Effect of Cu doping on the photocatalytic activity of InVO₄ for hazardous dye photodegradation under LED light and its mechanism

Mohamed Faisala, Anwar Iqbal a,*, Farook Adam a and R. Jothiramalingamb

a School of Chemical Sciences, Universiti Sains Malaysia, Penang 11800, Malaysia
b Surfactant Research Chair, Department of Chemistry, College of Sciences, King Saud University, Riyadh 11451, Saudi Arabia
*Corresponding author. E-mail: anwariqbal@usm.my

ABSTRACT

Cu doped InVO₄ (xCu-InVO₄ (x = 0.06–0.15 wt %) was synthesized by a facile one-pot hydrothermal method for the removal of methylene blue (MB) under LED light irradiation. The X-ray photoelectron spectroscopy (XPS) analysis indicated the coexistence of V⁵⁺ and V⁴⁺ species due to the O-deficient nature of the xCu-InVO₄. The synthesized photocatalysts displayed a morphology of spherical and square shaped particles (20–40 nm) and micro-sized rectangle rods with a length range of 100–200 μm. The xCu-InVO₄ exhibited superior adsorption and photodegradation efficiency compared to pristine InVO₄ and TiO₂ due to the presence of O₂ vacancies, V⁴⁺/V⁵⁺ species, and Cu dopant. The optimum reaction conditions were found to be 5 mg L⁻¹ (MB concentration), pH 6, and 100 mg of photocatalyst mass with a removal efficiency and mineralization degree of 100% and 96.67%, respectively. The main active species responsible for the degradation of MB were *OH radicals and h⁺. Reusability studies indicated that the 0.13Cu-InVO₄ was deactivated after a single cycle of photocatalytic reaction due to significant leaching of V⁴⁺ and Cu²⁺ species.

Key words: Cu doping, InVO₄, LED, methylene blue, visible light

HIGHLIGHTS

- xCu-InVO₄ (x = 0.06 – 0.15 wt%) were synthesized via the hydrothermal method.
- 0.13Cu-InVO₄ active under the LED light irradiation for MB removal.
- Optimized catalytic conditions displayed complete MB removal with >96% mineralization.
- 0.13Cu-InVO₄ deactivated after first use due to V⁴⁺ and Cu²⁺ species leaching.
INTRODUCTION

Since discovering the ability of TiO₂ electrodes in water splitting by Fujishima & Honda 1972, heterogeneous semiconductor photocatalysis has been broadly utilized in various fields, including water purification, selective organic transformations, and CO₂ reduction (Wen et al. 2017). However, due to the large bandgap of TiO₂ (3.2 eV) and low sensitivity towards visible light (Liang et al. 2021), the potential of other semiconductors such as ZnO, ZnS, BiVO₄, g-C₃N₄, Cds, and CdSe was explored. Zou et al. (2000) reported the suitability of InNbO₄ and InTaO₄ with bandgap energy of 2.5 eV and 2.6 eV as photocatalysts. This discovery has led Ye et al. (2002) to investigate whether Nb and Ta can be replaced with vanadium(V) for the synthesis of InVO₄. The group successfully synthesized the InVO₄ with a much narrower bandgap (2.0 eV) than InNbO₄ and InTaO₄. The InVO₄ catalyst was able to produce H₂ from water under visible light irradiation.

Due to its various potential properties such as narrow bandgap energy of ~2.0 eV, chemical stability, non-toxicity, and photo-corrosion resistivity, InVO₄ is considered as a promising visible-light active photocatalyst with great potential in various photocatalytic applications (Guo et al. 2016; Lin et al. 2016; Yuan et al. 2019). However, ineffective charge-carrier separation in its pure form severely restricts its application in photocatalysis (Chaison et al. 2017). Since the discovery of its photocatalytic activity, InVO₄ has been modified by forming integrated photocatalytic systems such as BiVO₄/InVO₄ (Guo et al. 2015), TiO₂/InVO₄/RGO (Lin et al. 2015a, 2015b), In₂S₃/InVO₄ (Yuan et al. 2019), InVO₄/β-AgVO₃ (Yang et al. 2019), InVO₄-g-C₃N₄/rGO (Hafeez et al. 2020), InVO₄/ZnFe₂O₄ (Wang et al. 2020a, 2020b), Ag-SnS₂@InVO₄ (He et al. 2020), and AgBr/Ag₂MoO₄@InVO₄ (Zhang et al. 2020a, 2020b, 2020c). Although heterojunction formation is efficient in lowering the recombination rate of photo-excited species, it still suffers from two major drawbacks. The first is that the addition of a guest photocatalyst will lead to active sites blockage and lowering the interactions between the catalyst surface and the substrate, which would finally decrease the catalytic activity. Secondly, the guest material is also believed to lower light penetration due to the shielding effect (Zhu & Wang 2017).

On the other hand, metal ion doping offers a better alternative in suppressing the rapid recombination of electron/hole (e⁻/h⁺) pairs. By adding charge trapping sites (dopants), the recombination rate will be quenched, and the lifespan of the photo-excited species will be prolonged to enhance the photocatalytic activity of the semiconductor (Imam et al. 2018). In the past, InVO₄ based photocatalysts were successfully modified with metals including Pt (Yan et al. 2012), Ag (Lin et al. 2015a, 2015b), Cu (Wetchakun et al. 2017), Bi (Wang et al. 2020a, 2020b), Yb and Tm (Zhang et al. 2020a, 2020b, 2020c).
In this study, different amounts of Cu were incorporated into the lattice of InVO₄ via a one-pot hydrothermal method under optimized reaction conditions. The detailed physicochemical properties of the photocatalysts were systematically characterized and studied before and after the photocatalytic reaction. An in-depth investigation on the visible-light-driven photodegradation of methylene blue (MB) under a low-cost homemade LED fixed photoreactor was also carried out. The Cu-InVO₄ prepared by Wetchakun et al. (2017) required higher temperature and longer heating time. The photocatalytic activities of the Cu-InVO₄ were investigated using a 50 W halogen lamp with a glass filter to block the UV components. In this research, lower heating temperature (180 °C) and shorter time (12 h) were used.

MATERIALS AND METHODS

Chemicals

Indium(III) nitrate hydrate (In(NO₃)₃·H₂O, 99.9%) and sodium metavanadate (NaVO₃, ≥98.0%) were purchased from Sigma-Aldrich. Copper(II) nitrate trihydrate (Cu(NO₃)₂·3H₂O, 99.5%) and ascorbic acid (99.5%) were purchased from QREC. All chemicals were analytical grade and used without any further purification.

Preparation of InVO₄

In a typical synthesis procedure, 2 mmol of In(NO₃)₃ was dissolved in 35 mL of deionized water under magnetic stirring followed by the addition of an equimolar amount of NaVO₃. The mixture was stirred vigorously for 2 h before being transferred into a 50 mL Teflon-lined stainless-steel autoclave and was placed horizontally in an oven at 180 °C for 12 hours. The yellowish InVO₄ powder was then separated from the mother liquid by centrifugation and washed alternatively with ethanol and water three times. The InVO₄ powder was dried at 60 °C for 24 h.

Synthesis of Cu doped InVO₄

The doping process was carried out according to the synthesis of pristine InVO₄ with some modifications. The Cu(NO₃)₂ (2.5–10 mole%) was added to the mixture of In(NO₃)₃–NaVO₃ solution. The photocatalysts were labelled as xCu-InVO₄ (x = 0.06, 0.10, 0.13 and 0.15) based on the wt% of Cu determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) analysis.

Characterization of the photocatalyst

The functional groups of the photocatalysts were determined using the Fourier Transform Infrared Spectroscopy (FT-IR) analysis (FT-IR 2000 Perkin Elmer). The crystal structure was determined by X-Ray diffraction (XRD) analysis (Bruker D8 Advance, current = 40 mA and voltage = 40 kV) under Cu Kα radiation (1.5406 Å). The mean crystal size of the prepared photocatalysts was evaluated using the Scherrer’s Equation (Gerawork 2021), as shown in Equation (1):

$$D_p = \frac{k \lambda}{\beta \cos(\theta)}$$

where $D_p$ is the average crystal diameter (nm), $k$ is the Scherrer’s constant (0.94), $\lambda$ is the wavelength of the Cu Kα radiation (0.15406 nm), $\beta$ is the full width of half maximum (FWHM) of the highest peak, which is located at $2\theta \approx 33^\circ$, and $\theta$ is the exact location of the peak in the $2\theta$ range (Yao et al. 2009; Dianat 2018). The scanning electron microscopy (SEM) (FEI Quanta 650 FEG SEM) was used to obtain the morphology, whereas the high-resolution transmittance electron microscopy (HRTEM) with field emission (TECNAI G2 20S-TWIN, FEI HRTEM 200 kV) was utilized to study the morphology. The surface elemental composition was obtained by X-ray photoelectron spectroscopy (XPS) (Ulvac- PHI Quantera II) equipped with monochromatic Al-Kα (hv = 1,486.6 eV) X-ray power source. The adventitious carbon peak (C1s) was used as a reference and calibrated to 284.8 eV (Oswald et al. 2018). The photocatalyst’s textural properties were investigated by nitrogen adsorption-desorption (NAD) analysis using Micromeritics ASAP 2020 Surface Adsorption Porosimeter. Data collected from the diffuse reflectance UV-Vis spectroscopy (UV-Vis DRS) (Perkin Elmer UV-Vis spectrophotometer, Lambda 35) was used to calculate the bandgap energy using Kubelka-Munk model (Wang et al. 2016a, 2016b). The point of zero charge (PZC) was estimated by pH drift method with some modifications (Jiao et al. 2017).

Photocatalytic study

The photodegradation of methylene blue (MB) was conducted using a homemade reactor equipped with a commercially available 36 Watts LED (Flying Butterfly Lamp company) lamp as the irradiation source. The lamp was placed directly
above the reaction mixture with 8.5 cm between the lamp and the reaction mixture (Figure S1 in Supplementary Information). The MB solution (200 mL of 5 mg L\(^{-1}\)) was stirred with the photocatalyst under the dark condition for 60 minutes to achieve adsorption-desorption equilibrium. Subsequently, the solution was irradiated with LED light. An aliquot (5 mL) was collected in 15-minute intervals and then filtered using 0.2 μm syringe filters. The reaction mixture was then analysed using a UV-Vis spectrometer (Shimadzu 2600 UV-Vis). The dye removal efficiency was calculated using Equation (2) where \(C_0\) and \(C_t\) are the initial MB concentration and MB concentration after a given time from light irradiation, respectively.

\[
\text{Removal}\% = \frac{(C_0 - C_t)}{C_0} \times 100
\]  

The Langmuir-Hinshelwood model was used to study the photodegradation kinetics and to determine the rate of reactions. Pseudo-first-order and pseudo-second-order kinetics were expressed using Equations (3) and (4), respectively.

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

\[
\frac{1}{C_0} - \frac{1}{C_t} = -k't
\]

where \(C_0\), \(C_t\), \(t\), \(k\) and \(k'\) are the MB concentration at zero time, the MB concentration at a specific time of light irradiation, time (minutes), the pseudo-first-order rate constant (min\(^{-1}\)), and the pseudo-second-order rate constant (L mol\(^{-1}\) min\(^{-1}\)), respectively. Mineralization studies were performed using ion chromatography analysis (Metrohm 792 Basic IC) by detecting SO\(_4^{2-}\) ions.

**RESULTS AND DISCUSSION**

**Photocatalyst characterization**

**FT-IR analysis**

The FT-IR spectra of the pristine InVO\(_4\) and \(x\)Cu-InVO\(_4\) (\(x = 0.06-0.15\)) are shown in Figure 1(a). The IR peak located at 452 cm\(^{-1}\) is assigned to the V – O – V vibrations (Liu et al. 2016), whereas the peaks at 767 cm\(^{-1}\) and 902 cm\(^{-1}\) are assigned to the V – O – In vibration (Lai et al. 2018). The peak associated with the contraction and expansion vibrations of V – O bond can be seen at 950 cm\(^{-1}\) (Yao et al. 2009). The two bands located at 1,630 cm\(^{-1}\) and 3,434 cm\(^{-1}\) are attributed to the surface hydroxyl groups’ stretching vibrations (–OH) and adsorbed water molecules, respectively (Zhang et al. 2015; Kumar et al. 2018). The IR peaks related to the CuO or Cu\(_2\)O were not observed in the spectra of Cu doped InVO\(_4\) photocatalysts. The absence of these peaks suggests that the Cu was possibly incorporated within the framework of InVO\(_4\) instead of forming CuO or Cu\(_2\)O species on the catalyst’s surface. The IR peak at 1,586 cm\(^{-1}\) is attributed to the presence of Na\(_2\)V\(_6\)O\(_{16}\). This complex is usually formed when vanadium ions with ratios equal to or exceeding 3 of V/In precursors are used (Yao et al. 2009). Since the ratio used in this study was 1:1, the existence of the peak is concluded not to be caused by the presence of excess vanadium ion.

During the photocatalyst synthesis, when NaVO\(_3\) solution was added into the In(NO\(_3\))\(_3\) solution, the colour of the solution quickly changed from colourless to dark red. The formation of the red-coloured solution indicates the presence of vanadic acid (HVO\(_3\)). During the hydrothermal process, HVO\(_3\) species will be converted into [VO\(_2\)(H\(_2\)O)\(_4\)]\(^{+}\) and [H\(_2\)V\(_{10}\)O\(_{28}\)]\(^{4+}\) ions. These two ions will undergo protonation and deprotonation during the hydrothermal synthesis, forming neutral [VO(OH)\(_3\)](H\(_2\)O)\(_3\). Polycondensation of [VO(OH)\(_3\)](H\(_2\)O)\(_2\) species in the presence of Na\(^+\) ions will lead to the formation of Na\(_2\)V\(_6\)O\(_{16}\) (Chithaiah et al. 2012).

**XRD analysis**

The XRD diffractograms of the synthesized photocatalysts are shown in Figure 1(b). The diffractogram patterns are in agreement with the standard data of InVO\(_4\) in the orthorhombic phase (JCPDS No.48-0898). The absence of diffraction peaks related to CuO and Cu\(_2\)O further confirms the observation in the FT-IR analysis. Diffraction peaks ascribed to Na\(_2\)V\(_6\)O\(_{16}\) were not observed, possibly due to its low amount. A closer inspection at 2θ = 30–36° (Figure 1(c)) showed that the three diffraction peaks experienced shifting compared to the pristine InVO\(_4\), indicating changes in the framework of InVO\(_4\). The doped metal can either fill up the voids between the host material’s atoms or replace the host material’s atoms. The first is known as interstitial doping, whereas the second is known as substitutional doping. The metal doping position can be assumed based on the Hume-Rothery principle, which states that atoms’ substitution will only occur if the difference between...
the substituted and substituting metals' electronegativities is less than 20% (Mathew et al. 2018). Since the difference between copper electronegativity (1.95) and indium electronegativity (1.78) is 8.7%, and between copper and vanadium electronegativities (1.63) is 16.41%, it is assumed that Cu doping into InVO₄ is in substitutional positions.

For 0.06Cu-InVO₄, the XRD peaks shifting to the lowest angle is ascribed as an effect of Cu²⁺ substituting V⁵⁺ (He et al. 2018). As for 0.10Cu-InVO₄, the XRD peaks shifted slightly to the right compared to 0.06Cu-InVO₄, possibly due to the substitution of In³⁺ by Cu²⁺. As the doping amount increased, shifting to a lower angle was observed but to a lesser extent compared to 0.06Cu-InVO₄. This observation could be due to the substitution of both In³⁺ and V⁵⁺ by Cu²⁺ but with more tendency towards replacing V⁵⁺.

The main dominant peak of InVO₄ of the (112) plane located at approximately 2θ = 33.1° was used to calculate and study the effect of Cu doping on the crystal size using Scherrer's equation. Additionally, based on previous efforts, the effect of doping on the lattice distortion degree of orthorhombic structured semiconductors can be measured using the a/b lattice constants ratio (Chen et al. 2018). The lattice constants were calculated using the formula:

$$\frac{1}{d_{hkl}^2} = \frac{k^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

where \(d_{hkl}\) is the d-spacing of a single plane. Also, \(h, k,\) and \(l\) are the Miller index of that same plane. Moreover, \(a, b,\) and \(c\) are the lattice constants.

Figure 1(d) illustrates the effect of Cu doping on the orthorhombic lattice distortion and the crystal size values obtained from the XRD analysis. It can be clearly seen that increasing the amount of doped Cu leads to an increase in the
orthorhombic distortion value with no change of the crystal size until 0.13 wt.% of Cu was doped into the catalyst. However, when the doping amount further increased to 0.15 wt.%, both the orthorhombic distortion and crystal size dropped significantly. The orthorhombic distortion was minimum for 0.06Cu-InVO4 due to the substitution of solely V5+ by Cu2+ ions. The distortion becomes significant for 0.10Cu-InVO4 due to the dual replacement of In3+ and V5+ by Cu2+. In addition, the sudden drop in both orthorhombic distortion and crystal size for 0.15Cu-InVO4 can be ascribed to the excessive crystal distortion and defects, which might have caused the crystals to break down into smaller crystals.

**HRTEM analysis**

The TEM and HRTEM images of the photocatalysts are shown in Figure 2. The lattice fringes and interplanar spacing were determined using Fast Fourier Transformation (FFT) software. Based on the TEM images, pristine InVO4 and xCu-InVO4 (x = 0.06–0.15) photocatalysts consisted of irregularly shaped oval and spherical nanoparticles.

The orthorhombic InVO4 XRD diffractogram contains 33 peaks and consequently 33 (hkl) planes. However, only four different d-spacing values were detected for each photocatalyst due to the different scanning areas. The pristine InVO4 was found to have d-spacing values that correlate to the hkl planes of (024), (111), (310), and (040). For 0.06Cu-InVO4, the hkl planes detected were (202), (220), (130), and (112), whereas the hkl planes of (042), (310), (222), and (200) were found in 0.10Cu-InVO4. The hkl planes present in 0.13Cu-InVO4 were (020), (040), (222), and (310). For 0.15Cu-InVO4, (004), (042), (150), and (114) hkl planes were detected.

The histograms were fitted using Gaussian distribution fitting to determine the photocatalyst’s average particle size as illustrated in Figure S2. The estimated particle size obtained was found to be 44.21 ± 0.66 nm, 35.05 ± 0.32 nm, 38.46 ± 0.82 nm, 38.61 ± 1.59 nm, and 37.54 ± 1.09 nm for InVO4, 0.06Cu-InVO4, 0.10Cu-InVO4, 0.13Cu-InVO4, and 0.15Cu-InVO4, respectively. The particles obtained are bigger than the particle size reported by Wetchakun et al. (2017). Generally, higher hydrothermal reaction temperature often leads to bigger particle size. However, in this research, smaller particle size was obtained due to different ratios of the reactants used compared to Wetchakun et al. (2017).

**N2 adsorption-desorption studies**

Table S1 illustrates the N2 adsorption-desorption isotherms of all the synthesized catalysts. At higher relative pressure region (P/P0 = 0.8–1), pristine InVO4 and xCu-InVO4 (x = 0.06–0.15) catalysts displayed type IV isotherms with H3 hysteresis loops, suggesting the presence of mesopores in the samples (Sing et al. 1985; Hoan et al. 2020; Zhang et al. 2020a, 2020b, 2020c). To further confirm the presence of such pores, Barrett-Joyner-Halenda (BJH) pore size distribution studies were carried out.

As illustrated in Figure S3, the photocatalysts have a bimodal pore system centred on ~5.7 nm and ~40 nm. The relatively smaller pores (inset) are ascribed to the mesopores within the InVO4 cracks, whereas the larger pores are believed to be due to the formation of larger mesopores or macropores between the InVO4 particles (Zhang et al. 2020a, 2020b, 2020c). As shown in Table S1, the BET surface area of the doped InVO4 was slightly lower compared to the pristine InVO4. A similar trend was observed in the total pore volume of the photocatalysts. This observation can be attributed to the low content of doped Cu2+. In addition, the small differences between the ionic radii of In3+ (0.08 nm), Cu2+ (0.075 nm), and V5+ (0.059 nm) do not significantly contribute to the changes in the surface area or pore volume. Nonetheless, Cu doping was found to enhance the pore width until 0.13 wt.%, whereas a further increase in Cu amount leads to a drop in the pore width.

**Point of zero charge (PZC) analysis**

The PZC of the photocatalysts was determined to be in the range of pH 2.32–2.58, as illustrated in Figure S4, similar to previous reports (Lamdab et al. 2015). The protonation and deprotonation of the catalyst surface will take place depending on the pH of the solution. At pH values below the pHPZC, the catalyst surface will be positively charged, whereas at pH above the pHPZC the surface will have a total negative charge. The effect of solution pH on the surface charge of the xCu-InVO4 (x = 0.06–0.15) can be summarized in Equations (6) and (7):

\[(\text{pH} < \text{PZC}): \text{InVO}_3\text{H} + \text{H}^+ \rightleftharpoons \text{InVO}_3\text{H}_2^+ \quad (6)\]

\[(\text{pH} > \text{PZC}): \text{InVO}_3\text{H} + \text{OH}^- \rightleftharpoons \text{InVO}_3^- + \text{H}_2\text{O} \quad (7)\]
Figure 2 | The TEM and HRTEM images of (a,b) InVO₄, (c,d) 0.06Cu-InVO₄, (e,f) 0.10Cu-InVO₄, (g,h) 0.13Cu-InVO₄, and (i,j) 0.15Cu-InVO₄, respectively.
UV-Vis DRS analysis

Figure 3(a) displays the absorbance spectra of the pristine InVO₄ and xCu-InVO₄ (x = 0.06–0.15). The absorbance edge of InVO₄ was noticed to experience a slight red shift towards higher wavelength values with Cu doping, indicating increased sensitivity towards visible light. The Kubelka-Munk function was used to determine the direct bandgap of the synthesized photocatalysts, as illustrated in Figure 3(b). The bandgap values are listed in Table S2. The bandgap of pristine InVO₄ was found to be 3.0 eV, which is higher than the usually reported bandgaps of InVO₄ (2.0–2.4 eV) (Ye et al. 2002; Wang et al. 2016a, 2016b). The high bandgap found in this study is due to the use of different concentrations of precursors and different synthesis temperatures. These factors affect the synthesized material’s optical properties (Jacob & Jerome Das 2016; Lestari et al. 2016).

In addition, the redshift also indicates the formation of a new band state located between the conduction band (CB) and valence band (VB) of the InVO₄. It is expected that xCu-InVO₄ (x = 0.06–0.15) will have better photocatalytic performance under visible light irradiation compared to pristine InVO₄ due to the smaller bandgap and enhanced Vis light-harvesting (He et al. 2018).

It is crucial to determine the CB and VB exact positions to understand the possible photocatalytic reaction mechanisms. The values of the energy bands were determined using the Equations:

\[ E_{CB} = \chi - E^e - 0.5E_g \]  
\[ E_{VB} = E_{CB} + E_g \]  

where \( E_{CB} \) and \( E_{VB} \) are the CB and VB energy potentials, respectively. The \( E_g \), \( E^e \), and \( \chi \) are the semiconductor’s bandgap, free electrons’ energy vs. hydrogen (4.5 eV), and the total electronegativity of the semiconductor (\( \chi = 5.74 \) eV for InVO₄), respectively. The values of \( E_{CB} \) and \( E_{VB} \) were calculated by substituting these values in Equations (8) and (9) and listed in Table S2.

Photoluminescence (PL) analysis

The PL analysis provides valuable information regarding electron migration and trapping efficiency. Generally, a lower PL emission intensity suggests a higher e⁻/h⁺ separation efficiency and a prolonged photo-excited charge carriers’ lifespan (Priya et al. 2020). Figure 4 shows the PL spectrum of pristine and xCu-InVO₄ (x = 0.06–0.15). All the photocatalysts illustrate very strong photoluminescence properties with intensity peaks mainly present in the green region of visible emission (~550 nm). The Cu doping has significantly influenced the peak intensities.
As proven by XRD, Cu$^{2+}$ replaced V$^{5+}$ sites at low doping concentrations (0.06Cu-InVO$_4$) and replaced both In$^{3+}$ and V$^{5+}$ active sites at higher doping levels. Since the PL emission peak of InVO$_4$ originates from the VO$_4^{3-}$/CO charge-transfer transition (Shih et al. 2015; Li & Xu 2018), the behaviour of the PL phenomena is correlated with V$^{5+}$ relative concentration in the nano-composites. Based on the obtained results, it can be concluded that substitution of V$^{5+}$ ions by Cu$^{2+}$ ions is highly efficient in enhancing the separation of photoinduced electron/hole pairs and provides better trapping sites compared to pristine InVO$_4$.

The XRD analysis also indicates that 0.10Cu-InVO and 0.13Cu-InVO$_4$ have the largest crystallite size (44 nm). It has been reported that larger crystallites have a lower number of atoms in grain boundaries and on the surface, hence increasing the light scattering efficiency compared to smaller crystals. As a result, the PL intensity of these photocatalysts appeared to be higher compared to 0.15Cu-InVO$_4$ (35 nm). The 0.06Cu-InVO$_4$ has lower PL intensity compared to 0.10Cu-InVO$_4$ and 0.13Cu-InVO$_4$, even though they have similar crystallite size. This trend is possibly due to the lower degree of orthorhombic distortion and even distribution of Cu species on the surface (Lee et al. 2015).

**XPS analysis**

The XPS analysis was carried out only for 0.13Cu-InVO$_4$ as a representative for the rest of the photocatalysts. As illustrated in Figure 5(a), the survey scan of 0.13Cu-InVO$_4$ shows the presence of indium (4d, 4p, 4s, 5d, 5p, 5s, and MNN transitions), vanadium (3p, 3s, 2p, 2s, and LMM transitions), oxygen (1s and KLL transitions), and carbon (1s transition). The MNN, LMM, and KLL are Auger peaks that provide information on the Auger transitions’ existing vacancies. Carbon originates from the instrumental environment. The existence of In3d, V2p, and O1s indicates the successful fabrication of InVO$_4$. However, Cu transitions, which should appear at B.E. ~932 eV and ~953 eV for Cu 2p transitions, were not detected (Wang et al. 2014; Moongraksathum et al. 2018). This is ascribed to the low amount of Cu in the sample. The XPS detection limit for most elements (including Cu) is 0.1 at.% – 1.0 at.% (Shard 2014; Lamers et al. 2018). The Cu concentration detected in 0.13Cu-InVO$_4$ was only 0.13%.

The narrow scan of In3d illustrates two peaks at 444.31 eV and 451.89 eV corresponding to In3d$_{5/2}$ and In3d$_{3/2}$ valence states, respectively (Figure 5(c)) (Li et al. 2009; Yang et al. 2019; Hafeez et al. 2020). Moreover, the deconvolution of V2p (Figure 5(c)) peaks shows the characteristic peaks at 517.12 eV and 524.62 eV that are assigned to V2p$_{3/2}$ and V2p$_{1/2}$, respectively, contributing to V$^{5+}$ (Silversmit et al. 2004; Ma et al. 2015; Zhou et al. 2018). The peaks located at 516.75 eV and 523.16 eV are ascribed to the surface V$^{4+}$ species (Motola et al. 2018; Han et al. 2019). Based on the Principle of Electroneutrality, the reduction of V$^{5+}$ to V$^{4+}$ can be ascribed to the oxygen vacancies produced during the hydrothermal synthesis (Wetchakun et al. 2017). The formation of oxygen vacancies can be attributed to two reasons, Cu$^{2+}$ doping (He et al. 2018) and the high applied pressure during the hydrothermal synthesis (Abdul-Rahman et al. 2019), which would weaken the V–O bond and further facilitate the removal of the oxygen attached to V, causing a reduction in V charge to form V$^{4+}$ moieties. The presence of oxygen vacancy sites and V$^{4+}$ species is highly crucial in photocatalytic activities, as will be explained later. Additionally, the asymmetrical O1s (Figure 5(d)) peak can be deconvoluted into two peaks located at 529.78 eV and 530.69 eV. These peaks originated from the lattice oxygen and surface adsorbed oxygen species, respectively (Wang et al. 2013a, 2013b; He et al. 2018; Liu et al. 2020).

**Figure 4** | The PL phenomena of pristine and xCu-InVO$_4$ ($x = 0.06–0.15$).
Table S3 illustrates the molar ratios of different species present on the surface of 0.13Cu-InVO₄. The molar ratios were calculated using the area of the peaks and the relative sensitivity factors (R.S.F) of each peak. In an ideal case of InVO₄, the molar ratio of V:In should be 1:1; however, in 0.13Cu-InVO₄ it is slightly less. This can be ascribed to the fall in V concentration due to Cu substitutional doping. Moreover, O:In and O:V ratios should theoretically be 4:1, yet the decrease in the actual ratios further confirms the formation of extrinsic O-vacancies and establishes that the 0.13Cu-InVO₄ is oxygen-deficient. Furthermore, the obtained V⁴⁺/V⁵⁺ molar ratio is higher than previously reported values for InVO₄ (0.184–0.430) (Wang et al. 2013a, 2013b), indicating relatively more surface-active sites.

Photocatalytic performance

Effect of Cu doping on the photocatalytic activity of InVO₄

The effect of Cu doping on the photocatalytic activity of InVO₄ was tested in the photodegradation of MB under LED light irradiation. As a comparison, the reaction was also carried out using TiO₂ and pristine InVO₄. As shown in Figure 6(a), the removal of MB was negligible under photolysis conditions. A similar observation was noticed when TiO₂ was used as the photocatalyst. The adsorption percentage of the photocatalysts were in the order of 0.13Cu-InVO₄ (62.3%) > 0.10Cu-InVO₄ (48.6%) > 0.15Cu-InVO₄ (45.9%) > 0.06Cu-InVO₄ (33.4%) > InVO₄ (10.4%). The enhancement in the adsorption properties is ascribed to a relatively high V⁴⁺/V⁵⁺ ratio (He et al. 2018), oxygen vacancies and defects induced from the Cu doping (Sun et al. 2019). In addition, Cu itself (Ma et al. 2010; Tan et al. 2011) and the surface hydroxyl groups can enhance the adsorption of organic pollutants (Fu et al. 2011; He et al. 2018).

The removal of MB by the synergetic effect of adsorption and photocatalysis was highest for 0.13Cu-InVO₄ (78.6%) followed by 0.10Cu-InVO₄ (68.2%), 0.15Cu-InVO₄ (59.4%), 0.06Cu-InVO₄ (45.3%), and pristine InVO₄ (10.1%). The insensitivity of the pristine InVO₄ towards visible light is attributed to its wide bandgap (3.0 eV), which prevented the
electrons from being excited to the VB from the CB under visible light irradiation. In addition, semiconductors with a wide bandgap have a high rate of recombination of $e^-/h^+$ pairs. The Cu dopant has been identified to play a few crucial roles: (1) it increases the sensitivity of the photocatalysts towards visible light absorption by reducing the bandgap, and (2) it acts as an electron reservoir, therefore prolonging the lifespan of photoinduced charge.

The kinetics of the photodegradation of MB using TiO$_2$, pristine InVO$_4$ and $x$Cu-InVO$_4$ ($x = 0.06$–$0.15$) were fitted into pseudo-first- (Figure 6(b)) and pseudo-second-order kinetics (Figure 6(c)) models. The Langmuir-Hinshelwood constants are provided in Table 1, where $k$, $k'$, and $R$ represent pseudo-first-order reaction rate constants ($\text{min}^{-1}$), the pseudo-

**Figure 6** | (a) The MB removal efficiency by TiO$_2$, photolysis, pristine and Cu doped InVO$_4$ with the corresponding (b) pseudo-first-order and (c) pseudo-second-order kinetics of MB photocatalytic degradation by TiO$_2$, pristine and Cu doped InVO$_4$ ([MB] = 5 mg L$^{-1}$, catalyst dosage = 50 mg and pH = 6, LED irradiation).

**Table 1** | The rate constants and correlation coefficient values of pseudo-first- and pseudo-second-order kinetics for the used catalysts for MB degradation

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pseudo-first-order</th>
<th>Pseudo-second-order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k \times 10^{-3}$ (min$^{-1}$)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>–</td>
<td>0.88005</td>
</tr>
<tr>
<td>InVO$_4$</td>
<td>–</td>
<td>0.0336</td>
</tr>
<tr>
<td>0.06Cu-InVO$_4$</td>
<td>1.82</td>
<td>0.98341</td>
</tr>
<tr>
<td>0.10Cu-InVO$_4$</td>
<td>4.24</td>
<td>0.99552</td>
</tr>
<tr>
<td>0.13Cu-InVO$_4$</td>
<td>4.90</td>
<td>0.99823</td>
</tr>
<tr>
<td>0.15Cu-InVO$_4$</td>
<td>2.58</td>
<td>0.99346</td>
</tr>
</tbody>
</table>
second-order reaction rate constant (L mol\(^{-1}\) min\(^{-1}\)), and correlation regression coefficient, respectively. The negligible rate constant value of pristine InVO\(_4\) and negative R\(^2\) can be explained by the desorption of some traces of the MB molecules without undergoing photodegradation when exposed to the LED light irradiation due to its relatively large bandgap (3.0 eV) and fast recombination rate of e\(^-\)/h\(^+\) pairs. The \(x\)-Cu-InVO\(_4\) (\(x = 0.06\)–\(0.15\)) photocatalysts showed good fitting using pseudo-second-order kinetics as their correlation regression coefficient (R) values were closer to 1 compared to those of pseudo-first-order. Since only a handful of researchers have reported the modification of InVO\(_4\), it is difficult to pinpoint the exact reasons for \(x\)-Cu-InVO\(_4\) (\(x = 0.06\)–\(0.15\)) pseudo-second-order kinetics rather than pseudo-first-order kinetics. The photocatalysts’ distinct physicochemical properties compared to InVO\(_4\) and the conditions used during the photocatalytic reaction (i.e., light source, precursor concentration, treatment temperature and time) may have favoured pseudo-second-order kinetics. All the \(x\)-Cu-InVO\(_4\) (\(x = 0.06\)–\(0.15\)) photocatalysts illustrated superior photo-activity, and Cu doping was found to significantly increase the rate constants compared to pristine InVO\(_4\). The maximum rate constant was obtained with 0.13Cu-InVO\(_4\) catalyst with a pseudo-second-order rate constant of 0.0197 min\(^{-1}\). Due to the enhanced photocatalytic activity of 0.13Cu-InVO\(_4\), it was used for the optimization of other parameters.

**Effect of initial solution pH on MB removal**

The effect of the solution pH on the photocatalytic degradation of MB was investigated in the range of pH 2–9. The MB removal profiles are shown in Figure 7(a). At pH values below the PZC of the 0.13Cu-InVO\(_4\) (pH 2.4), the surface of the catalyst will be protonated and becomes positively charged, whereas, at pH values above 2.4, the concentration of OH\(^-\) ions in the MB solution will increase and cause the deprotonation of the catalyst surface and amplify a negatively charged catalyst.
surface (Zawawi et al. 2017). The removal of MB was highest when the pH was increased from pH 2 to pH 6. At this range, the electrostatic interactions between the cationic MB and negatively charged 0.13Cu-InVO₄ surface were strongest. As a result of the strong electrostatic interactions, more MB molecules will be adsorbed on the catalyst for photocatalytic reactions. The removal percentage started to decrease significantly when the pH was increased. The drop in the MB removal is possibly due to forming a stable hydroxyl-MB complex, reducing the electrostatic attraction between the dye molecules and the 0.13Cu-InVO₄ surface (Sabar et al. 2020). The formation of the hydroxyl-MB complex was prominent at pH 9 compared to pH 7 due to the solution’s high pH and a larger amount of −OH ions that will compete with the catalyst over bonding with MB molecules.

Effect of irradiation source on MB removal

The ability of 0.13Cu-InVO₄ in removing MB under solar irradiation was investigated as well. The pseudo-second-order rate constant was higher when solar irradiation was used. As shown in Table 2, the intensity of visible light irradiation was five times higher in solar radiation compared to the LED light. In addition, solar light contains 29.7–34.4 W m⁻² UV, whereas the UV light was not detected in the LED light. The combination of visible and UV light can produce more reactive oxygen species compared to visible light alone (Zawawi et al. 2017). Hence, higher photocatalytic activity was observed. However, the correlation coefficient (R²) for solar light is lower than that of the LED light (Figure 7(b)). The lower R²-value is ascribed to the inconsistency of solar radiation due to atmospheric and weather changes. The LED light radiation has several advantages compared to solar radiation. Besides being stable, it has no UV portion and poses fewer cancer risks to humans (Sabar et al. 2020).

In addition, the LED lights are reliable, inexpensive, and produce high light intensity under relatively low electrical power with less heat generated than fluorescence and mercury lamps. Due to these facts, the use of LED lights in photocatalytic systems has been growing rapidly during the last few years (Salehi et al. 2012; Izadifard et al. 2015; Jo & Tayade 2014; Reza et al. 2017; Alkaykh et al. 2020; Hameeda et al. 2020).

Effect of photocatalyst mass on MB removal and mineralization degree

The photocatalyst mass effect on the removal and mineralization degree of MB is shown in Figure 7(d). The MB removal increased from 76.2% to 96.0% when the photocatalyst mass was increased from 50 to 75 mg. The further increase of the mass resulted in the complete removal of the MB molecules. As the amount of photocatalyst mass is increased, more surface-active sites are available for the adsorption of the dye molecules and absorption of photons. This will eventually lead to a higher number of dye molecules reacting on the catalyst surface, and more active species will be formed (Kiwaan et al. 2020). Since sulfur is positioned at the centre of the MB triaromatic rings, the formation of SO₄²⁻ ions indicates the cleavage of the resonance stabilized aromatic rings (Abdul-Rahman et al. 2019). Therefore, the mineralization degree was evaluated by monitoring the formation of SO₄²⁻ traces in the reaction mixture.

The SO₄²⁻ concentration was found to be 0.592, 1.303, 1.363, 0.703, and 0.05 mg L⁻¹ when the photocatalyst mass was 50, 75, 100, 125, and 150 mg, respectively. Since the molecular weights of MB and SO₄²⁻ are 319.85 g mol⁻¹ and 90.06 g mol⁻¹, respectively, the complete mineralization of 5 mg L⁻¹ of MB would produce 1.41 mg L⁻¹ of SO₄²⁻ ion. Therefore, the mineralization degree of MB was found to increase significantly from 42.0% to 92.4% when the mass was increased from 50 to 75 mg and further increased to 96.7% when 100 mg of the photocatalyst was used. Although the removal of MB remained 100% when the photocatalyst mass was above 100 mg, the concentration of SO₄²⁻ was significantly reduced to 0.703 mg L⁻¹ and 0.05 mg L⁻¹, corresponding to a mineralization degree of 49.86% and 3.55%, respectively. Excessive photocatalyst mass increases the light scattering and lowers the light penetration into the photocatalyst surface (Van de Moortel et al. 2020). Besides, particle agglomeration (particle-particle interaction), which usually takes place at a high concentration of photocatalyst particles, would lower the total surface area of the photocatalyst in the system (Tetteh et al. 2020). As a result, the mineralization process will be suppressed. At the same time, the removal remained at 100% due to higher adsorption efficiency.

<table>
<thead>
<tr>
<th>Irradiation source</th>
<th>Vis Intensity (W m⁻²)</th>
<th>UV Intensity (W m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LED</td>
<td>68.9</td>
<td>0.00</td>
</tr>
<tr>
<td>Solar</td>
<td>358–389</td>
<td>29.7–34.4</td>
</tr>
</tbody>
</table>
Free radicals scavenging studies

Scavenging tests were performed to identify the main active species responsible for the photocatalytic degradation of MB using 0.13Cu-InVO₄. Isopropyl alcohol (IPA), ethylenediaminetetraacetic acid (EDTA), and ascorbic acid (AA) were used as scavengers for ·OH, h⁺, and O₂, respectively. Figure 8(a) illustrates the effect of chemical scavengers on the photocatalytic activity of 0.13Cu-InVO₄. The addition of IPA and EDTA caused a slight decrease in the MB removal percentage, whereas AA did not affect the photodegradation efficiency. The results indicate that ·OH and h⁺ are the main active species in the photodegradation, whereas O₂ had no contribution to the photodegradation process. In ·OH and h⁺ scavenging cases, the drop in the removal% was low, attributed to the high MB adsorption efficiency.

Proposed photodegradation mechanism

The results obtained from scavenging studies are in good agreement with the findings from the CB and VB calculations. The CB energy (−0.23 eV) of the 0.13Cu-InVO₄ was found to be not negative enough to produce O₂ as compared to the reduction potential of O₂ to ·O₂, which is −0.33 eV (Xiao et al. 2013; Imam et al. 2018). However, the CB energy (−0.23 eV) is more negative than the reduction potential of O₂/H₂O₂ (+0.695 eV − +0.682 eV). Hence, the photocatalyst can reduce O₂ to H₂O₂, which then will react with the e⁻ to form ·OH (Jiang et al. 2012; Wen et al. 2017; Karbasi et al. 2020). The positively charged holes of VB (h⁺) are more positive than the reduction potential of OH⁻ /OH (+2.38 eV) (Hou et al. 2017; Huang et al. 2020; de Melo Santos Moura et al. 2021), which allows it to oxidize hydroxyl ions to form hydroxyl radicals. In addition, the h⁺ is a strong oxidizing agent that can directly degrade MB (Garcia-Segura & Brillas 2017). Based on these findings, a possible pathway for the degradation process is illustrated in Equations (10)–(16).

\[
\begin{align*}
Cu – InVO₄ + hv & \rightarrow e^- + h^+ & (10) \\
e^- + Cu^{2+} & \rightarrow Cu^+ & (11) \\
2e^- + O₂ + 2H^+ & \rightarrow H₂O₂ & (12) \\
e^- + H₂O₂ & \rightarrow ·OH & (13) \\
h^+ + OH^- & \rightarrow ·OH & (14) \\
·OH + MB & \rightarrow CO₂ + H₂O & (15) \\
h^+ + MB & \rightarrow CO₂ + H₂O & (16)
\end{align*}
\]

First, the visible light absorbed by the catalyst will lead to the migration of electrons from the VB to the CB (e⁻), leaving positively charged holes in the VB (h⁺) (Equation (10)). Instead of direct recombination with h⁺, the photo-excited electrons...
will be trapped by the doped Cu$^{2+}$ by reducing it to Cu$^+$ (Cu$^{2+}$/Cu$^+$ : + 0.161 eV vs. NHE) (Equation (11)), which will extend the lifetime of the e$^-$/h$^+$ species, allowing it to react with other species (Wetchakun et al. 2017). Then, the e$_{CB}$ will react with the O$_2$ and H$^+$ to form H$_2$O$_2$, which will eventually form 'OH (Equations (12) and (13)). On the other hand, the h$^+$ may undergo two separate reactions; first, it will directly react with the MB molecules to oxidize and mineralize them (Equation (16)). Second, h$^+$ will also react with the available hydroxyl anions (OH$^-$) in the solution to form 'OH (Equation (14)). Finally, the 'OH produced will react with the MB molecules and degrade them into harmless products that will eventually turn into CO$_2$ and water (Equation (15)). The results are summarized and illustrated in Figure 8(b).

**Reusability studies**

Reusability studies were carried out to determine the regeneration efficiency and stability of 0.13Cu-InVO$_4$. Prior to reusability, the 0.13Cu-InVO$_4$ was washed with alkaline water (pH 11–12) to remove the adsorbed MB. The 0.13Cu-InVO$_4$ was found to be deactivated after only one cycle, as shown in Figure S5(a). The adsorption efficiency of the used 0.13Cu-InVO$_4$ was even less than that of fresh, pristine InVO$_4$. The spent 0.13Cu-InVO$_4$ was re-characterized using FT-IR, XRD, ICP-OES, and XPS to identify the cause of the deactivation. The complete removal of MB from the photocatalyst surface was confirmed by the FT-IR analysis (Figure S5 (b)). The XRD analysis of the spent photocatalyst did not indicate any crystal structural change compared to the fresh diffractogram as illustrated in Figure S5(c).

The ICP-OES analysis detected vanadium (3.902 mg L$^{-1}$) and copper (0.326 mg L$^{-1}$) in the photocatalytic reaction mixture. The significant leaching of these species is believed to be due to excessive O$_2$ vacancies that would weaken the bonds between the atoms, causing leaching of V and Cu species. Another reason is that V$^{4+}$ species are the prominent vanadium species in the 0.13Cu-InVO$_4$ as proven by XPS, with a molar ratio of 0.704 of V$^{4+}$/V$^{5+}$. Since the original oxidation state of vanadium in InVO$_4$ is V$^{5+}$, the presence of high moieties of V$^{4+}$ species would destabilize the structure and weaken the V–O–In bonds due to the unnatural structure of the semiconductor. In addition, crystal size and lattice distortion calculations obtained from XRD results showed that the crystal size of 0.13Cu-InVO$_4$ increased from 43.98 nm to 73.29 nm and the orthorhombic lattice distortion (a/b ratio) slightly decreased from 0.67444 to 0.67187. The changes suggest that the crystals undergo an aggregation process to form larger crystals with less lattice distortion and better stability to overcome the significant loss of V atoms from the sample.

Figure S6(a) illustrates the comparison of the overall XPS scan between the freshly synthesized 0.13Cu-InVO$_4$ vs. the used 0.13Cu-InVO$_4$, and narrow scans of In3d (Figure S6(b)), V2p (Figure S6(c)), and O1s (Figure S6(d)). Table S4 provides detailed information regarding the oxidation states and elemental composition of fresh and used 0.13Cu-InVO$_4$. As evident in Figure S6, the overall scan comparison shows that both used and fresh 0.13Cu-InVO$_4$ comprise the same elemental composition of In, V, and O, corresponding to InVO$_4$, and C resulting from the instrumental environment. Moreover, no peaks ascribed to sulfur, nitrogen, or chloride were observed, further confirming the complete removal of the adsorbed MB from the photocatalytic reaction. In addition, leaching of V was also confirmed as its atomic% dropped from 16.8% to 13% and V/In molar ratio significantly fell from 0.95 to 0.61 (Table 3). The decrease in O/In molar ratio can be ascribed to V leaching. When the vanadium atoms were leached, the oxygen atoms bonded to them leached as well. This also explains the decrease in the lattice oxygen portion (increase in O$_{ads}$/O$_{latt}$ molar ratio).

The V$^{4+}$/V$^{5+}$ molar ratio has significantly dropped by almost 81% after the photocatalytic degradation. The drop indicates that most of the V atoms that were leached are V$^{5+}$ species. As previously mentioned, V$^{4+}$ surface species are highly crucial in photocatalytic reactions, as they provide active surface sites (Wang et al. 2013; He et al. 2018). Based on the obtained results, it can be concluded that the loss of adsorption and photocatalytic abilities of InVO$_4$ are mainly attributed to the leaching of surface V$^{4+}$ moieties coupled with the loss of Cu$^{2+}$ dopants. These findings also confirm that V$^{4+}$ species were the main contributors to the photocatalytic activity of InVO$_4$. Additionally, considering V/In weight ratios of pristine fresh InVO$_4$ and used 0.13Cu-InVO$_4$ being equal to 0.6011 and 0.4734, this explains the deactivation of used 0.13Cu-InVO$_4$.

| Table 3 | The elemental composition of fresh and used 0.13Cu-InVO$_4$ using XPS |
|---|---|---|---|---|---|---|---|
| In3d at.% | V3p at.% | O1s at.% | V/In | O/In | O$_{ads}$/O$_{latt}$ | V$^{4+}$/V$^{5+}$ |
| Fresh catalyst | 17.68% | 16.80% | 65.52% | 0.95 | 3.71 | 0.51 | 0.70 |
| Used catalyst | 21.33% | 12.96% | 65.71% | 0.61 | 3.08 | 0.62 | 0.13 |
To further investigate the chemical changes that may have occurred, the positions of deconvoluted In3d, V3p, and O1s peaks are compared and presented in Table S4. It can be noticed that In3d and O1s peaks shifted slightly to higher binding energy values, whereas V2p peaks all experienced a shift towards lower binding energies. Chemical shifts in XPS indicate changes in surface compositions and oxidation states. In general, shifting to higher binding energy occurs due to the decrease of the electron density on the respective element. Therefore, the positive shifting of O1s and In3d peaks can be explained by the following: in the bonds of In–O–V–O–In of InVO4, when V is oxidized from V4+ to V5+, the electron density around oxygen and indium atoms will drop because of the loss of an electron from the neighbouring V atoms. The O1s peak shift (+0.26 eV and +0.20 eV) was relatively higher than that of In3d (+0.17 eV and +0.15 eV) because the O atoms are directly linked to the V atom, making it more affected by the changes in the oxidation states of vanadium. As for the opposite chemical shift behaviour of V2p peaks, when V4+ moieties were lost and V5+ species became the prominent, vanadium oxidation state, therefore becoming less electron-dense, consequently, neighbouring In and O atoms became relatively more electron-dense compared to V atoms, hence causing the V2p peaks to experience a negative shift in binding energy values.

CONCLUSION

In this work, Cu doped InVO4 was successfully synthesized via a facile one-pot hydrothermal synthesis technique. The bandgap of InVO4 was found to drop with the increase in Cu content due to the formation of an intermediate energy level (Cu2+/Cu+). Due to the low Cu concentration used, the surface area, particle size, and morphology of the synthesized photocatalysts were not significantly influenced by the modifications. However, the PL phenomena and the crystal structure were found to be significantly influenced by Cu doping. The XRD analysis suggests that Cu2+ prefers to substitute the V5+ at low doping amounts, whereas at higher concentration, both In3+ and V5+ started to be substituted; however, with more tendency towards V5+ position replacement. The synergistic effect of adsorption and photodegradation due to the presence of Cu dopants, the presence of V4+ moieties, and the O-deficits on the catalyst surface significantly enhanced the photocatalytic activity of the InVO4. The photodegradation of 0.13Cu-InVO4 was best described by pseudo-second-order kinetics. The MB removal’s optimum conditions were pH = 6, MB initial concentration of 5 mg L⁻¹, and nanocomposite mass of 100 mg, which displayed a complete MB removal with >96% mineralization degree after 120 minutes of LED light radiation. The poor reusability of 0.13Cu-InVO4 is ascribed to the leaching of Cu2+ and V4+ species.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support received from Universiti Sains Malaysia Research University Grant (RUI) (1001/PKIMIA/8011083).

DECLARATION OF COMPETING INTEREST

The authors have no competing interest to declare.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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First received 19 March 2021; accepted in revised form 13 June 2021. Available online 24 June 2021