co³⁺ redox coupling. The developed heterojunction delivered a limit of detection of 39 nM, a 10–300 nM linear range and high selectivity for Cr(vi) together with satisfactory stability and reliability in real-sample detection.

This study validates that rational design of heterointerfaces is crucial in advancing metal hydroxide–oxide catalysts. Bridging the gap between materials science and device engineering will be essential for developing the next generation of portable environmental diagnostic tools.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting the findings of this study are available from the corresponding author upon request.

Supplementary information (SI): Scherrer equation calculation, comparison of kinetic parameters of synthesized nanocomposites with other reported materials, photoluminescence spectra (PL) of TMB oxidation reaction confirming the generation of ·OH radicals, PXRD analysis on the catalyst recovered after five consecutive cycles. See DOI: <https://doi.org/10.1039/d5na01116g>.

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