

Earth-abundant CZTS/MIL-125-NH₂ heterojunctions for enhanced visible-light Cr(VI) reduction: Interfacial charge dynamics and mechanistic insights

Yesica Di Iorio

ydiiorio@mdp.edu.ar

National University of Mar del Plata

C. Javier Pereyra

Universidad de la República de Uruguay

Ricardo Marotti

Universidad de la República de Uruguay

Enrique Dalchiele

Universidad de la República de Uruguay

Joaquín Nigro

National University of Mar del Plata

Cristina Ramírez

National University of Mar del Plata

Matías E. Aguirre

National University of Mar del Plata

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Abstract

The development of efficient, stable, and earth-abundant photocatalysts for the reduction of highly toxic Cr(VI) under visible light remains a significant challenge. Herein, a novel heterojunction system is reported based on the integration of Cu₂ZnSnS₄ (CZTS) kesterite nanoparticles (size ~ 10 nm) into the titanium-based metal–organic framework MIL-125-NH₂. A series of MIL-125-NH₂/CZTS nanocomposites with varying CZTS loadings (5, 10, 25, and 50 wt%) was synthesized via a solvothermal approach in the presence of preformed CZTS nanoparticles. Structural (XRD, Raman, SEM) and optical (DRS) analyses confirm the formation of intimate heterointerfaces with preserved crystallinity and extended visible-light absorption up to 800 nm. Mott–Schottky analysis reveals that the NC25 composite (25% CZTS) exhibits a high carrier density ($5.7 \times 10^{22} \text{ cm}^{-3}$) and an optimized flat-band potential, promoting efficient charge transfer. Photoelectrochemical measurements demonstrate that NC25 delivers a significantly enhanced photocurrent response ($73.3 \mu\text{A cm}^{-2}$ at 0 V vs Ag/AgCl), outperforming both individual components and layered architectures. Under visible-light irradiation, the NC25 nanocomposite achieves a remarkable Cr(VI) reduction rate constant of $3.4 \times 10^{-2} \text{ min}^{-1}$, approximately twice that of pristine MIL-125-NH₂. Wavelength-dependent photocatalytic kinetics reveal a 22-fold decrease in the reduction rate when the excitation shifts from 440 nm (dual excitation) to 568 nm (selective CZTS excitation) confirming that synergistic photoexcitation is essential for efficient charge separation, consistent with a type-II heterojunction. This work highlights the pivotal role of interface design in MOF-based hybrid systems, offering a cost-effective and non-toxic alternative for solar-driven environmental remediation.

1.- Introduction

Designing systems that convert solar energy into stored chemical energy or use it to degrade pollutants is a key research field for addressing energy and environmental challenges [1, 2]. A wide variety of semiconductors, including oxides, sulfides, and metal–organic frameworks (MOFs), have been used as active materials to generate charge carriers (electrons and holes) under visible-light irradiation for hydrogen production via water splitting and for the reduction of heavy metals such as Cr(VI) [3–5]. However, photoinduced electron–hole pairs form an unstable excited state highly prone to recombination, the main limitation of these systems [6]. Scarce-element materials such as CuInGaSe₂ are often used to enhance photovoltaic efficiency for energy conversion and hydrogen generation. Strategies to improve charge separation include defect minimization, additional processing steps, or stratified architectures [7–9]. However, these strategies increase costs and complicate large-scale implementation.

An alternative and widely explored approach to enhance photocatalytic efficiency is the construction of heterojunctions by coupling a semiconductor with a second material, which generates band structures that favor charge transfer and separation. Among these, systems composed of two semiconductors with type-II band alignment are particularly attractive [10]. In such a configuration, the photogenerated electrons from the higher conduction band of one semiconductor are transferred to the lower conduction

band of the other, while the holes migrate in the opposite direction, resulting in spatial charge separation and reduced recombination. These electrons can trigger high-energy multielectron reduction reactions, such as the conversion of CO₂ or Cr(VI) into fuels and less toxic products, respectively [11, 12]. However, these systems often involve complex architectures, expensive materials or toxic species [13]. Therefore, the development of energy conversion and photocatalytic systems capable of mediating useful processes under visible-light excitation, based on low-cost, readily available, and biocompatible materials, remains a challenge.

MOFs are three-dimensional crystalline materials composed of metal clusters and organic linkers, featuring high surface areas and tunable properties for applications in gas storage, sensing, pollutant adsorption, and bio-catalysis [14]. Additionally, Ti-based MOFs incorporating aminated terephthalate linkers exhibit semiconductor-like behavior with relatively narrow band gaps, enabling photoactivity under visible-light irradiation [15]. MIL-125-NH₂ is derived from 2-aminoterephthalic acid with a band gap of around 2.7 eV and a highly negative conduction band potential (≈ -0.6 V vs. NHE) [16], which makes it a widely used photocatalyst for mediating environmentally relevant processes. However, the low electrical conductivity of these systems leads to a high recombination rate of photogenerated charge carriers [17]; therefore, an effective strategy to enhance their photocatalytic performance is to couple them with another material that improves charge separation. The modification of this MOF with inorganic sulfides, whose band positions are generally suitable for forming type-II heterojunctions, has been explored for hydrogen generation and Cr(VI) photoreduction using CdS, CdInS₄, and ZnIn₂S₄ [18, 19]. Nevertheless, while these systems exhibit good efficiency, they often require costly precursors or may lead to the formation of toxic species under photocatalytic conditions. In this context, a safer, less expensive, and largely unexplored alternative is the use of kesterite Cu₂ZnSnS₄ (CZTS). CZTS is a quaternary sulfide composed of earth-abundant and non-toxic elements, with a relatively narrow band gap and a high absorption coefficient, which makes it a promising absorber for photovoltaic devices as a replacement for traditional Cu(In,Ga)Se₂ [20]. However, the presence of less-absorbing secondary phases and crystalline defects that act as recombination centers severely limits its application both as an absorber and as a photocatalyst [21]. In this context, the hot-injection method has recently emerged as an effective strategy, where the rapid addition of the sulfide source at high temperature enables the synthesis of highly pure and crystalline CZTS [21]. Moreover, CZTS exhibits a highly negative conduction band [46], which, combined with its high absorption capacity, suggests that the modification of MIL-125-NH₂ with CZTS would result in a system with maximized charge separation and an extended visible light response.

Herein, the synthesis and characterization of MIL-125-NH₂/CZTS nanocomposites are presented. Progressive modification of the MOF with CZTS nanoparticles modulates the optical and electronic properties, enabling more efficient interfacial charge transfer and significantly improved photocatalytic Cr(VI) reduction compared to the individual components, with the optimal composition reflecting a balance between carrier density and interfacial interactions, highlighting the role of interface design.

2.- Materials and methods

2.1- Materials

2-aminoterephthalic acid, dimethylformamide, ethanol, isopropyl alcohol, acetonitrile, titanium(IV) isopropoxide, and titanium diisopropoxide bis(acetylacetonate) were purchased from Sigma-Aldrich. Copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, Aldrich), Zinc chloride anhydrous (ZnCl_2 , Alfa Aesar), Tin (II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, Alfa Aesar), and sulfur (S, Aldrich); oleylamine (OLA, Aldrich) and toluene (Aldrich) were used as received without further purification. Fluorine-doped tin oxide (FTO) ($\text{SnO}_2:\text{F}$, Zhuhai Kaivo Electronic Components Co., Ltd.) was used as the device substrate material electrode.

2.2- Synthesis

2.2.1-Synthesis of metal-organic framework: MIL-125-NH₂ particles

Following the solvothermal procedure described by Ahmed and coworkers [22], the MIL-125-NH₂ was prepared by a one-step solvothermal method as follows: 0.2643 g of 2-aminoterephthalic acid was dissolved in 12 mL of a mixture of DMF and methanol (9:1) under stirring for 15 minutes until dissolution at room temperature. Finally, 220 μL of titanium isopropoxide was added, and the reaction mixture was kept stirring vigorously for 10 minutes. The mixture was transferred to the autoclavable reactor and heated at 150°C for 16 hours at 2°C min⁻¹. After the solvothermal reaction, the yellow-green solid was separated by centrifugation at 7500 rpm for 10 minutes, and then the product was washed with portions of 10 mL DMF/MeOH (9:1) and MeOH three times. Finally, the solid was stored.

2.2.2- Synthesis of CZTS nanoparticles

CZTS nanoparticles were synthesized by hot injection method [23]. In a typical synthesis, 0.2634 g of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (1.2 mmol), 0.341 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (2 mmol), and 0.2268 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (1 mmol) were placed in a three-neck flask and dissolved in 10 mL of oleylamine, which acts as a solvent, surfactant, and capping ligand. And heated at 140°C for 30 minutes under a nitrogen atmosphere. Then, it was heated to 240°C, and once this temperature was reached, 5 mL of oleylamine containing 0.16 g of colloidal sulfur (5 mmol) previously dissolved at 80°C was quickly added under anaerobic conditions. The reaction mixture turned black and was kept at 240°C for 90 minutes while maintaining an inert atmosphere. Then, it was allowed to cool to 60°C, and 15 mL of isopropanol:toluene (8:1 v/v) was added and allowed to stand overnight. Subsequently, the solid was isolated by centrifugation at 7500 rpm for 10 minutes and washed twice with isopropanol:toluene (8:1).

2.2.3- Synthesis MIL-125-NH₂/CZTS nanocomposite

The hybrid material was obtained following the same processes to synthesize MIL-125-NH₂ particles, adding different quantities of pre-synthesized CZTS nanoparticles in the precursor solution to achieve

the following nominal chalcogenide:MOF ratios 5:95, 10:90, 25:75, and 50:50 w/w, hereafter referred to as NC5, NC10, NC25, and NC50, respectively. Solid washing was performed in the same way as described above.

2.3- Films preparation

Substrate preparation. The glass/FTO substrates (1 cm × 2.5 cm) were washed consecutively with aqueous detergent solution, water, and isopropyl alcohol/deionized water 1:1 solution in an ultrasonic bath for 10 min. The cleaned substrates were dried under a nitrogen flow and finally exposed to ozone for 5 minutes.

The photoelectrode architecture consisted of a multilayer configuration of FTO//compact TiO₂//mesoporous TiO₂//active layer (MIL-125-NH₂, CZTS, or MIL-125-NH₂/CZTS nanocomposite).

Two TiO₂ blocking layers [24, 25], consisting of a compact and mesoporous layer, were deposited between the FTO substrate and the active nanocomposite layer. The compact TiO₂ was deposited by spin coating from a 1:10 solution of titanium bis(acetylacetonate) in ethanol at 3000 rpm for 30 s onto the FTO. After deposition, the substrates were dried on a hot plate at 120°C for 10 min and annealed at 450°C for 30 min with a heating rate of 20°C min⁻¹. A mesoporous TiO₂ layer was then deposited from a 1:7 solution of titanium bis(acetylacetonate) in ethanol at 3000 rpm for 30 s, followed by sintering at 500°C for 30 min using the same heating rate. Before the deposition of each subsequent layer, the TiO₂-coated FTO substrates were “thermally activated” at 120°C for 5 min.

Spin coating was employed to deposit the active layers using two consecutive deposition cycles (2000 rpm for 20 s) with intermediate drying at 120°C for 15 min. MIL-125-NH₂ films were prepared from an isopropanolic dispersion (8 mg mL⁻¹) sonicated for 2 h and deposited onto the FTO/TiO₂ substrate. For the layered architecture, CZTS films were obtained from an ethanolic suspension (218 mg mL⁻¹) sonicated for 15 min and spin-coated onto the pre-deposited MOF layer. Nanocomposite films were fabricated from an isopropanolic dispersion (125 mg mL⁻¹) of the MIL-125-NH₂/CZTS composite, sonicated for 15 min, and deposited directly onto the FTO/TiO₂ substrate.

2.4- Characterization

The crystalline structure of the samples was analyzed by powder X-ray diffraction (XRD). Measurements were performed using an X'Pert PRO (PANalytical) powder diffractometer, with Cu K_α radiation operated at 40 kV and 30 mA. Diffraction patterns were recorded in the 2θ range from 5° to 70° with a scanning rate of 0.04° s⁻¹. The obtained patterns were analyzed using X'Pert HighScore software.

The surface morphology of the films was examined by scanning electron microscopy (SEM) using a JEOL JSM-6460LV instrument.

Localized Raman spectra were acquired using a Renishaw in Via Reflex confocal Raman microprobe operating in backscattering configuration with a 50× objective and a 785 nm excitation laser. Spectra

were collected using an integration time of 20 s, 2 accumulations, and 0.5% laser power.

Semi-quantitative elemental analysis was performed by X-ray fluorescence (XRF) using a PANalytical MiniPal 2 (PW4025) spectrometer equipped with a Cr anode X-ray tube. Measurements were conducted at 20 kV and 10 μ A without the use of a Ti filter.

The diffuse reflectance spectra (DRS) of the samples were measured with an integrating sphere (Ocean Optics ISP-REF), and a halogen lamp was used as a source of optical excitation. The reflected signal was coupled into a spectrometer (Ocean Optics S2000) with an optical fiber (50 μ m diameter).

The DRS (R_D) signal was converted into an experimental absorbance α_{exp} using the Kubelka-Munk function (F_{K-M}) [26]:

$$F_{K-M} = \frac{(1 - R_D)^2}{2R_D} \propto \alpha_{exp}$$

The electrochemical characterization was performed with the film deposited on FTO serving as the working electrode, while a platinum ring and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. Mott-Schottky measurements were performed using an SRS potentiostat (EC301) coupled to a MokuGo frequency response analyzer, which generated the AC perturbation (amplitude = 25 mV) and recorded the impedance response. Capacitance measurements were performed over a potential range of -1 to 0.8 V vs Ag/AgCl using an AC perturbation of 25 mV amplitude at a frequency of 1200 Hz [27, 28]. All the measurements were performed in a 0.2 M Na_2SO_4 aqueous solution. To avoid undesired effects on the samples, the current density during capacitance measurements was kept below 200 $\mu\text{A cm}^{-2}$ according to established criteria [29].

All electrochemical and photochemical measurements were carried out at room temperature in a quartz cell using a three-electrode configuration with a Pt mesh as counter electrode and Ag/AgCl as reference electrode. Prior to each experiment, the electrolyte or reaction solution was purged with high-purity nitrogen (N_2 , 99.99%) for at least 20 min to remove dissolved oxygen.

For the photoelectrochemical characterization, the working electrode consisted of the film deposited on FTO, and measurements were performed in a 0.5 M Na_2SO_4 aqueous solution using a commercial potentiostat/galvanostat (TEQ-04). The potential was swept from -0.5 to 1.0 V at a scan rate of 25 mVs^{-1} . Current density-voltage (J-V) curves were recorded under chopped illumination using a Xenon lamp as the light source equipped with a 400 nm cut-off filter, with back-side illumination through the conductive substrate (FTO/ TiO_2 /sample configuration).

For the photocatalytic experiments, irradiation was provided by a high-pressure Hg-Xe lamp for polychromatic irradiation coupled to a Kratos-Schoeffel monochromator to select the desired wavelength. Photocatalysis was carried out in 3 cm^3 square quartz cells containing the photocatalyst

suspension (1 mg mL^{-1}) in $\text{K}_2\text{Cr}_2\text{O}_7$ solution ($5.4 \times 10^{-4} \text{ M}$, phosphate buffer 0.1 M , pH 7) with triethylamine (10 mM) as a sacrificial donor. For polychromatic experiments a 400 nm cutoff filter was used to avoid direct photoreduction of dichromate. Prior to irradiation, the suspension was stirred in the dark for 30 min .

The concentration of Cr(VI) was monitored using the diphenylcarbazide colorimetric method by following the absorbance of the Cr –diphenylcarbazide complex at 540 nm [30]. Photon flux was determined by chemical actinometry using phenylglyoxylic acid [31], ferrioxalate [32], and Reinecke's salt method [33] depending on the irradiation wavelength. Control experiments performed in the absence of a photocatalyst, under dark conditions, or without the sacrificial donor (triethylamine) confirmed that Cr(VI) reduction does not occur under these conditions (see Supplementary Information, Figure S11).

3.- Results and discussion

3.1- Structural characterization

The crystalline structure of MIL-125-NH_2 , CZTS nanoparticles, and the resulting nanocomposites was investigated by powder X-ray diffraction (XRD), and the corresponding patterns are shown in Fig. 1a. The diffraction patterns of the individual samples were similar to those previously reported [34, 35]. For MIL-125-NH_2 , the diffraction peaks are consistent with the pristine MIL-125 isoform, where the most dominant Bragg reflections correspond to the (101) and (002) crystal planes [34], confirming the formation of the characteristic tetragonal framework. In the case of pure CZTS, all diffraction peaks match well with the kesterite structure reported in the JCPDS-26-0575. The three most intense peaks located at 28.5° , 47.4° , and 56.3° can be attributed to the (112), (220), and (312) planes, respectively.

As shown in the Fig. 1b, the incorporation of increasing amounts of CZTS nanoparticles in the synthesis of MIL-125-NH_2 can be reflected by the gradual increase in the intensity of the diffraction peaks associated with CZTS. This behavior indicates the successful incorporation of the semiconductor nanoparticles within the composite materials while preserving the crystalline structure of MIL-125-NH_2 .

To further confirm the phase purity of the CZTS nanoparticles and exclude the presence of secondary phases, Raman spectroscopy was performed (Fig. S1). The Raman spectrum of CZTS exhibits the characteristic symmetric A_1 vibrational mode located at 336 cm^{-1} , which corresponds to the vibration of sulfur atoms within the kesterite lattice [36]. Furthermore, the absence of vibrational modes corresponding to secondary phases such as CuS , ZnS , SnS , SnS_2 and Cu_3SnS_3 confirms that the CZTS nanoparticles are the only phase obtained through this synthetic method. For MIL-125-NH_2 , Raman bands at 800 , 825 , 1250 , 1414 , 1570 , and 1620 cm^{-1} correspond to Ti-O vibrations and organic linker modes [9b]. The Raman spectra of the nanocomposites (not shown) exhibit the characteristic bands of both MIL-125-NH_2 and CZTS, confirming that both phases retain their structural integrity upon incorporation into the hybrid material. However, due to the high fluorescence background of the

composite samples, the spectra are not presented here. This observation, together with the XRD results, indicates that the solvothermal synthesis in the presence of preformed CZTS nanoparticles does not induce significant structural degradation of either component.

The elemental composition of the nanocomposites was further analyzed by X-ray fluorescence (XRF) (Fig. S2). The elemental ratios obtained are close to the expected stoichiometry. As the CZTS content in the synthesis increases, the relative proportions of Cu, Zn, and Sn progressively increase, confirming the successful incorporation of CZTS nanoparticles within the MOF matrix. The presence of Ti, Cu, Zn, and Sn is consistent with the formation of the MIL-125-NH₂/CZTS heterostructure.

The morphology of the samples was examined by scanning electron microscopy (SEM), and representative images are presented in the Supplementary Information (Figure S3). The MIL-125-NH₂ synthesized by the solvothermal method forms homogeneous hexagonal disk-like particles with an average size of approximately 400 nm, in agreement with previous reports for solvothermally synthesized MIL-125-NH₂ particles [38]. The CZTS nanoparticles (Figure S3b) appear as aggregated clusters of small primary particles, consistent with the crystallite size of ~ 10 nm estimated from XRD analysis. When CZTS nanoparticles are incorporated during the MOF synthesis, a gradual change in particle morphology is observed. The particles progressively adopt a more irregular and predominantly tetrahedral shape. In addition, the average particle size slightly decreases while the surface roughness increases. These observations suggest that CZTS nanoparticles are deposited on the external surface of the MOF crystals during growth, modifying the morphology and surface characteristics of the particles. The resulting materials therefore resemble a heterostructured architecture in which the CZTS nanoparticles decorate the surface of the MIL-125-NH₂ crystals, rather than being incorporated into the MOF pores.

3.2- Optical properties and band gap determination

The optical properties of semiconductor materials play a key role in determining their photoelectrochemical and photocatalytic performance, since the absorption coefficient, band gap energy (E_g), and electronic structure directly influence light harvesting and charge transfer processes.

To evaluate the influence of CZTS incorporation on the optical behavior of the materials, diffuse reflectance Visible spectra of MIL-125-NH₂, CZTS nanoparticles, and the corresponding nanocomposites were recorded in the 400–1000 nm spectral range. The experimental absorbance spectra (α_{exp}) derived from diffuse reflectance are shown in Fig. 2.

The spectra show that MIL-125-NH₂ exhibits strong absorption in the near UV region with a sharp absorption edge around ~ 450 nm, which is characteristic of this MOF and associated with ligand-to-metal charge transfer transitions within the Ti–O clusters of the framework. This absorption typically appears between 2.44 and 2.72 eV according to previous reports [39–44]. As a consequence, MIL-125-NH₂ displays very limited absorption in the visible region.

In contrast, CZTS nanoparticles display strong absorption throughout the visible region of the spectrum, extending well beyond 800 nm. This behavior is typical of kesterite-type CZTS semiconductors and reflects their relatively narrow band gap.

Thus, when CZTS nanoparticles are incorporated into the MOF matrix, the absorbance spectra of the nanocomposites progressively develop a second absorption feature at lower photon energies. This additional contribution becomes more pronounced as the CZTS content increases and is associated with the optical transition of the CZTS semiconductor phase. The progressive emergence of this low-energy absorption edge confirms that the incorporation of CZTS nanoparticles effectively extends the optical response of the MOF-based material toward the visible region.

After accounting for the free carrier contribution, Tauc analysis was performed assuming direct allowed electronic transitions, which is appropriate for both CZTS and MIL-125-NH₂. Representative Tauc plots are shown in Fig. 3, while the extracted band gap energies are summarized in Table 1.

Table 1
Optical band gap values
obtained from Tauc plots for
MIL-125-NH₂, CZTS
nanoparticles, and MIL-125-
NH₂/CZTS nanocomposites.

CZTS	E _{g1} (eV)	E _{g2} (eV)
	1.652	---
MOF	---	2.85
NC5	1.735	2.752
NC10	1.724	2.845
NC25	1.652	2.753
NC50	1.639	---

For the nanocomposite materials, two distinct optical transitions are identified: the lower-energy band gap (E_{g1}) corresponds to the CZTS semiconductor phase, while the higher-energy band gap (E_{g2}) originates from the MIL-125-NH₂ framework.

The band gap of CZTS nanoparticles was determined to be approximately 1.65 eV, which is close to the values typically reported for kesterite-type CZTS semiconductors [46]. Slight deviations toward higher energies may arise from quantum confinement effects commonly observed in CZTS nanocrystals with sizes below ~ 7 nm [47–52].

For MIL-125-NH₂, band gap energies between 2.75 and 2.85 eV were obtained. These values are slightly higher than the commonly reported range (2.44–2.72 eV), which may be attributed to variations in the

degree of amino functionalization within the MIL-125 framework [39–43].

For the nanocomposite materials, two distinct optical transitions can be identified. The lower-energy transition corresponds to the CZTS semiconductor phase, while the higher-energy transition originates from the MOF framework.

This confirms that CZTS extends the optical response of the MOF toward the visible region. The MOF framework may participate in charge separation and transport processes, while the electronic interaction between both components is expected to facilitate the separation of photogenerated charge carriers at the interface, which is a key factor for improving the photoelectrochemical and photocatalytic performance of the materials.

A deeper analysis of the electronic structure and band alignment between the two components will be discussed in the following section based on Mott–Schottky measurements.

3.3- Electronic properties: Mott–Schottky analysis

The electronic properties of the nanocomposite films were investigated by Mott–Schottky analysis to determine the semiconductor type, carrier density (N_D), and flat band potentials (E_{FB}). Measurements were performed at 1200 Hz in the potential range from – 1.0 to 0.8 V vs. Ag/AgCl using FTO/TiO₂/sample films, as described in the Experimental section. A 0.2 M Na₂SO₄ aqueous solution was used as a supporting electrolyte, with a Pt ring and Ag/AgCl electrodes acting as counter and reference electrodes, respectively.

Figure 4 shows the Mott–Schottky plots ($1/C^2$ vs. applied potential) for FTO/TiO₂ substrates and the MOF/CZTS nanocomposites with increasing CZTS loadings. For reference, the Mott–Schottky response of a pristine CZTS film deposited on FTO/TiO₂ is also included (Figure S7). The pristine CZTS film exhibits a negative slope in the linear region (Figure S7), confirming its intrinsic p-type character, consistent with previous reports [37, 53]. In contrast, the FTO/TiO₂ substrate, the MIL-125-NH₂ film, and all the MOF/CZTS nanocomposites display positive slopes (Fig. 4), indicating an apparent n-type behavior. This apparent n-type response is attributed to the dominant capacitive contribution of the underlying n-type FTO/TiO₂ blocking layer and the n-type MOF matrix, which are in direct contact with the electrolyte and contribute significantly to the measured capacitance at the selected frequency (1200 Hz). This apparent n-type behavior, governed by the substrate and the depletion layer of the n-type semiconductor, is well-documented [54]. Nevertheless, the positive shift of E_{FB} with increasing CZTS content (Fig. 4 and Table 2) confirms the formation of a p-n heterojunction.

The E_{FB} values, extracted from the intercept of the linear region with the potential axis (using Eq. 1), are summarized in Table 2. For the MOF film, $E_{FB} \approx -0.57$ V vs. Ag/AgCl, while for NC5 it remains similar (-0.56 V), indicating that a low CZTS loading has a minimal effect on the band bending. As the CZTS loading increases, E_{FB} shifts positively, reaching values approaching that of the pure CZTS film (≈ -0.22 V vs. Ag/AgCl for NC50) [37].

The carrier density (N_D) was calculated from the slope of the linear region of the Mott–Schottky plots using the standard relationship:

$$\frac{1}{C^2} = \frac{2}{e\epsilon_0\epsilon_r N_D A^2} \left(V - V_{FB} - \frac{kT}{e} \right)$$

1

where C is the measured capacitance, e is the elementary charge, ϵ_0 is the vacuum permittivity ($8.854 \times 10^{-14} \text{ F cm}^{-1}$), ϵ_r is the dielectric constant of the semiconductor (taken as 6.7 for CZTS [37]), and A is the geometric area of the electrode (0.25 cm^2).

As shown in Table 2, N_D values vary with CZTS incorporation, with NC10 exhibiting the highest carrier density ($9.4 \times 10^{22} \text{ cm}^{-3}$), while NC25 shows a slightly lower but still significant N_D ($5.7 \times 10^{22} \text{ cm}^{-3}$). This trend indicates that while an optimal CZTS content (25 wt%) provides the most efficient electronic coupling between the MOF matrix and the kesterite nanoparticles, the carrier density alone does not determine the overall performance. The superior photoelectrochemical and photocatalytic activity of NC25 (Sections 3.4 and 3.5) suggests that interfacial quality and charge-transfer dynamics are also critical factors.

The enhanced carrier density in NC25 correlates with its photoelectrochemical performance (Section 3.4). The decrease in N_D for NC50 may be attributed to agglomeration of CZTS nanoparticles or partial blocking of the MOF pores, which hinders effective charge transfer at the heterojunction.

The flat-band potentials were converted to the normal hydrogen electrode (NHE) scale using the relation $E_{\text{NHE}} = E_{\text{Ag/AgCl}} + 0.210$ (at 25°C). For the n-type semiconductors (MOF and composites), the conduction band edge (E_{CB}) was approximated as $E_{\text{CB}} \approx E_{\text{FB}} - 0.1 \text{ V}$, and the valence band edge (E_{VB}) was calculated as $E_{\text{VB}} = E_{\text{CB}} + E_g$. For the p-type CZTS, the valence band edge was estimated as $E_{\text{VB}} \approx E_{\text{FB}} + 0.1 \text{ V}$, and the conduction band edge was calculated as $E_{\text{CB}} = E_{\text{VB}} - E_g$, using the optical band gap determined from Tauc analysis (Table 1). The resulting band edge positions are compiled in Table 2.

Table 2
Carrier density (N_D), flat-band potential (V_{FB}), and derived band edge positions for the MOF/CZTS nanocomposites with different CZTS loadings.

CZTS	$N_D / (\text{cm}^{-3})$	$E_{FB} / (\text{V vs Ag/AgCl})$	$E_{FB} / (\text{V vs NHE})$	E_{CB} / V	E_{VB} / V
	$1.8 \times 10^{23} \text{ }^a$	0.28	0.49	-1.06 ^b	0.59 ^b
MOF	2.7×10^{22}	-0.57	-0.36	-0.46	2.39
NC5	8.3×10^{21}	-0.56	-0.35	-0.45	1.285
NC10	9.4×10^{22}	-0.47	-0.26	-0.36	1.364
NC25	5.7×10^{22}	-0.36	-0.15	-0.25	1.402
NC50	5.0×10^{22}	-0.22	-0.01	-0.11	1.529

^a For the pristine CZTS film, the negative slope of the Mott–Schottky plot (Figure S7) confirms its p-type character. The acceptor density (N_A) was estimated from the absolute value of the slope.

^b Estimated as $E_{VB} \approx E_{FB} + 0.1 \text{ V}$ (vs NHE) and $E_{CB} = E_{VB} - E_g$, using $E_g = 1.652 \text{ eV}$.

The Mott–Schottky analysis of the pristine CZTS film (Figure S7) confirms its intrinsic p-type character, as evidenced by the negative slope of the $1/C^2$ vs. V plot. The flat-band potential (E_{FB}) of the CZTS film is 0.28 V vs. Ag/AgCl (0.49 V vs NHE), which is in good agreement with previous reports for kesterite CZTS [60]. The acceptor density ($N_A \approx 1.8 \times 10^{23} \text{ cm}^{-3}$) is within the typical range for CZTS nanocrystals synthesized by the hot-injection method [36]. For this p-type semiconductor, the valence band edge was estimated as $E_{VB} \approx E_{FB} + 0.1 \text{ V} = 0.59 \text{ V}$ vs NHE, and the conduction band edge was calculated as $E_{CB} = E_{VB} - E_g = -1.06 \text{ V}$ vs. NHE, using the optical band gap of 1.65 eV (Table 1). These values, together with the band positions of the MOF/CZTS nanocomposites (Table 2), confirm the staggered band alignment characteristic of a type-II heterojunction, which is expected to facilitate interfacial charge transfer.

The evolution of the carrier density and flat-band potential as a function of CZTS loading is presented in the Supplementary Information (Figure S8), and the corresponding values are summarized in Table 2. The observed trends indicate that the electronic properties of the MOF/CZTS system can be effectively tuned by controlling the semiconductor content within the MOF matrix. The NC25 composition, which exhibits the highest photocurrent response and photocatalytic activity, combines a high carrier density with an optimized interfacial structure that facilitates charge separation and interfacial electron transfer. To further evaluate the photoinduced charge separation and transport properties of the materials, photoelectrochemical measurements were performed.

3.4- Photoelectrochemical properties

The photoelectrochemical response of the MOF/CZTS systems was investigated to evaluate the efficiency of photogenerated charge separation and transport in the hybrid materials.

Photoelectrodes were fabricated on FTO substrates using a TiO_2 interlayer consisting of compact and mesoporous TiO_2 films, which provides a large interfacial contact area and facilitates electron transport toward the conductive substrate. This architecture is widely used in photoelectrochemical devices due to the favorable electron injection properties of TiO_2 [24].

Prior to the photoelectrochemical measurements, the thickness of the MOF layer was optimized by varying the number of spin-coating deposition cycles. The corresponding photocurrent responses revealed the presence of an optimal film thickness, which maximizes the photocurrent density. A detailed analysis of this optimization study is provided in the Supplementary Information (Figure S9). Based on these results, two deposition cycles were selected for all subsequent experiments.

To evaluate the influence of the material architecture, three configurations were investigated: individual semiconductor films (MOF and CZTS), layered structures (MOF||CZTS), and nanocomposite films containing different CZTS loadings. The photocurrent density measured at 0 V vs. Ag/AgCl were $5.45 \mu\text{A cm}^{-2}$ (MOF), $4.17 \mu\text{A cm}^{-2}$ (CZTS), $29.96 \mu\text{A cm}^{-2}$ (layered MOF||CZTS), and $73.25 \mu\text{A cm}^{-2}$ (NC25), as shown in Figure S10.

Both pristine semiconductors exhibit relatively low photocurrent responses, which can be attributed to rapid recombination of photogenerated carriers within their bulk structures. The layered MOF||CZTS structure shows a significant improvement in photocurrent generation ($29.96 \mu\text{A cm}^{-2}$) compared to the individual components, indicating that the combination of both semiconductors promotes interfacial charge transfer.

An even stronger enhancement is observed for the nanocomposite architecture. In particular, the NC25 sample exhibits the highest photocurrent density ($73.25 \mu\text{A cm}^{-2}$) among the investigated materials, which is approximately 15 times higher than that of the pristine MOF and 2.5 times higher than the layered structure. This drastic improvement can be attributed to the nanocomposite arrangement, which not only maximizes the interfacial contact area between the two semiconductors but also promotes efficient charge separation driven by both the internal p–n junction electric field and the staggered band alignment. The type II charge transfer mechanism allows photogenerated electrons to migrate from CZTS to MOF (and subsequently toward the external circuit), while holes are transferred in the opposite direction. This interfacial charge transfer largely suppresses the recombination of photogenerated electron–hole pairs, resulting in a marked increase in the photoelectrochemical response.

The dependence of the photocurrent response on the nanocomposite composition is shown in Fig. 5. The photocurrent density increases with CZTS incorporation, reaching a maximum value for the NC25 sample, and decreases again for higher CZTS loading (NC50). The photocurrent densities at 0 V vs. Ag/AgCl were $51.6 \mu\text{A cm}^{-2}$ (NC5), $66.1 \mu\text{A cm}^{-2}$ (NC10), $73.25 \mu\text{A cm}^{-2}$ (NC25), and $45.2 \mu\text{A cm}^{-2}$

(NC50). This behavior indicates that an optimal semiconductor content exists for efficient charge transport within the hybrid structure.

The photocurrent density follows a similar trend to the carrier density (N_D) obtained from Mott–Schottky analysis (Section 3.3), although NC10 exhibits the highest N_D ($9.4 \times 10^{22} \text{ cm}^{-3}$) while NC25 shows the highest photocurrent ($73.25 \mu\text{A cm}^{-2}$). This indicates that while a high carrier density is beneficial, other factors such as interfacial quality and charge-transfer dynamics also play a crucial role in determining the photoelectrochemical performance. Notably, the enhanced photocurrent in NC25 cannot be attributed solely to a reduction in the optical band gap, as all nanocomposites exhibit similar CZTS band gap values ($E_g \approx 1.65 \text{ eV}$, Table 1). Instead, the superior performance is correlated with the optimized interfacial contact at this specific composition, which facilitates efficient charge separation and transport, despite NC25 not having the highest N_D . In contrast, the decrease in photocurrent for NC50 is consistent with the lower carrier density and possible agglomeration of CZTS nanoparticles, which hinders effective charge transfer at the heterojunction.

The enhanced photocurrent response observed for NC25 can therefore be attributed to efficient interfacial charge separation within the MOF/CZTS heterostructure. Based on the staggered band alignment derived from Mott–Schottky analysis and optical band gaps (Tables 1 and 2), the type-II heterojunction favors electron transfer from the CZTS conduction band to the MOF conduction band, and subsequently toward the TiO_2 layer and the external circuit. Under irradiation, the photogenerated holes are consumed by the sacrificial electron donor (triethylamine, TEA), while the electrons are collected at the working electrode, generating the observed anodic photocurrent.

A schematic representation of the proposed band alignment within the device architecture is presented in Scheme 1. In this configuration, the heterojunction formed between MIL-125- NH_2 and CZTS promotes spatial separation of photogenerated carriers, thereby reducing recombination and enhancing the overall photoelectrochemical activity of the nanocomposite.

The optimal photocurrent response obtained for NC25 indicates that an intermediate CZTS loading provides the best balance between carrier density and interfacial charge transfer efficiency within the hybrid system. These results establish a direct link between the electronic properties of the materials and their performance under illumination, which will be further explored in the context of photocatalytic Cr(VI) reduction (Section 3.5).

3.5- Photocatalytic Cr(VI) reduction

Based on its superior charge separation and transport properties, the photocatalytic activity of NC25 toward Cr(VI) reduction was investigated under visible-light irradiation ($\lambda > 400 \text{ nm}$). The temporal evolution of Cr(VI) concentration follows pseudo-first-order kinetics with respect to chromium

concentration: $\ln \left(\frac{C}{C_0} \right) = -k_{obs} \cdot t$.

The corresponding kinetic plots are shown in Fig. 6a for MIL-125-NH₂, CZTS, and the NC25 nanocomposite. Both individual semiconductors exhibit measurable photocatalytic activity, with the MOF showing higher reduction rates than CZTS. The apparent rate constants were $k_{\text{obs}} = 1.71 \times 10^{-2} \text{ min}^{-1}$ for MOF, $6.6 \times 10^{-3} \text{ min}^{-1}$ for CZTS, and $3.4 \times 10^{-2} \text{ min}^{-1}$ for NC25. Thus, the hybrid nanocomposite NC25 displays a significantly enhanced photocatalytic performance, with a rate constant approximately twice that of the pristine MOF and about five times higher than that of CZTS alone, clearly indicating a synergistic effect between both semiconductors.

Control experiments confirmed no reduction occurs without light, catalyst, or TEA (Figure S11).

The enhanced catalytic performance of the nanocomposite can be attributed to improved interfacial charge separation within the MOF/CZTS heterostructure. This interpretation is consistent with the photoelectrochemical measurements, which showed the highest photocurrent response for the NC25 composition (Section 3.4).

To further evaluate the influence of semiconductor composition, nanocomposites containing different CZTS loadings (NC5, NC25, and NC50) were investigated. As shown in Fig. 6b, the photocatalytic efficiency strongly depends on the semiconductor ratio within the hybrid structure. The apparent rate constants were $k_{\text{obs}} = 2.51 \times 10^{-2} \text{ min}^{-1}$ for NC5, $3.4 \times 10^{-2} \text{ min}^{-1}$ for NC25, and $1.57 \times 10^{-2} \text{ min}^{-1}$ for NC50. The NC25 composition exhibits the highest apparent rate constant, being approximately 1.4 times higher than NC5 and 2.1 times higher than NC50. Under the investigated conditions, complete reduction of Cr(VI) was achieved within 120 min for NC25.

The effect of photocatalyst concentration was also evaluated. The apparent rate constant remained essentially unchanged when the nanocomposite concentration was increased from 1 to 2 mg mL⁻¹ ($k_{\text{obs}} = 3.4 \times 10^{-2} \text{ min}^{-1}$ and $3.3 \times 10^{-2} \text{ min}^{-1}$, respectively), suggesting that the reaction rate is not limited by the available catalytic surface under the studied conditions. Instead, the photocatalytic activity appears to be governed by the interfacial charge-transfer dynamics within the nanocomposite.

To gain deeper insight into the origin of this synergistic effect, the wavelength-dependent photocatalytic activity was evaluated in the visible region (Fig. 7). Notably, a marked difference in performance was observed upon selective excitation. At 440 nm, where both MIL 125-NH₂ and CZTS are simultaneously excited, the nanocomposite achieved a remarkable reduction rate constant. In striking contrast, when the reaction was carried out at 568 nm—where the photon energy exclusively excites CZTS and is near its absorption edge—the rate constant dropped drastically, being approximately 22 times lower than at 440 nm. This dramatic decrease emphasizes that the synergistic excitation of both components is fundamental for achieving efficient interfacial charge transfer. The enhanced performance at 440 nm arises from the Type II pathway, where electrons migrate from the CZTS conduction band to the MOF, promoting spatial charge separation. Conversely, the poor performance at 568 nm confirms that excitation of CZTS alone leads to rapid charge recombination before interfacial transfer can occur. The

corresponding time-dependent Cr(VI) reduction curves at these selected wavelengths are provided in Fig. 7.

A full UV-Vis study (333–568 nm) with apparent quantum efficiencies (AQE) is provided in the Supplementary Information (Figure S12, Table S1). Although this extended characterization includes the UV region, where the maximum absolute AQE is observed (333 nm), the main conclusion regarding the visible-light-driven mechanism remains the sharp decline in efficiency when moving from 440 nm to 568 nm. This trend unequivocally confirms that the photoelectrochemical and photocatalytic synergy in the NC25 heterojunction is strictly governed by the simultaneous photoexcitation of both semiconductors in the visible spectrum, making the system highly attractive for visible-light-driven environmental remediation.

3.6-Interfacial Charge Dynamics and Mechanistic Interpretation

The combined photoelectrochemical and photocatalytic results provide strong evidence that the enhanced activity of the MOF/CZTS nanocomposite arises from efficient interfacial charge separation within the heterostructure. Based on the staggered band alignment derived from Mott–Schottky analysis (Table 2) and the wavelength-dependent photocatalytic activity (Fig. 7), a type II charge transfer pathway can be proposed for the hybrid system, as illustrated in Scheme 1.

The energy diagram constructed from the experimental data (Scheme 1, Table 2) reveals a staggered band alignment between the n-type MIL-125-NH₂ and the p-type CZTS. Under irradiation, both semiconductors absorb photons with energy equal to or greater than their respective band gaps (≈ 2.85 eV for MOF and ≈ 1.65 eV for CZTS), generating electron–hole pairs in each component. In a type II heterojunction, the photogenerated electrons in the CZTS conduction band (-1.06 V) are transferred to the MOF conduction band (-0.52 V), while the holes in the MOF valence band ($+2.23$ V) are transferred to the CZTS valence band ($+0.59$ V). This spatial separation of charge carriers reduces recombination and enhances the photocatalytic activity. The electrons accumulated in the MOF conduction band are sufficiently reducing to convert Cr(VI) to Cr(III) ($E^\circ \approx 0.51$ V vs NHE at pH 7), while the holes in the CZTS valence band are consumed by the sacrificial donor (triethylamine).

This type II interpretation is consistent with the composition-dependent trends already described: the photocurrent and Cr(VI) reduction rate both peak at NC25 (Sections 3.3–3.5), and the sharp activity drop upon shifting excitation from 440 to 568 nm (Fig. 7) confirms that electron transfer from CZTS to the MOF, rather than CZTS excitation alone, governs the photocatalytic response.

The sharp decrease in activity at 568 nm further corroborates this interpretation, as the reduced absorption coefficient of the kesterite nanoparticles at longer wavelengths leads to a lower density of photogenerated carriers and, consequently, a diminished photocatalytic response.

Although a Z-scheme pathway cannot be entirely ruled out, the presence of an intrinsic electric field at the p–n heterojunction and the observed photocurrent behavior are more consistent with a type-II charge-transfer mechanism. This interpretation is further supported by the sharp decrease in photocatalytic activity when moving from dual (440 nm) to single (568 nm) excitation, which aligns with the expected behavior of a type-II heterojunction.

Overall, nano-interface engineering within the MOF/CZTS hybrid promotes efficient charge separation and electron accumulation at the MOF conduction band, governing the photocatalytic reduction kinetics via a type II pathway enabled by the staggered band alignment and intimate p–n heterojunction.

4.- Conclusions

In this work, a series of MIL-125-NH₂/CZTS nanocomposites with varying nominal kesterite loadings (5, 10, 25, and 50 wt%) was successfully synthesized via a solvothermal approach. Comprehensive structural, optical, and electronic characterization confirms the formation of intimate heterointerfaces with preserved crystallinity and extended visible light absorption up to 800 nm.

Mott–Schottky analysis revealed that the nanocomposites exhibit an apparent n-type behavior, dominated by the underlying FTO/TiO₂ substrate and the MOF matrix, while the pristine CZTS film confirmed its intrinsic p-type character. The progressive positive shift of the flat band potential with increasing CZTS content, together with the high carrier density of NC25 ($N_D \approx 5.7 \times 10^{22} \text{ cm}^{-3}$) and its superior photoelectrochemical and photocatalytic performance, provides evidence of the formation of an intimate p–n heterojunction with optimal electronic coupling and charge transfer dynamics at the interface.

Photoelectrochemical measurements demonstrated that the NC25 nanocomposite delivers the highest photocurrent response ($73.3 \mu\text{A cm}^{-2}$ at 0 V vs. Ag/AgCl), outperforming both individual components and layered architectures. The photocurrent trend correlates with N_D , confirming enhanced charge separation.

The photocatalytic evaluation for Cr(VI) reduction under visible light irradiation showed that NC25 exhibits a remarkable rate constant of $3.4 \times 10^{-2} \text{ min}^{-1}$, approximately twice that of pristine MIL 125-NH₂ and five times that of bare CZTS. The wavelength-dependent photocatalytic kinetics provided direct evidence of the proposed Type II charge transfer mechanism. Notably, a drastic decrease in the reduction rate—approximately 22-fold—was observed when the excitation wavelength shifted from 440 nm (where both semiconductors are simultaneously excited) to 568 nm (where only CZTS absorbs light). This sharp contrast confirms that the synergistic photoexcitation of both components is essential to achieve efficient interfacial charge separation. The staggered band alignment, together with the optimized interfacial contact in the NC25 heterojunction, ensures that photogenerated electrons are effectively transferred from the CZTS conduction band to the MOF, thereby suppressing recombination and accumulating reducing electrons for the reduction of Cr(VI) to Cr(III).

This work highlights the pivotal role of interface design in MOF-based hybrid systems for solar-driven environmental remediation. The use of earth-abundant, non-toxic elements (Cu, Zn, Sn, S) and the avoidance of hazardous materials (e.g., Cd, Pb) make the MIL-125-NH₂/CZTS heterojunction a cost-effective and sustainable alternative for photocatalytic Cr(VI) reduction. These insights provide a foundation for designing next-generation MOF photocatalysts.

Declarations

Author Contribution

Y. D.I. : conceptualization, methodology, investigation (synthesis, characterization, photocatalytic and photoelectrochemical measurements), formal analysis, writing – original draft, writing – review & editing, visualization, project administration. C. J. P.: investigation (UV-Vis and Mott-Schottky studies), formal analysis, and writing – review & editing. R. M.: writing – review & editing. E. D.: formal analysis (Mott-Schottky). J. N.: investigation (photocatalytic Cr(VI) reduction experiments). C. R.: formal analysis and writing – review & editing. M. E. A.: resources, funding acquisition, and writing – review & editing. All authors read and approved the final manuscript.

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Scheme

Scheme 1 is available in the Supplementary Files section.

Figures

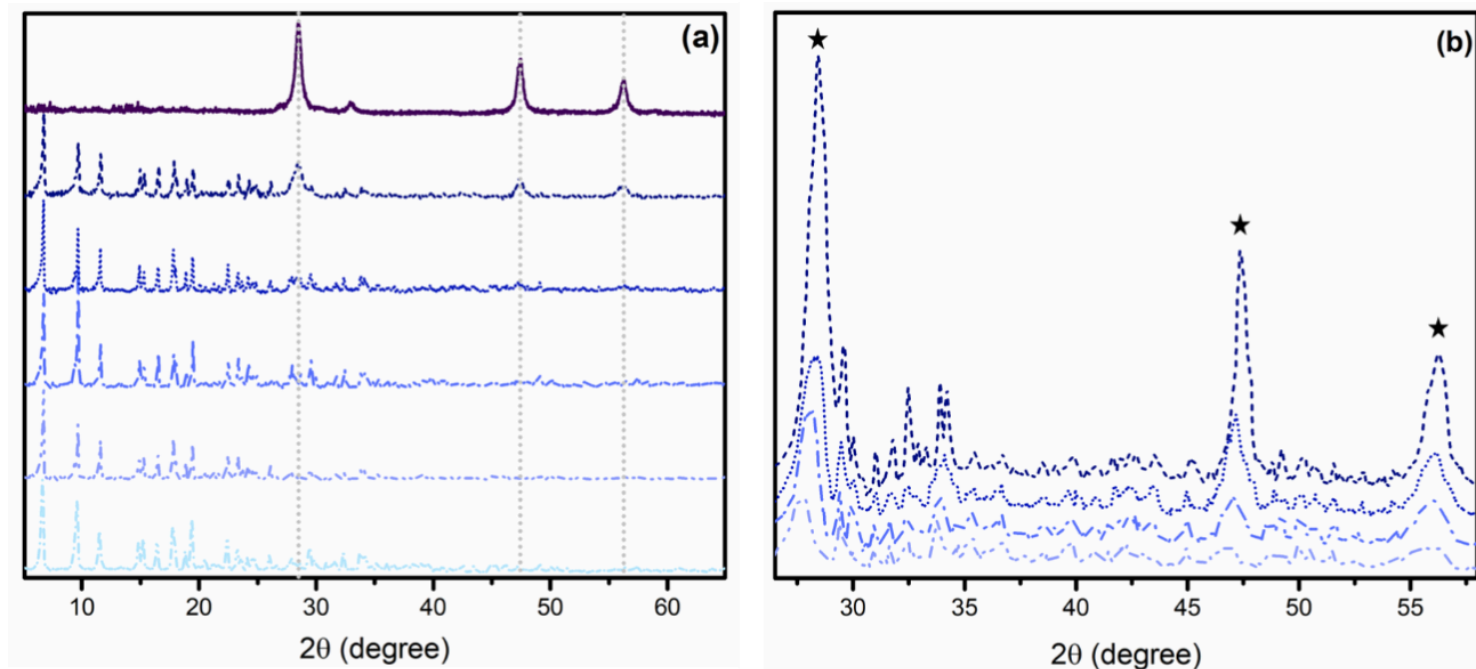


Figure 1

(a) XRD patterns of MIL-125-NH₂ (short dash dot), CZTS nanoparticles (line), and MIL-125-NH₂/CZTS nanocomposites (NC5 (dash dot dot), NC10 (dash dot), NC25 (short dot), and NC50 (short dash)). Vertical dashed lines mark characteristic CZTS peaks (JCPDS 26-0575). (b) Magnified region showing increased CZTS peak intensity (×) with loading, confirming kesterite incorporation without altering MOF structure

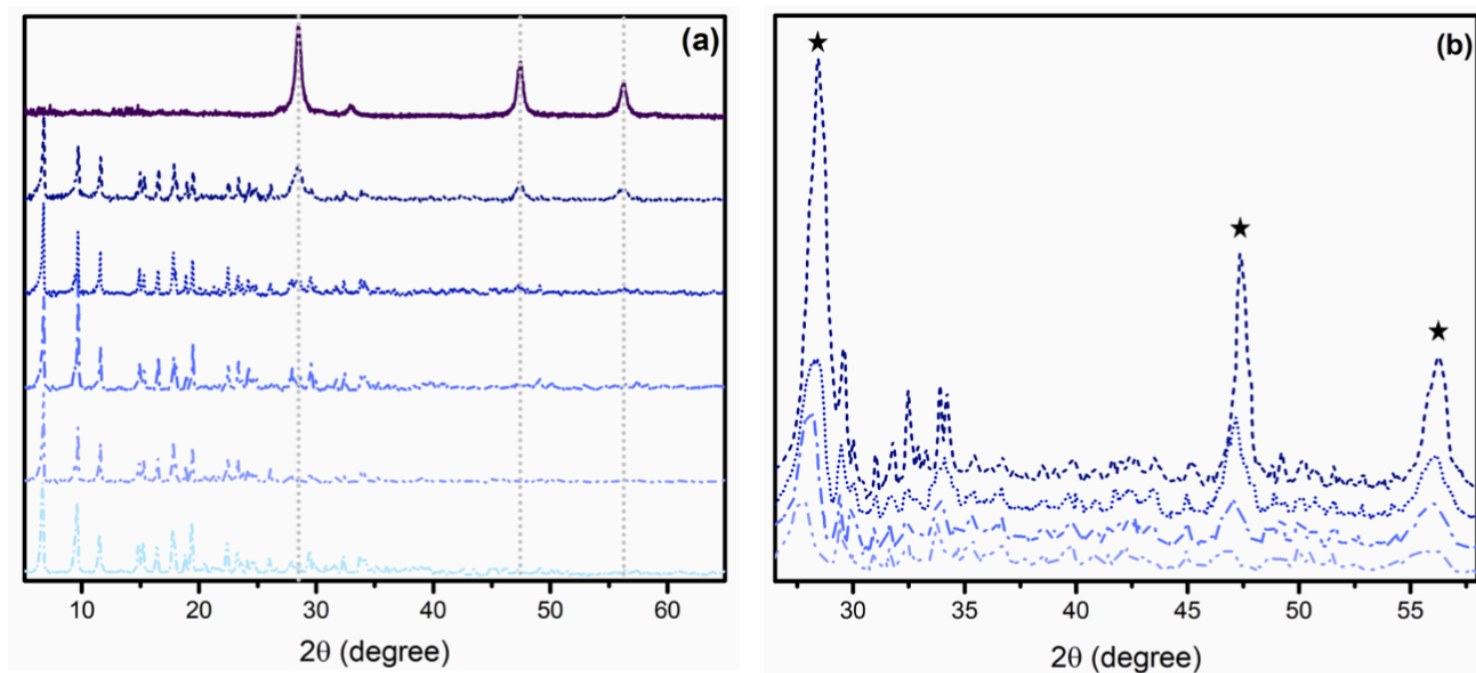


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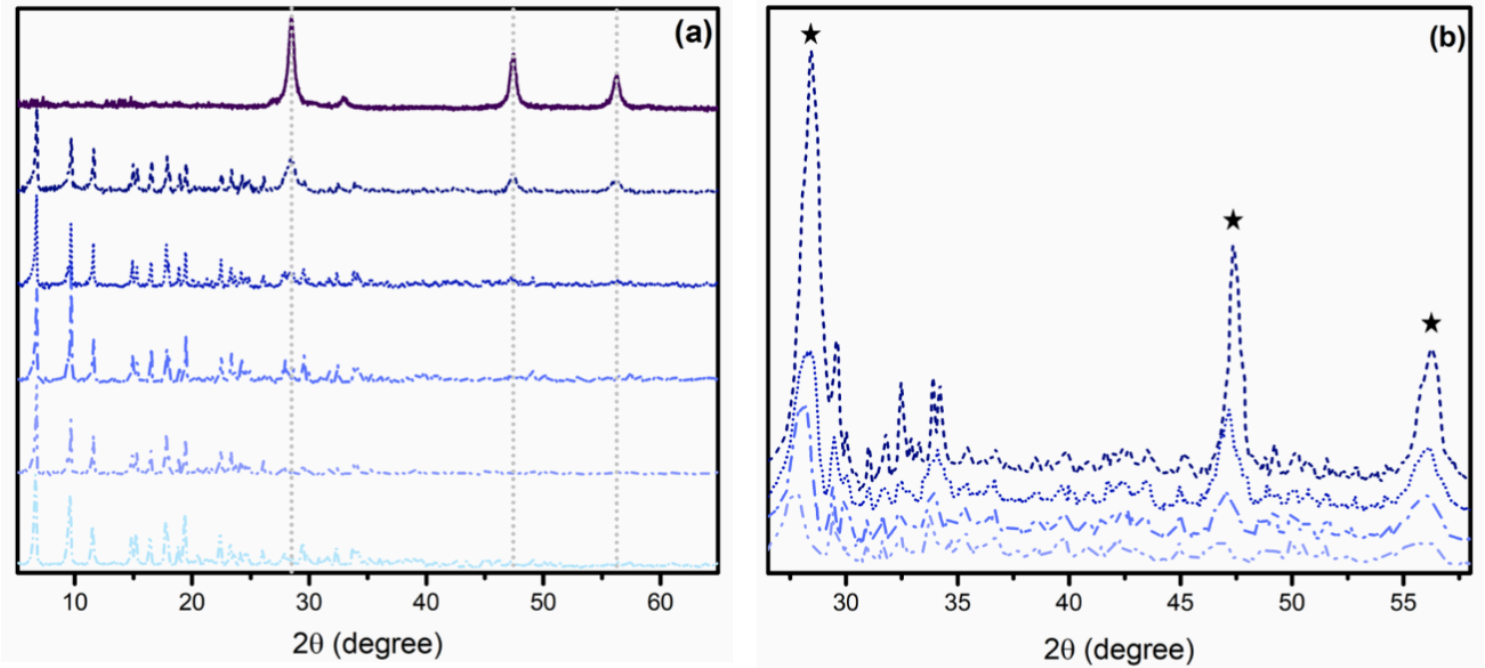


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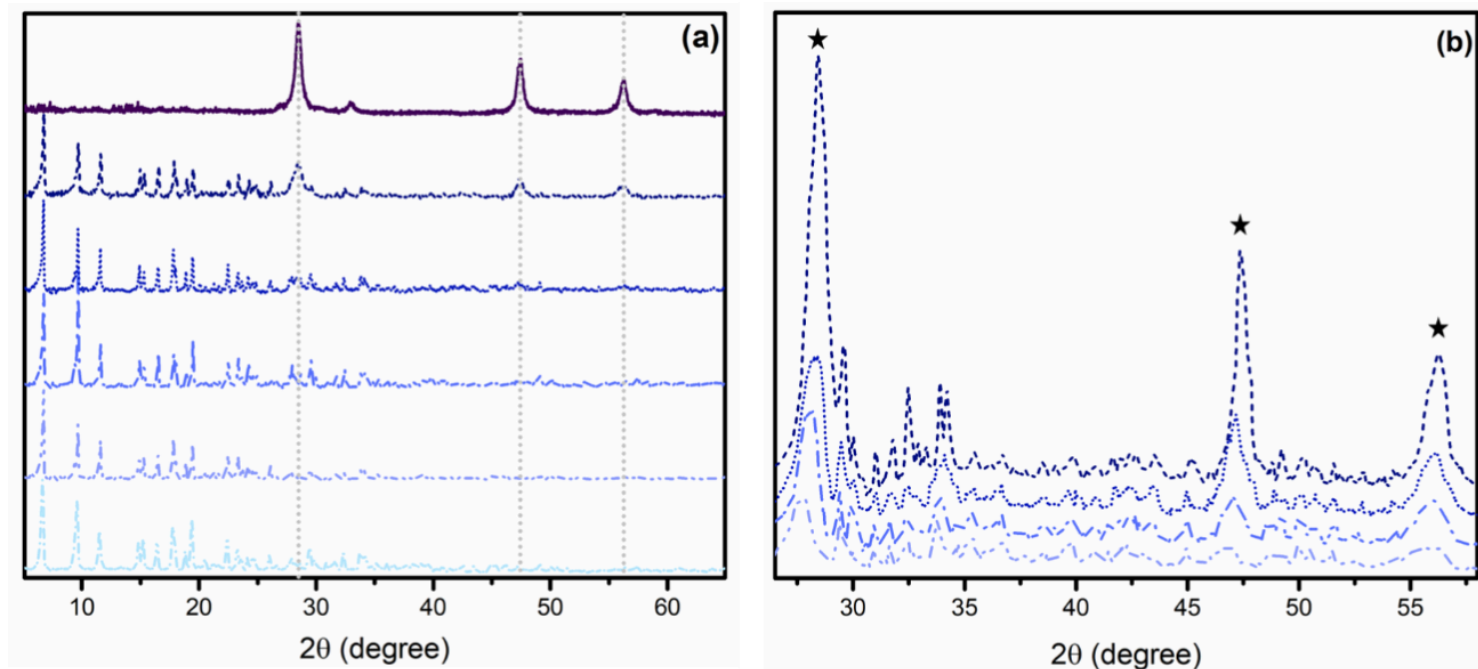


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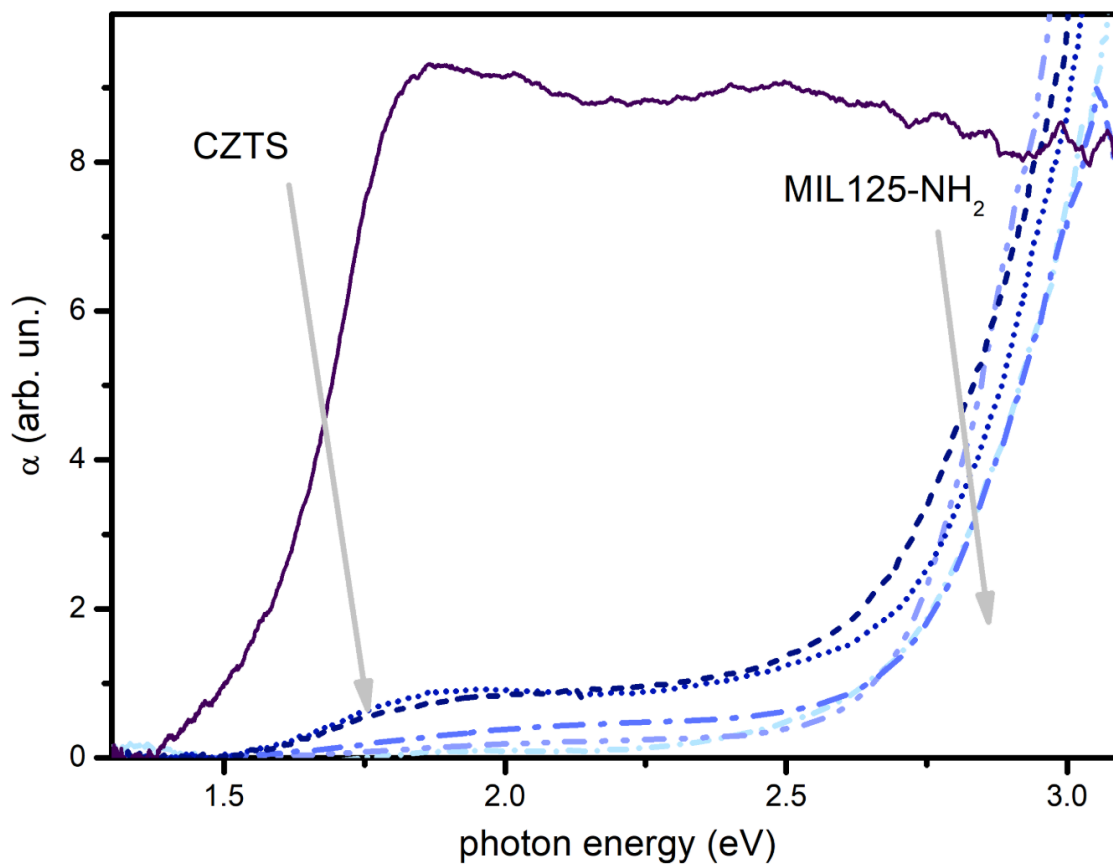


Figure 2

UV-Vis absorbance spectra (α_{exp}) of MIL-125-NH₂ (short dash dash), CZTS (line), and composites NC5 (dash dot dot), NC10 (dash dot), NC25 (short dot), NC50 (short dash). The second absorption feature at lower photon energies confirms that CZTS extends the optical response to the visible region

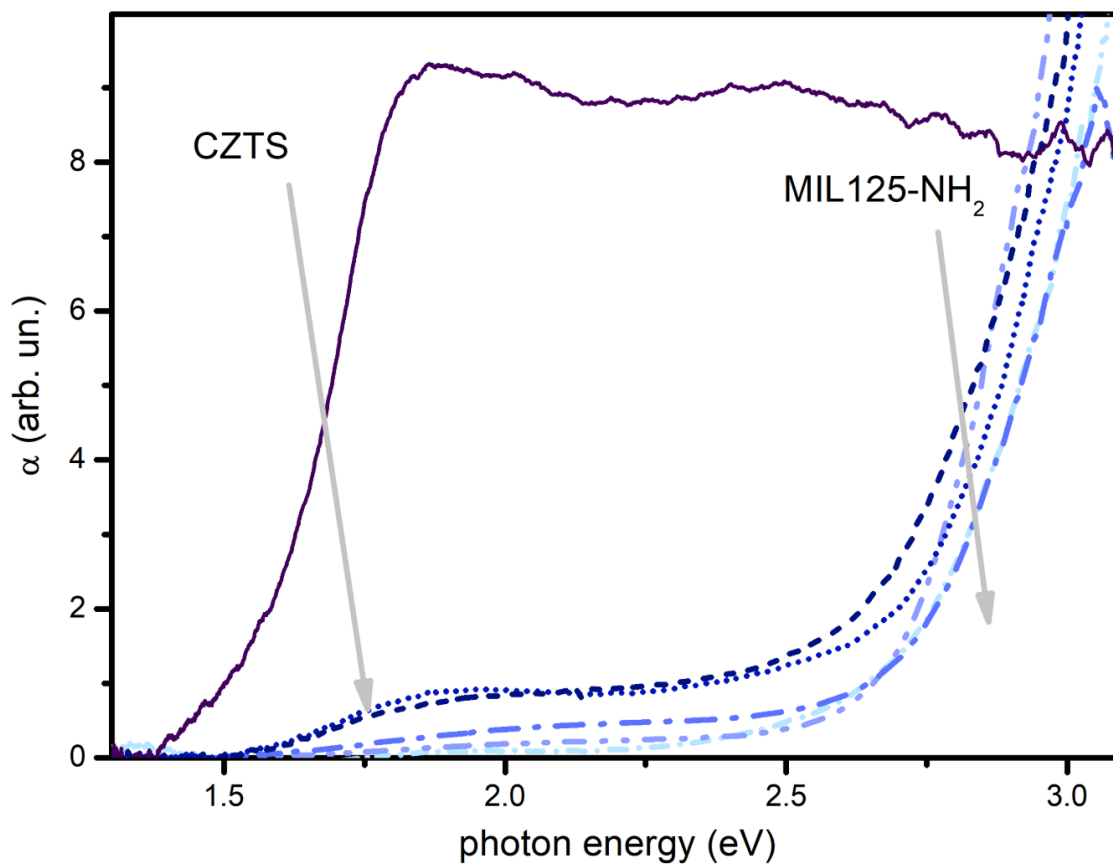


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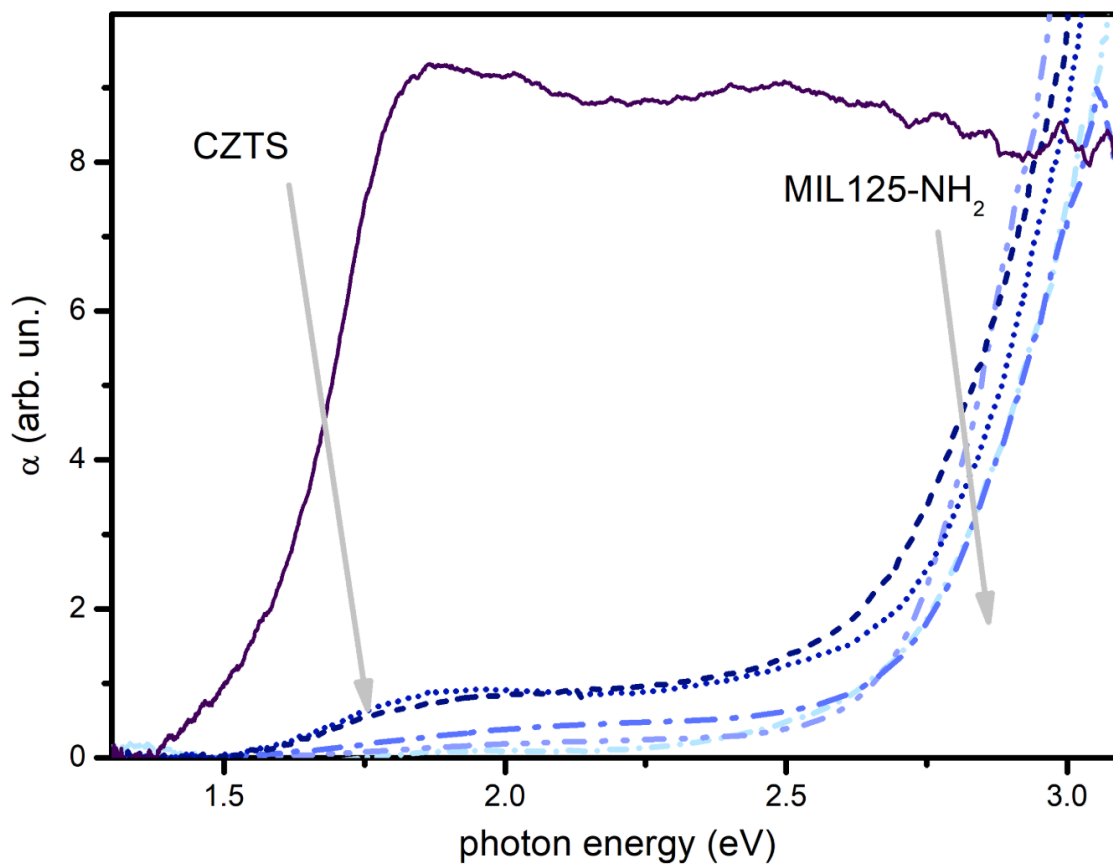


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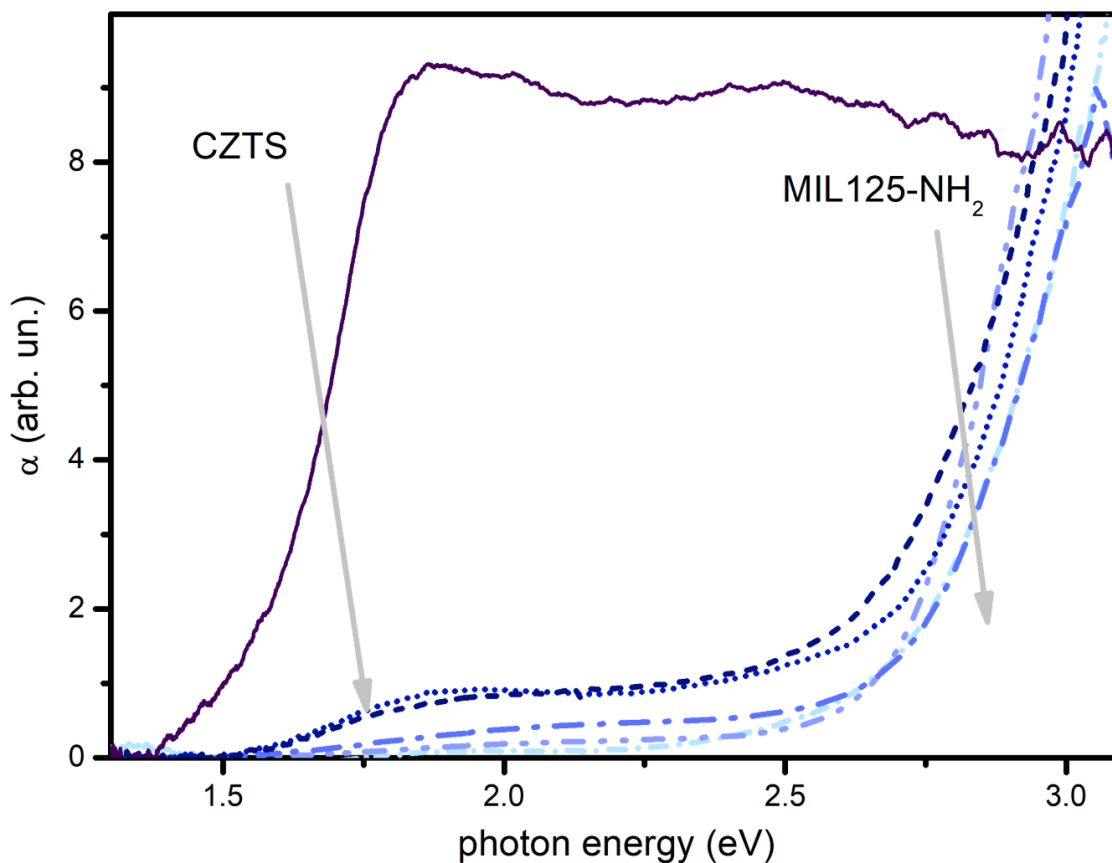


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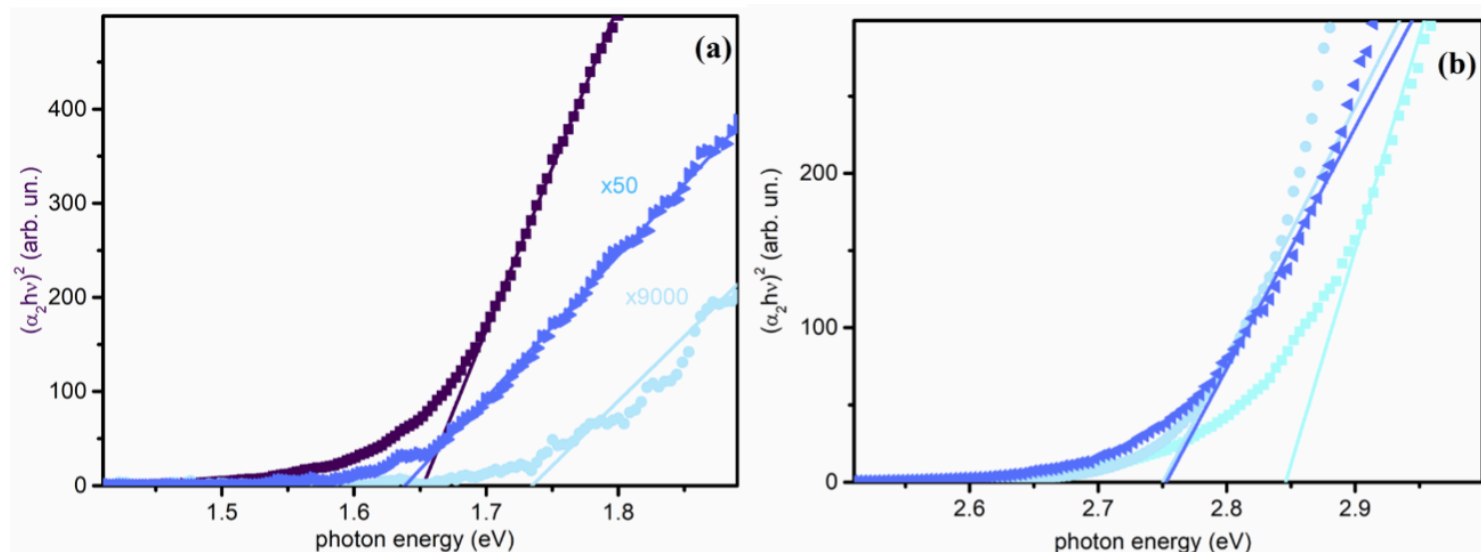


Figure 3

Tauc plots $(\alpha h\nu)^2$ vs photon energy for (a) CZTS and (b) MIL-125-NH₂ band gap determination. NC5 (circles), NC50 (triangles), and CZTS or MIL-125-NH₂ (squares). The lines represent linear fits. Intercepts with the energy axis yield the band gap energies summarized in Table 1

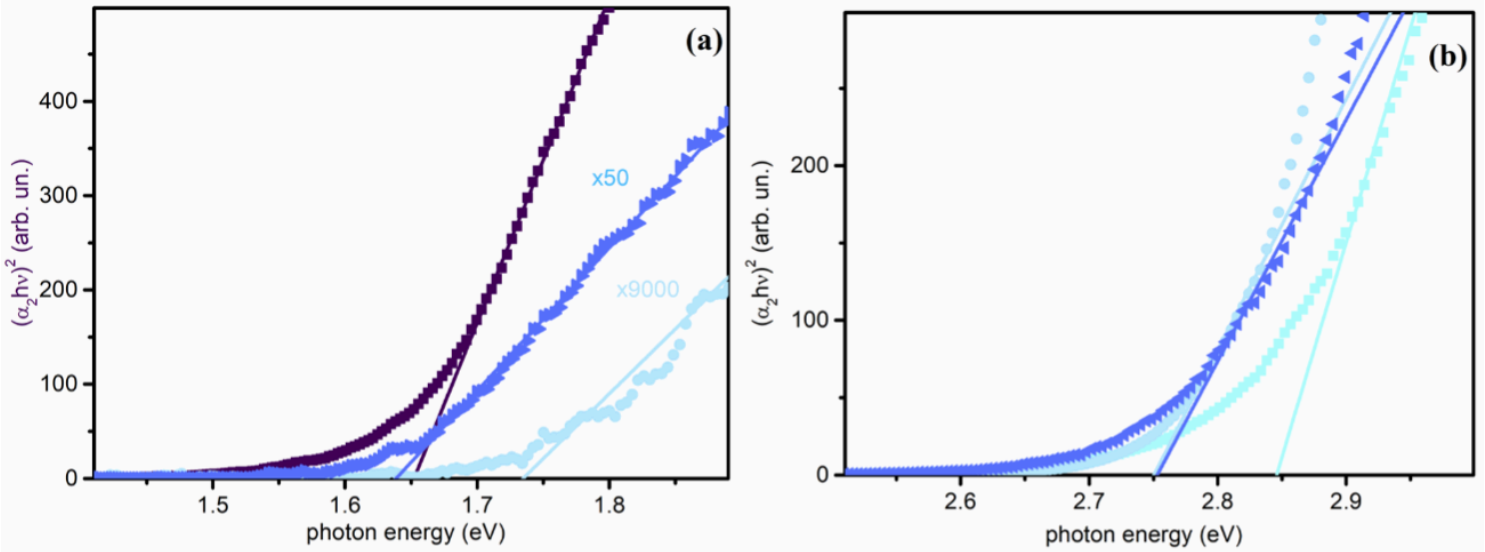


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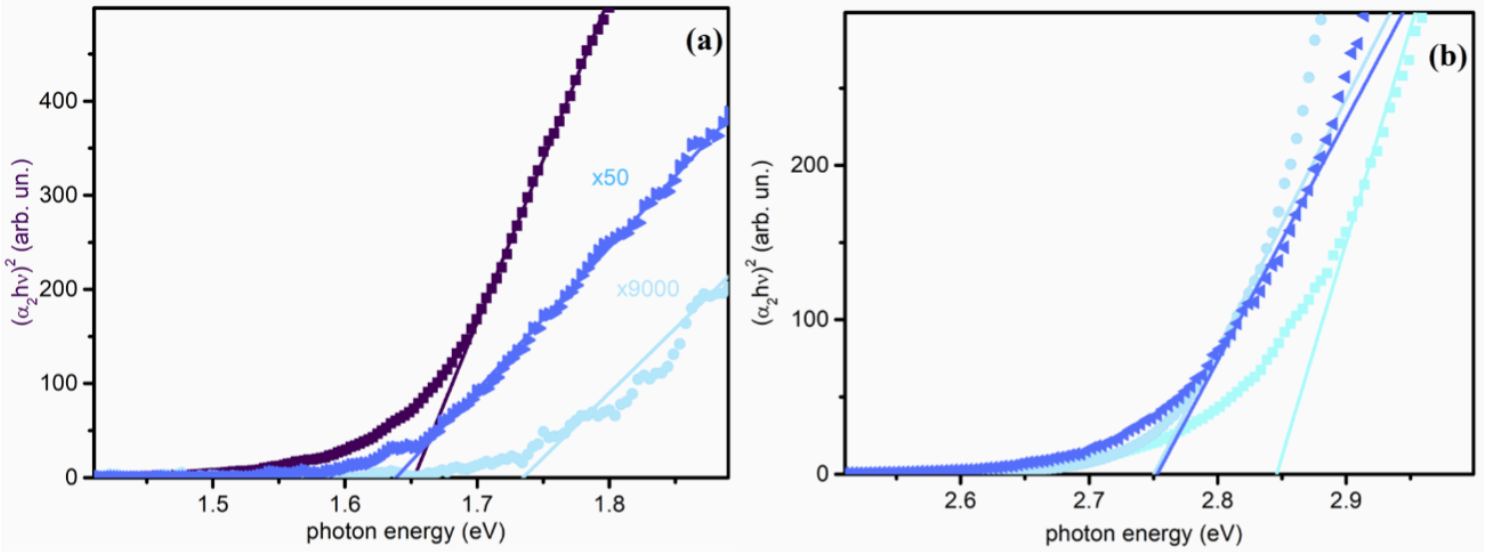


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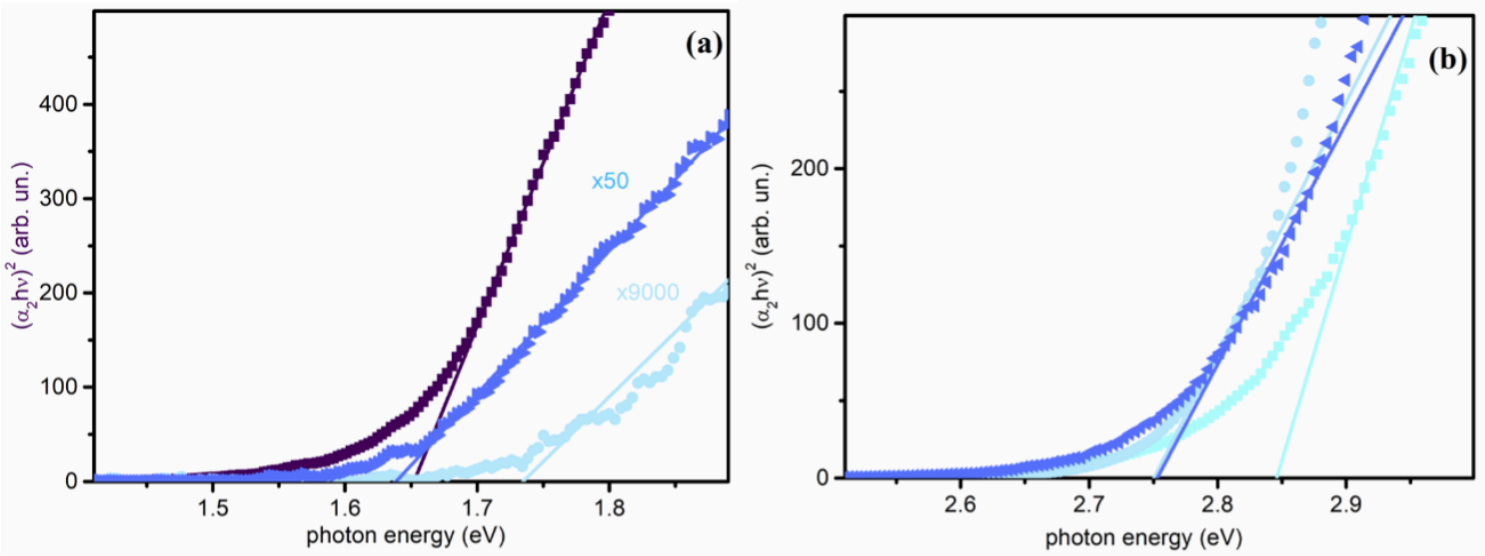


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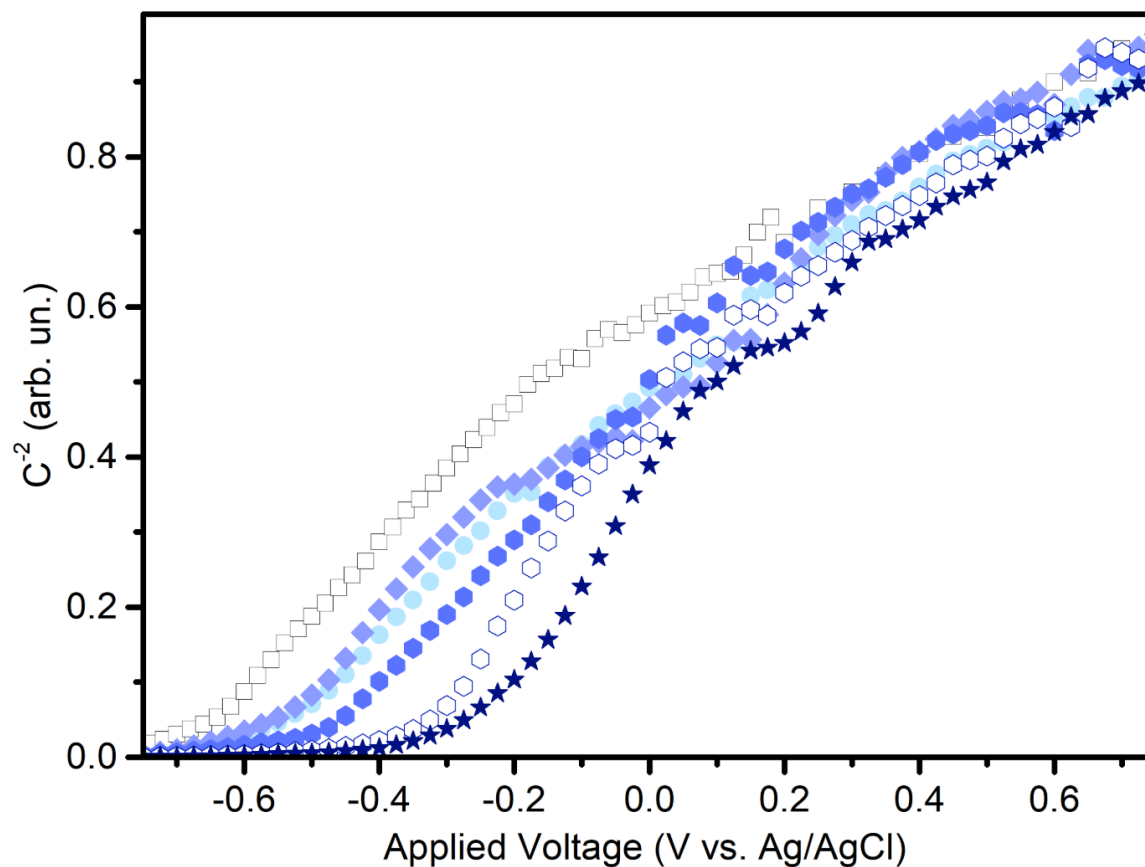


Figure 4

Mott-Schottky plots ($1/C^2$ vs potential) at 1200 Hz for FTO/TiO₂ (empty squares), MIL 125 NH₂ (circles), and MOF/CZTS composites NC5 (rhombus), NC10 (filled hexagon), NC25 (empty hexagon), NC50 (star) in 0.2 M Na₂SO₄. Positive slopes indicate apparent n-type behavior, dominated by substrate and MOF matrix. Shift to positive potentials with CZTS loading reflects p-n heterojunction formation

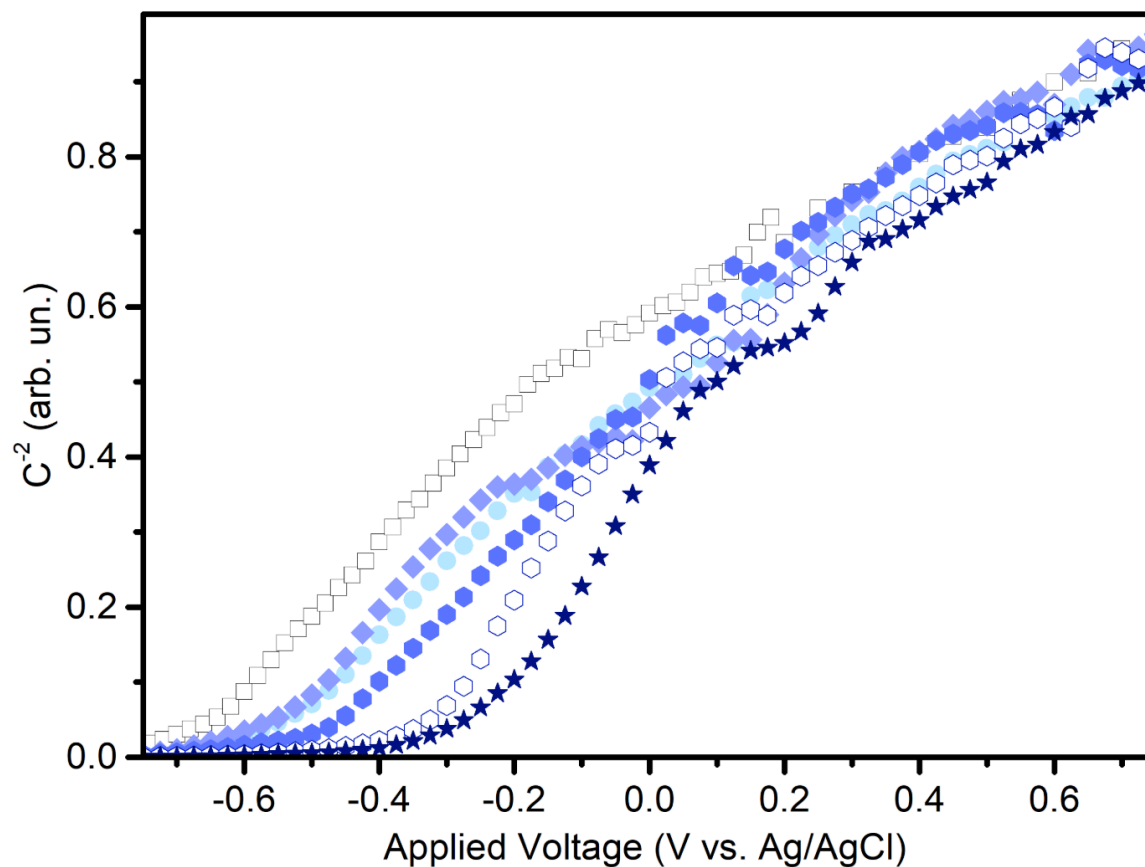


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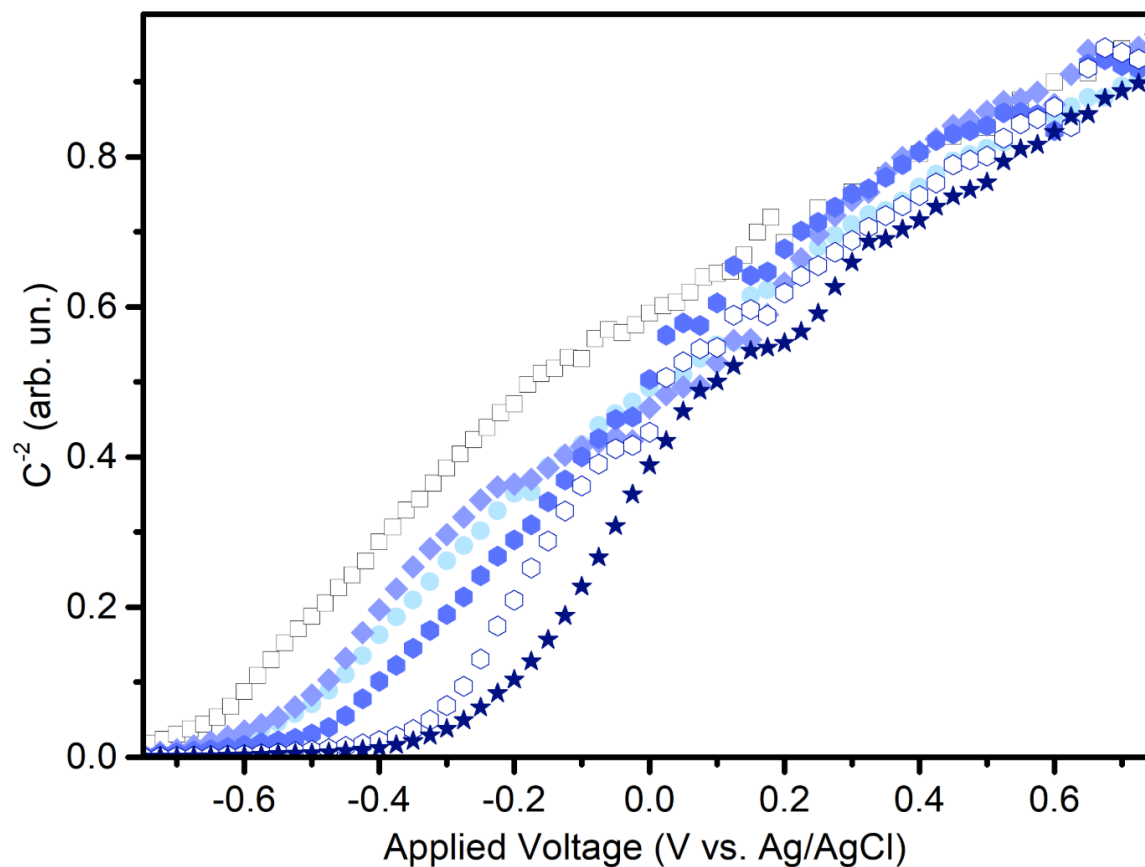


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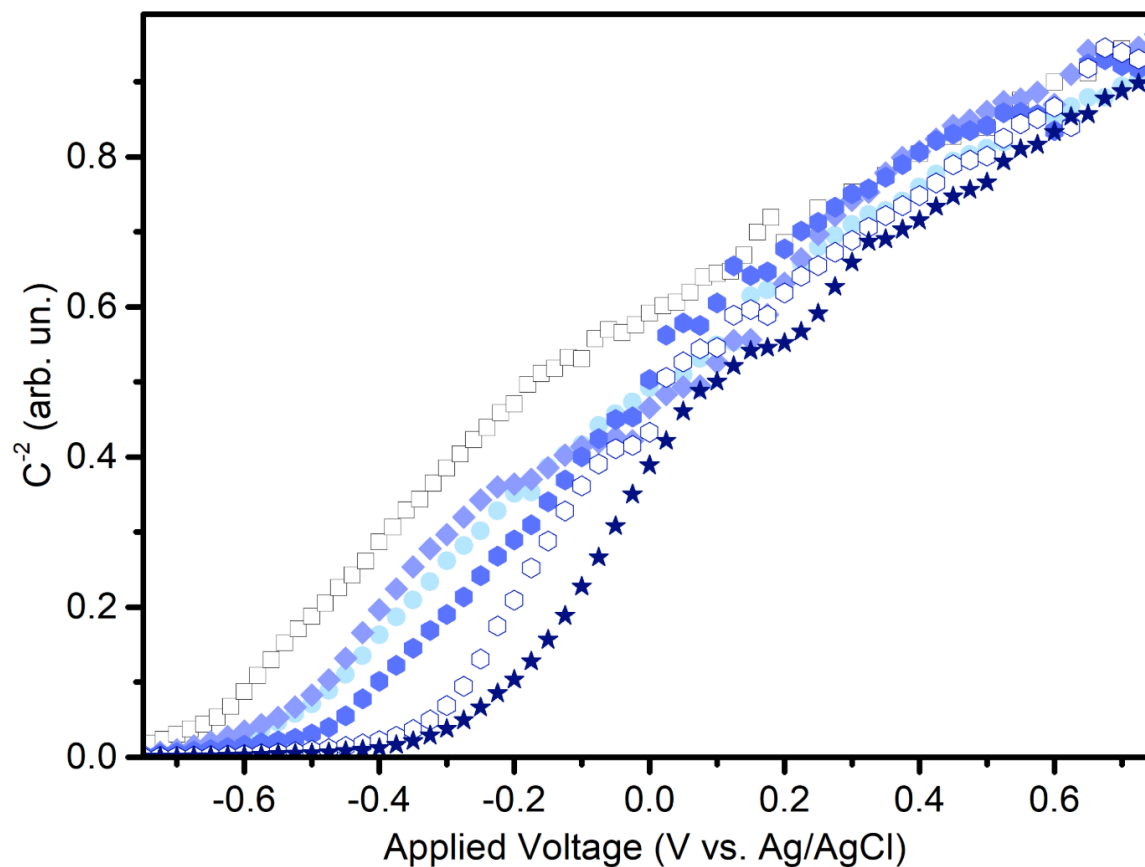


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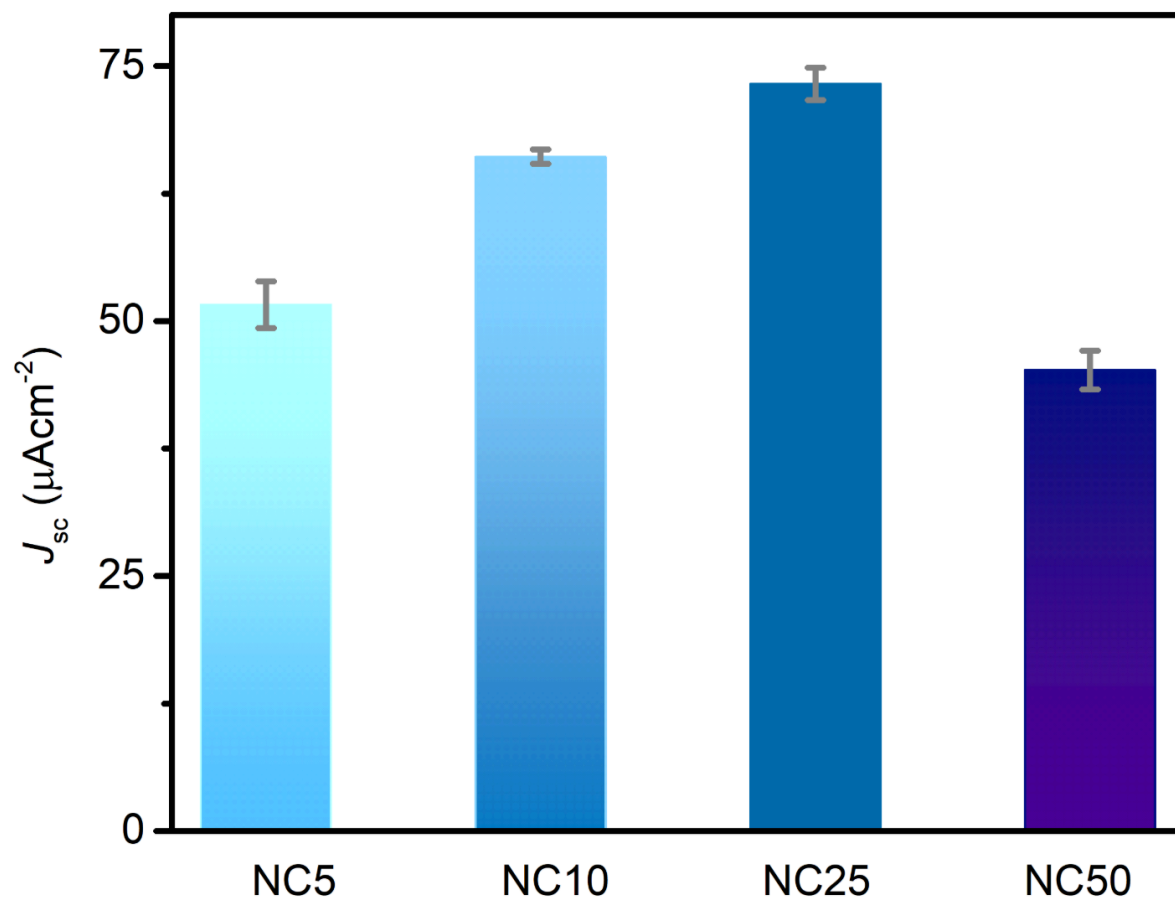


Figure 5

Photocurrent density at 0 V vs Ag/AgCl as a function of CZTS loading. Maximum at NC25 (73.3 $\mu A cm^{-2}$). Error bars: standard deviation from three measurements

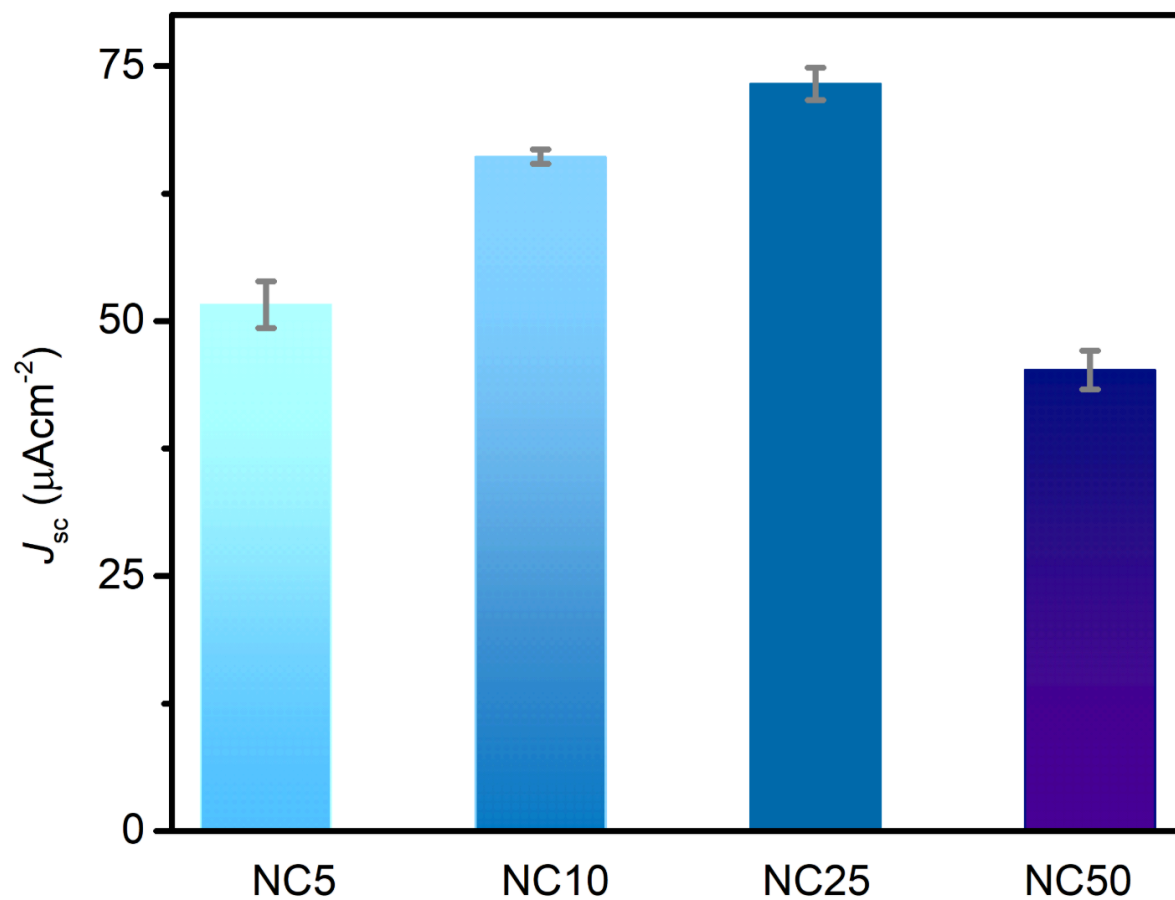


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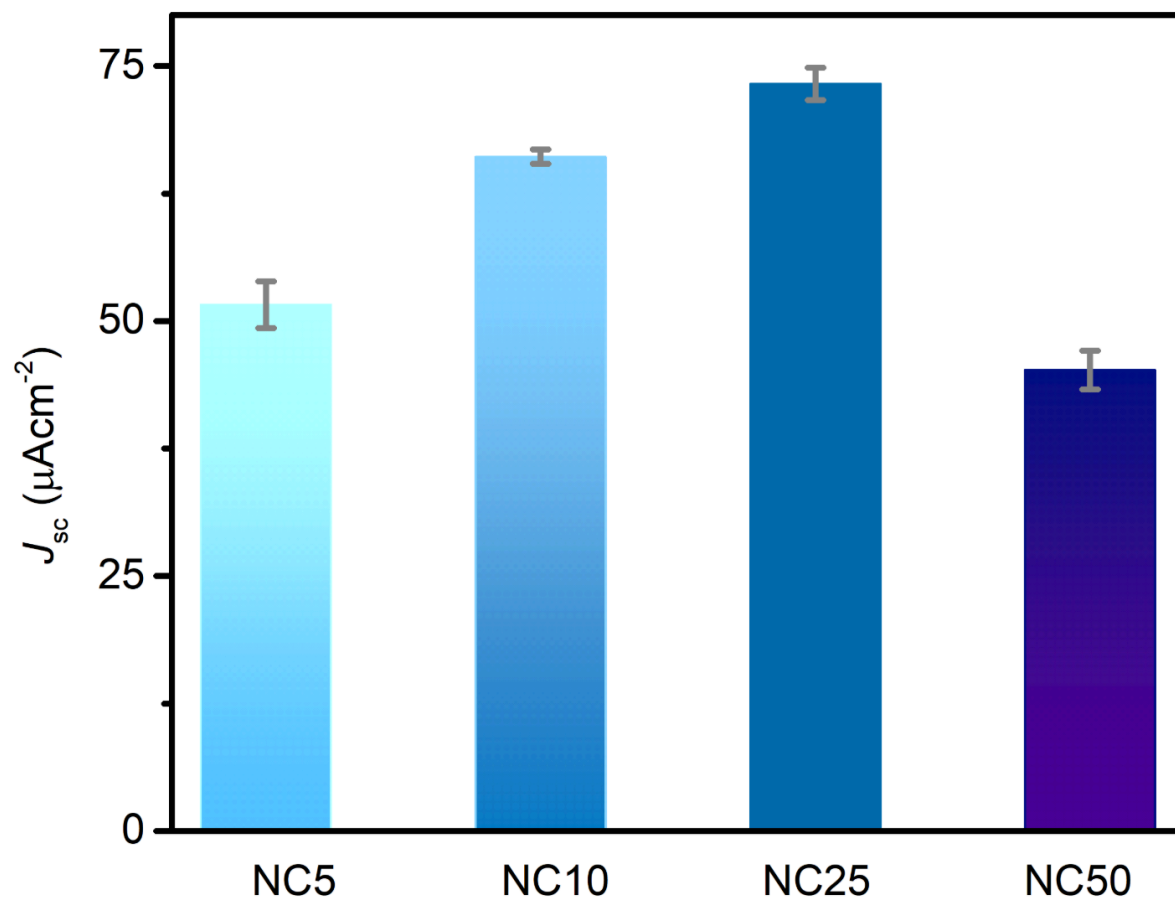


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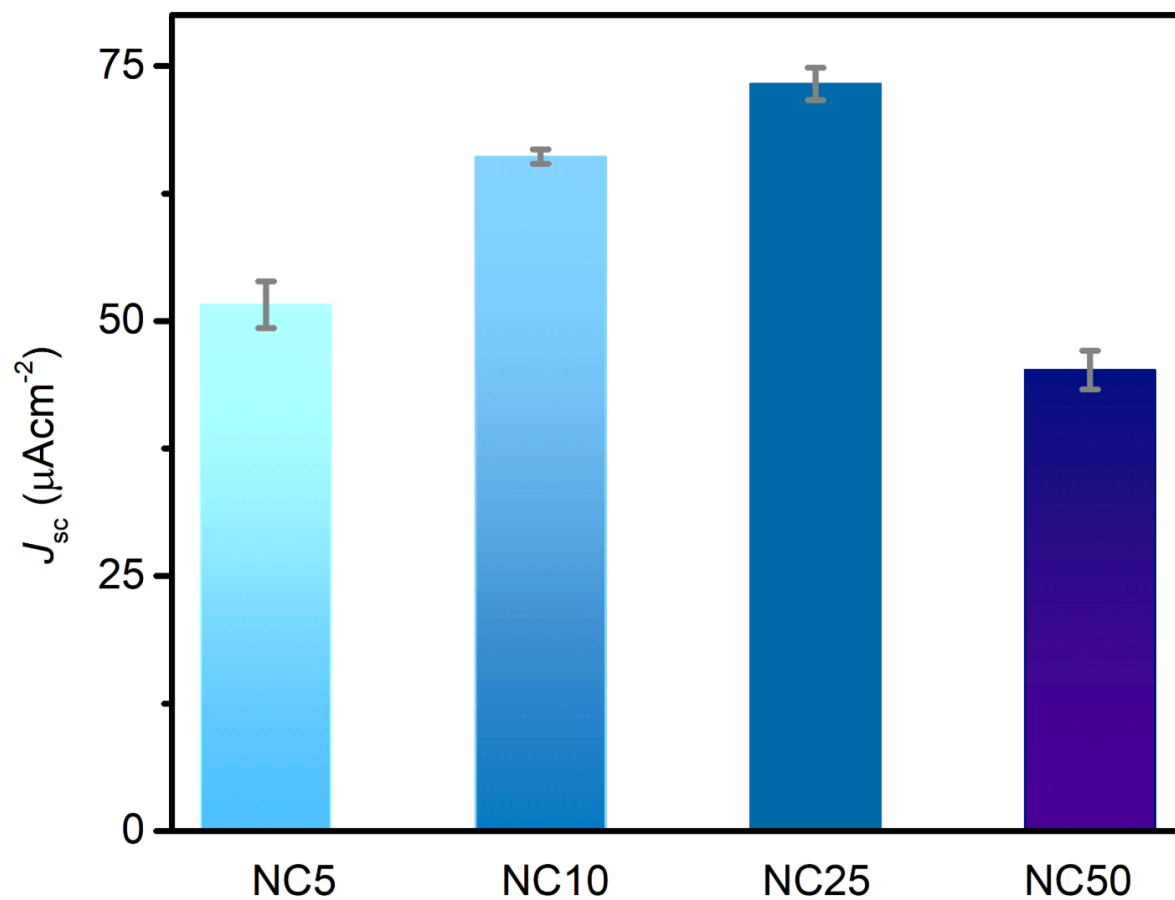


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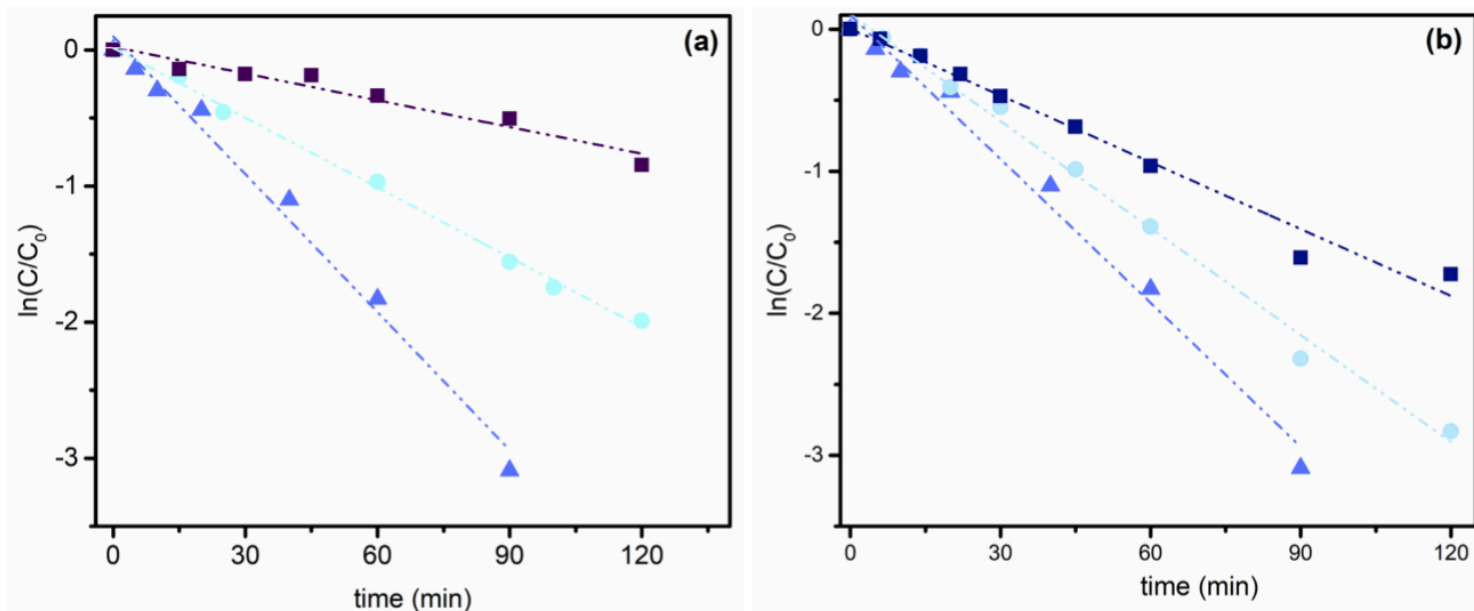


Figure 6

Photocatalytic Cr(VI) reduction. (a) Kinetic plots $\ln(C/C_0)$ vs time for MIL-125-NH₂ (circles), CZTS (squares), and NC25 (triangles) under visible light ($\lambda > 400$ nm). NC25 shows the highest k_{obs} ($3.4 \times 10^{-2} \text{ min}^{-1}$). (b) Comparison for NC5 (circles), NC25 (triangles), and NC50 (squares). Complete reduction within 120 min for NC25. Conditions: $[\text{Cr(VI)}]_0 = 5.4 \times 10^{-4} \text{ M}$, $[\text{TEA}] = 10 \text{ mM}$, catalyst 1 mg mL^{-1} , pH 7, N₂. Dashed lines represent linear fits

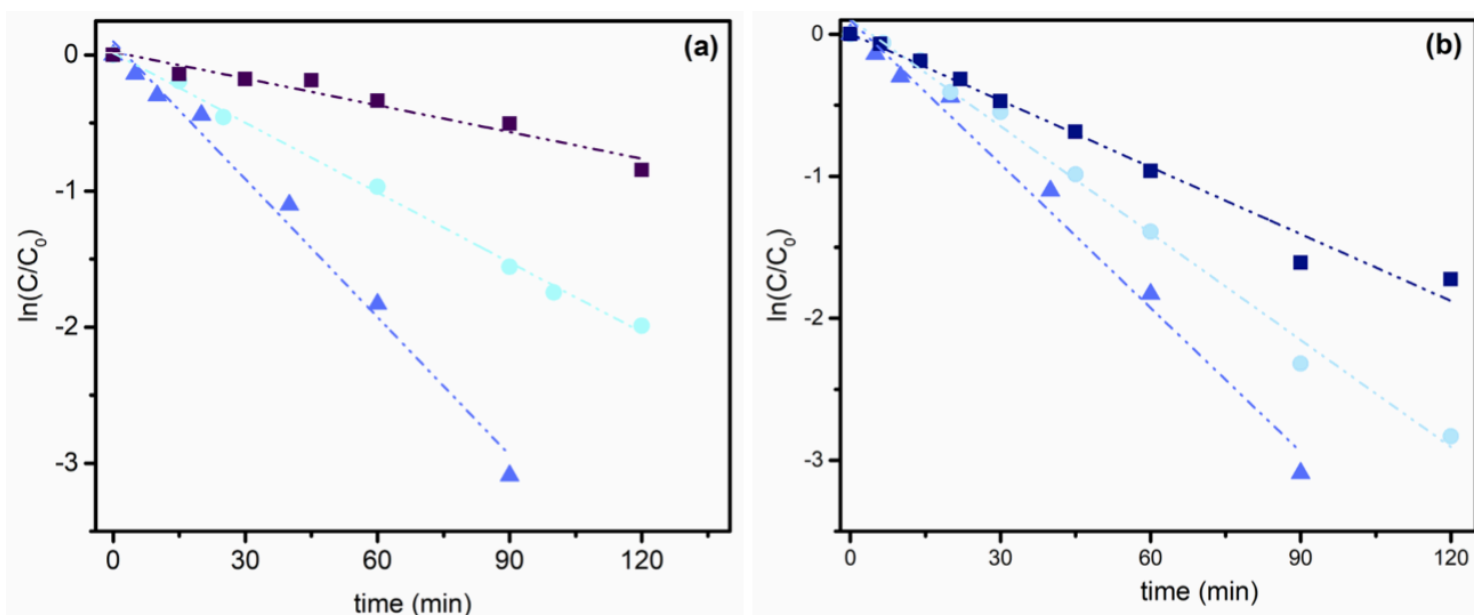


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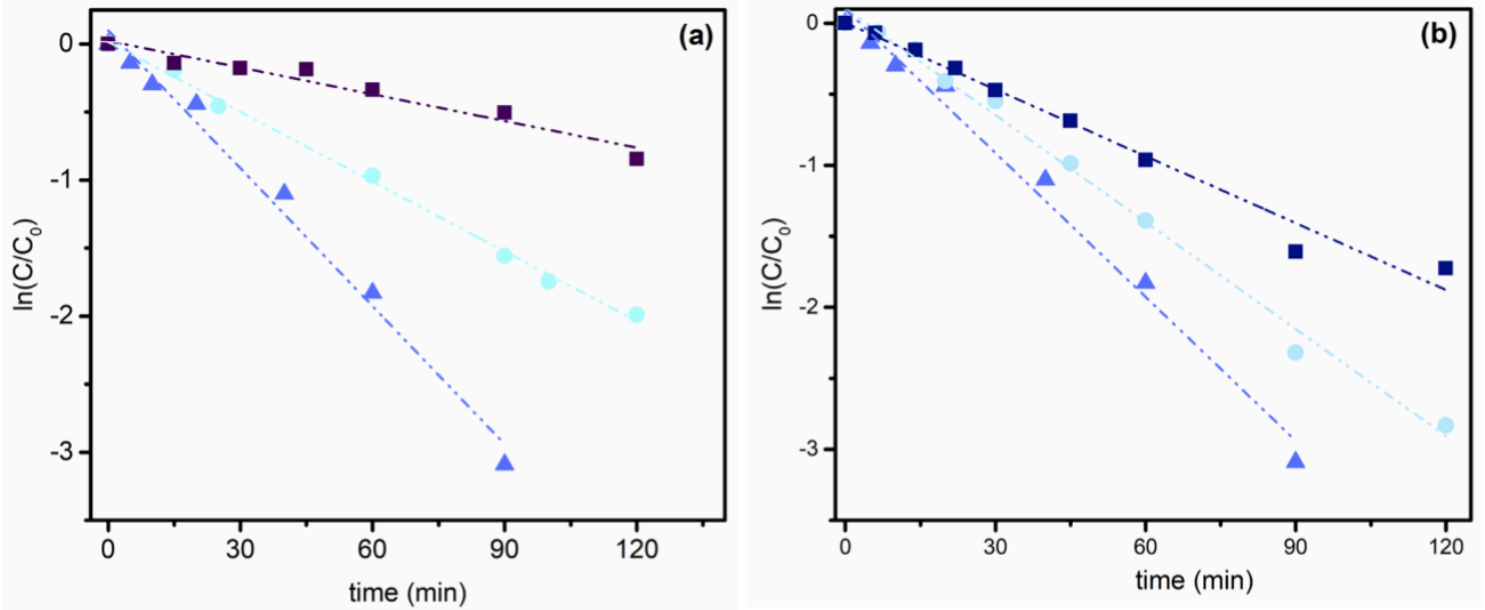


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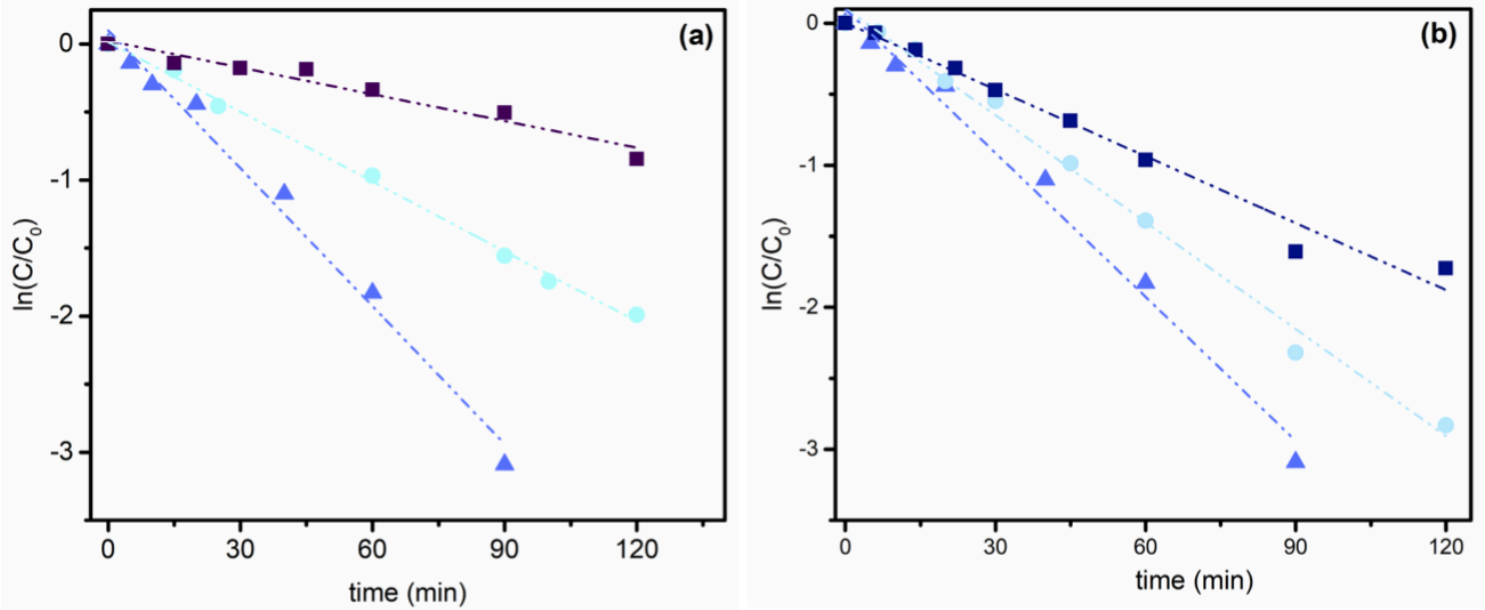


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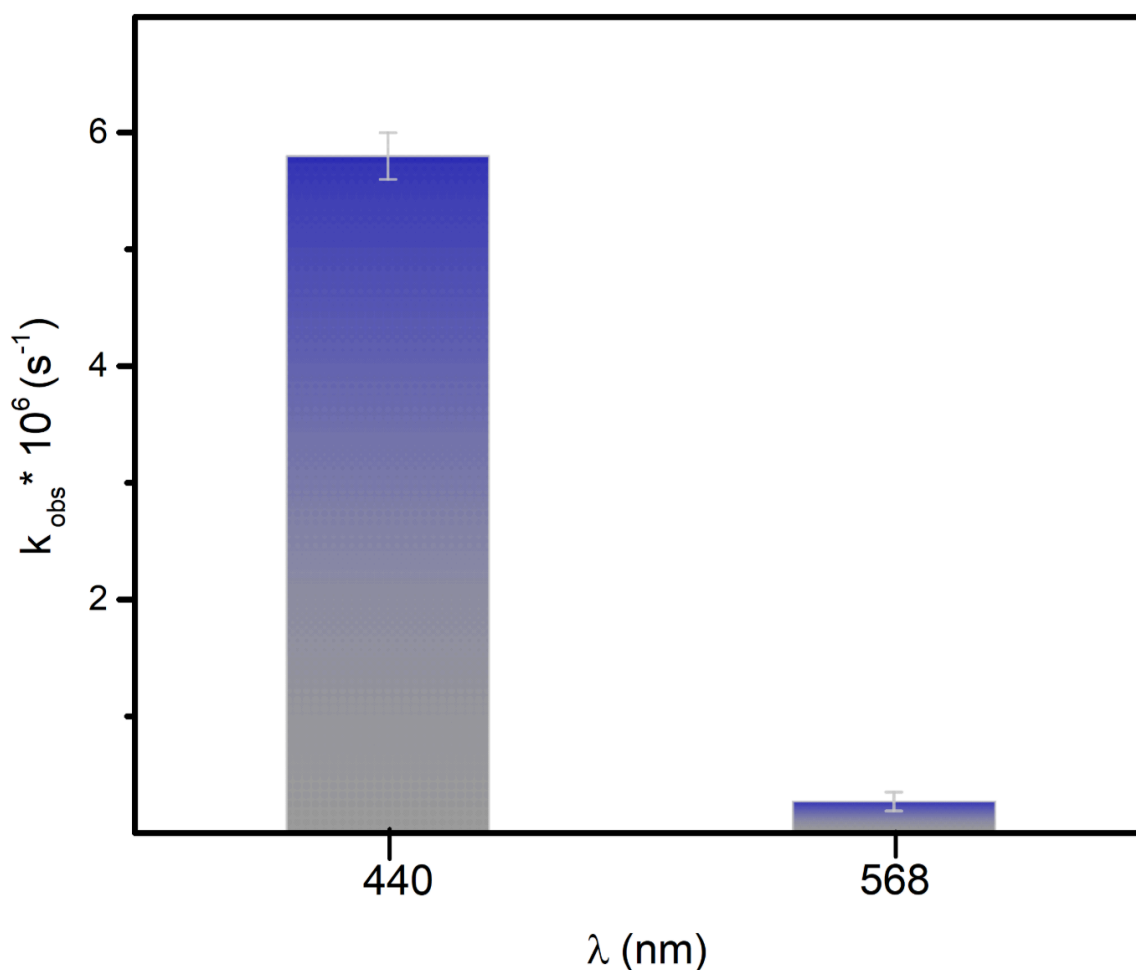


Figure 7

Comparison of apparent rate constants (k_{obs}) for Cr(VI) photoreduction using NC25 at 440 nm (simultaneous excitation) and 568 nm (selective excitation of CZTS). Error bars: SD from three measurements. Conditions: $[\text{Cr(VI)}]_0 = 5.4 \times 10^{-4} \text{ M}$, $[\text{TEA}] = 10 \text{ mM}$, catalyst 1 mg mL^{-1} , pH 7, N₂

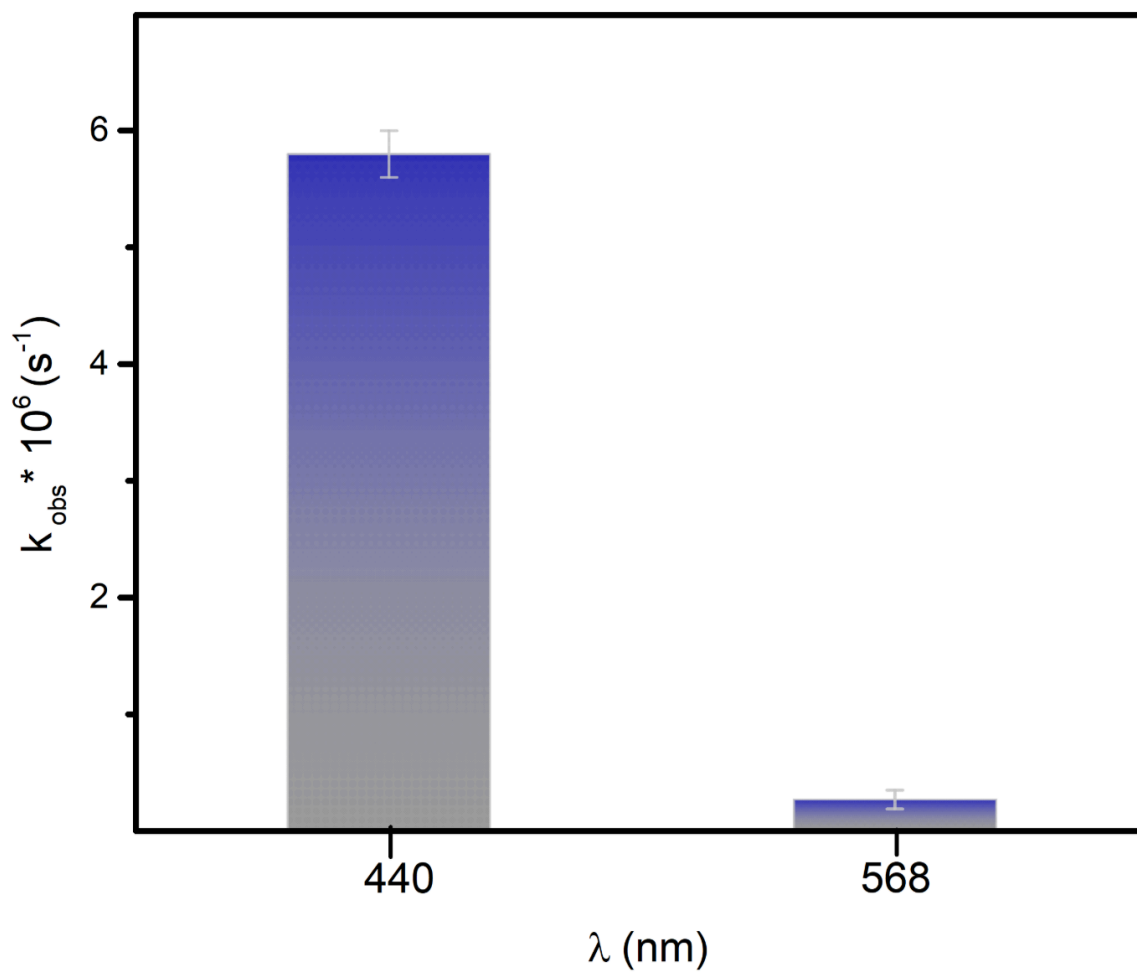


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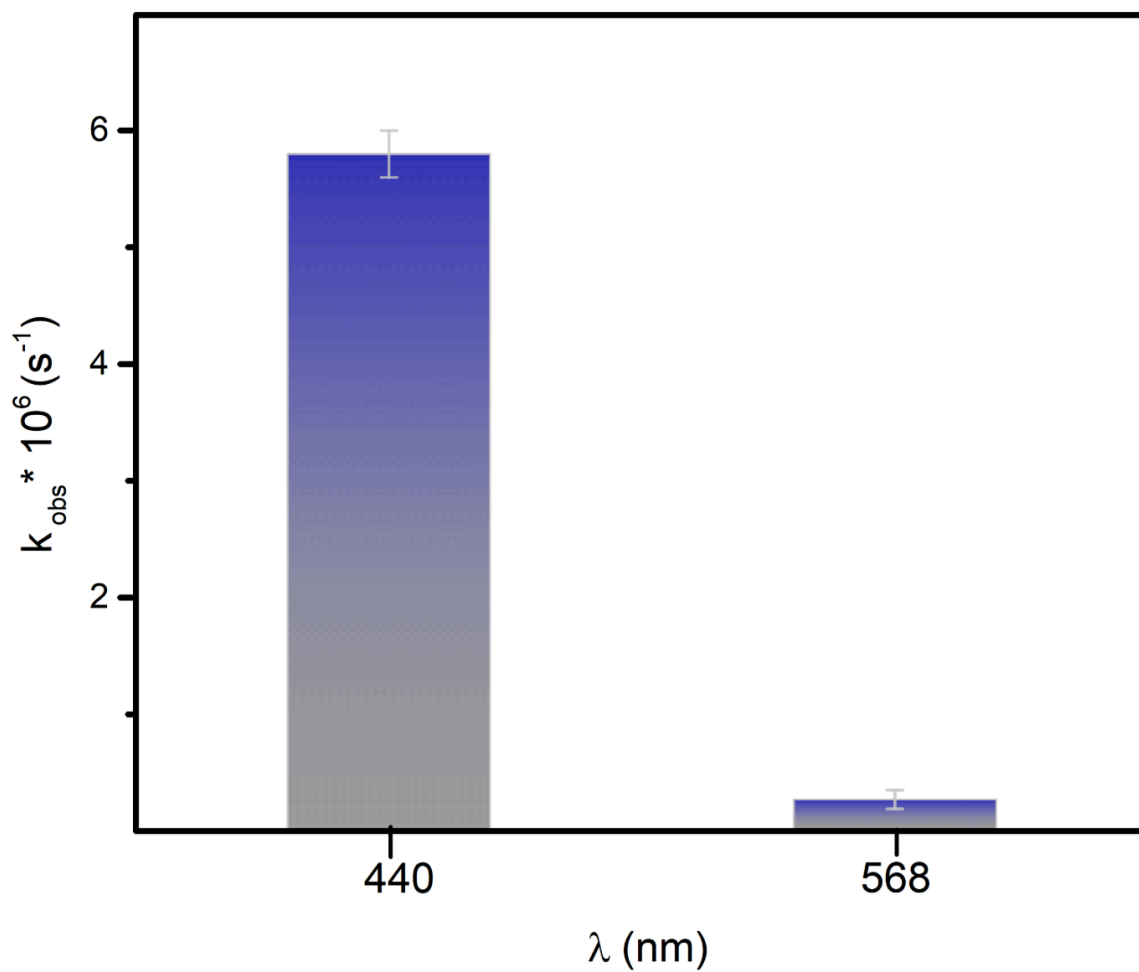


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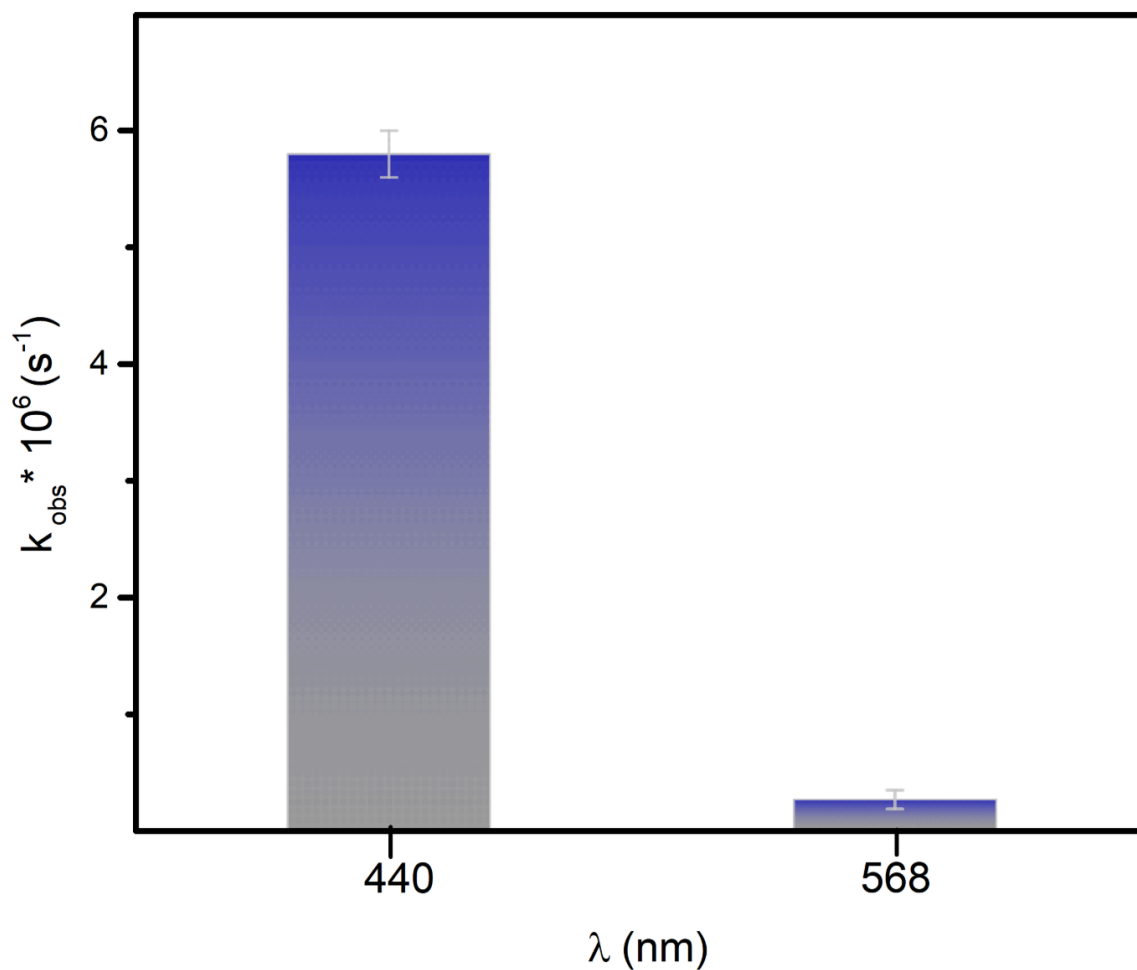


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Supplementary Files

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