



Development of CuCr_2O_4 nanocomposite adopting decoration with polyaniline for acridine orange dye degradation

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Abstract

In this investigation, polyaniline@ CuCr_2O_4 nanocomposites possessing diverse mass proportions of polyaniline (PANI): CuCr_2O_4 were fabricated. The photocatalytic action of the diverse synthesized specimens throughout the photocatalytic decoloration of acridine orange beneath Vis light illumination was elucidated. Consolidating polyaniline to CuCr_2O_4 nanospheres diminishes their specific surface areas from 100 to 90 m^2/g . TEM micrographs acknowledged that both CuCr_2O_4 and polyaniline@ CuCr_2O_4 nanocomposites have arisen as compatible nanospherical. It has been conducted that incorporating PANI to CuCr_2O_4 photo-catalyst did not alter the nanocomposites structure of the base CuCr_2O_4 . Furthermore, the microscopic content loading of PANI onto the surface of CuCr_2O_4 makes it hard to be clearly monitored. The photocatalytic disintegration of acridine orange dye underneath Vis light illumination practicing 0.06% polyaniline/ CuCr_2O_4 nanocomposites has reached 100% after 40 min adopting 2.0 g/L photo-catalyst dosage.

Keywords CuCr_2O_4 · PANI · Visible photo-catalyst · Acridine orange dye

Introduction

In the contemporary society, as long as there is population growth and expanding diverse industries there is an enlarged interest regarding environmental deterioration. Accordingly, many reviews have been assigned to expand highly adequate environmental degeneration approaches (Reddy et al. 2016; Rani et al. 2017; Haghghat Mamaghani et al. 2017; Szczepanik 2017). One of the most extensive compounds that engender environmental pollution is acridine orange (AO) dye. Acridine orange is a compound that could be utilized for diverse purposes like dyeing, lithography, leather manufacturing and printing ink (Xie et al.

2000). In addition, acridine orange (AO) dye has diverse biological applications (Girish et al. 2017). Simple methods of wastewater treatment failed to remediate acridine orange (AO) dye. Actually, the existence of this dye in wastewater poses a contemplative issue as it represents a major origin of aquatic pollution (Faisal et al. 2007). And so, assisting efficient design to remove this pollutant from aquatic environment has become an issue of great concern. Discrete regimes have been devoted to remediate this dye from environment including; advanced oxidation, electrochemical treatment, photolysis, chemical precipitation, chemical oxidation, etc. (Peng and Fan 2005). As long as it has great efficacy, advanced oxidation has been developed as one of the most meaningful approaches for dye deportation from wastewater. Obviously, advanced oxidation technique depends primarily on generation of active hydroxyl radicals by the aid of numerous manners like TiO_2 -interfered photocatalysis and $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$, $\text{H}_2\text{O}_2/\text{UV}$, $\text{H}_2\text{O}_2/\text{Vis}$ photolysis. Photo-catalysis, especially that of heterogeneous kind, has become one of the most relevant techniques to treat wastewater as it could effectively degrade pollutants beneath mild conditions and low-cost expenses generating harmless compounds (Szczepanik 2017; Chen and Cao 2005; Faisal et al. 2019). The heterogeneous photocatalyst should acquire so low bandgap energy (less than 3.0 eV) that it could absorb

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solar energy and hence it would be adopted in diverse applications (Wang et al. 2017). Nevertheless, the well-known photocatalysts (ZnS, ZnO, and TiO₂) that absorb only in UV zone are noticeable as impoverished photo-catalyst beneath Vis light irradiation (Girish et al. 2017; Faisal et al. 2007; Peng and Fan 2005). Therefore, several attempts have been performed to design efficient photocatalysts in the Vis zone (Wang et al. 2017; An et al. 2016; Meng and Zhang 2016; Sohabi et al. 2017; Aljhdali et al. 2018; Sobahi et al. 2018; Baoum et al. 2018; Sobahi and Amin 2019a, b). Among the recently designed photocatalysts for various purposes like super-capacitors, photocatalytic destruction of dyes, thermal decomposition reactions, and photocatalytic hydrogen evolution is copper chromite (CuCr₂O₄) photo-catalyst that acquires narrow bandgap energy (Yan et al. 2009; Yuan et al. 2014; Acharyya et al. 2015a, b, c; Paul et al. 2015; Sanoop et al. 2015; Mageshwari et al. 2015; Ma et al. 2016). Numerous successful approaches have been investigated to fabricate CuCr₂O₄ like; sol–gel (Lee et al. 2016), solid-state (Arboleda et al. 2014), co-precipitation (Delmon 2007) and hydrothermal (George and Sugunan 2008) regimes. Some features restrain the capability CuCr₂O₄ to be adopted in various applications like its limited light absorption. Thus, the challenge is the development of an efficient strategy to boost the photocatalytic activity of CuCr₂O₄ by modifying its efficiency to absorb light. Polyaniline (PANI) has been devoted to the photocatalytic operations as a result of its amazing aspects like its great capability to absorb Vis light, the exclusive transporting characteristics of its electrons and holes, its low price and the ease methods of its synthesis in comparison to decorating rare metals. Diverse reviews concluded that inclusion of PANI to photo-catalyst could boost the migration efficacy of charge transporters amid photo-catalyst and PANI. Many attempts have been achieved for constructing efficient nanocomposite decorated with polyaniline for example; PANI/BiVO₄ (Shang et al. 2009), PANI/TiO₂ (Radoicic et al. 2017), PANI/ZnO (Zhang et al. 2009), PANI/BiOCl (Wang et al. 2013), Ag₃PO₄@PANI (Liu et al. 2017) and PANI@CdS (Zhang and Zhu 2010). And so, CuCr₂O₄ could be modified via doping with PANI and the modification may involve extension of its light absorption zone as well as enhancement of the separation of the charge carriers which certainly leads to improved photocatalytic action. In this investigation, PANI/CuCr₂O₄ nanocomposite of excellent capability towards Vis light absorption has been established. The photocatalytic activity of the fabricated nanocomposite has been assessed via destruction of acridine orange dye beneath Vis light. The interface interaction amid CuCr₂O₄ and PANI might be the reason for the boosted photocatalytic destruction performance over PANI/CuCr₂O₄ nanocomposite. In addition, long-wavelength of illuminated light has been adopted to assure that inclusion of PANI broadens the light absorption zone with great efficacy.

Materials and experimental designs

Materials

All adopted chemicals in this examination were of analytical grade and were utilized as received. Aniline, absolute ethanol, ammonium persulphate and citric acid of about 99.5% purity were utilized. In addition, highly pure (96%) sodium hydroxide was applied. Besides, two different nitrate salts (copper nitrate tri-hydrate and chromium nitrate nonahydrate) and tetrahydrofuran (THF) were handled.

Photocatalysts Fabrication

Fabrication of PANI

The polymerization process at mild temperature has been addressed to attain PANI. Deionized water (80 mL) was utilized to dissolve definite quantity of citric acid and the resultant mix was agitated for about 20 min. After that, aniline (0.5 mL) was introduced to the previously prepared solution and the resultant mixture was agitated for about 0.5 h. Then, 20 mL of ammonium persulfate solution (0.25 M) was incorporated dropwise to the produced mix and the attained solution was agitated for 24 h. The temperature all over the investigation was kept between 0–5 °C. After all, the specimen was gathered, washed with ethanol many intervals and then left to dry for 6 h at 60 °C. Polyaniline (PANI) powder of green color has been received.

Fabrication of CuCr₂O₄ nanospherical

Deionized water (50 mL) was utilized to dissolve chromium nitrate nonahydrate (15.4 g) and copper nitrate tri-hydrate (5.54 g) to receive 1 M solution of the analogous nitrates. The resultant solution was intermixed with deionized water together with 1 M sodium hydroxide solution (50 mL) at 60 °C. pH was adjusted to be 7 amid precipitation. After reaction completion, the precipitate was left in the mother liquor for 5 h. After that, the produced system was dried at 90 °C and the yield was fired for 5 h at 500 °C to receive CuCr₂O₄ nanospherical.

Fabrication of CuCr₂O₄ nanocomposite decorated with PANI

CuCr₂O₄ photocatalysts decorated with PANI were designed at ambient temperature. CuCr₂O₄ powder (2.0 g) was introduced to 0.22 g L⁻¹ PANI/THF solution (0.75 mL) and the resultant mix was dissolved in ethyl alcohol (30 mL). After that, 2 M sodium hydroxide (15 mL) was incorporated dropwise to the former solution under constant agitation

that extended for 4 h. The attained solution was washed at numerous intervals with deionized water and left to dry for 24 h at 60 °C. Evidently, the gathered specimen of PANI/CuCr₂O₄ was designated as 0.02% PANI/CuCr₂O₄ nanocomposite (mass proportion of PANI: CuCr₂O₄ = 0.02%). In a similar way, different PANI/CuCr₂O₄ nanocomposites acquiring diverse mass proportions of PANI:CuCr₂O₄ as 0.04%, 0.06% and 0.08% were fabricated and designated as 0.04% PANI/CuCr₂O₄, 0.06% PANI/CuCr₂O₄ and 0.08% PANI/CuCr₂O₄ nanocomposites, respectively.

Characterization

XRD appliance was applied to interpret the crystalline phases of the fabricated specimens. Whereas, FTIR spectrometer was appropriated to register the transmittance mode of the FTIR spectra at room temperature. For X-ray photoelectron spectroscopy (XPS) assessments, a Thermo Scientific spectrometer was supported. In addition, transmission electron microscopy (TEM) of JEOL kind was devoted to analyzing the morphology as well as the architecture of the diverse fabricated specimens. Chromatech appliance of Nova 2000 kind was practiced to interpret the textural aspects of the formulated specimens. Moreover, bandgap magnitudes were assessed (estimated from diffuse reflectance spectra) via covering UV–Vis–NIR spectrophotometer. The fluorescence spectrophotometer (Shimadzu model) was supported to record the photoluminescence emission spectra (PL). Finally, Zahner Zennium electrochemical workstation was affirmed to register the transient photocurrent measurements.

Photocatalytic Examination

In this examination, an acridine orange (AO) dye was chosen as a typical example of pollutant to test its photocatalytic destruction over CuCr₂O₄ nanocomposite decorated with polyaniline. A concentration of 100 ppm corresponding to the degraded dye has been chosen and a Xe-arc lamp, that emits UV–Vis radiation, was selected to be the light source. In the photocatalytic investigation, we allow only the Vis light to be absorbed by the tested photocatalyst and so, UV light was prevented from absorption via utilization UV cut filter. 0.5 L of the tested dye (100 ppm) was blended with nanocomposite (CuCr₂O₄ decorated with polyaniline) and the system was continuously pumped by air to assure the existence of oxygen all over the reaction. The mix was continuously agitated for 0.5 h in dark to attain equilibrium of adsorption/desorption of the tested dye solution prior to irradiation. After that, the previous system was subjected to irradiation via the mentioned light source for 1 h. after definite intervals, 3 mL of suspension was extracted from the reaction medium. Centrifugation was performed to the withdrawn solution to detach the solid. Hence, UV/Vis/NIR

spectrophotometer was utilized to record the absorbance of the diverse specimens at 492 nm.

Results and discussion

XRD spectra were implemented to diagnose the crystallinity and phase composition of the fabricated neat CuCr₂O₄ as well as PANI@CuCr₂O₄ nanocomposite specimens (Fig. 1). XRD patterns of Fig. 1 reveal the presence of (112) (211) (202) (224) and (303) crystal planes correspond to neat CuCr₂O₄ (JCPDS 05-0657). On the other hand, no prescribed peaks of PANI were registered in the diffractograms of Fig. 1. This observation could be attributed to the very limited amount of the applied PANI in the nanocomposite. Furthermore, alteration of the intensities correlated to some diffractograms as a result of boosting the PANI dose has been observed. This alteration in intensity might be associated with the particle size reduction of CuCr₂O₄ nanospherical as the result of enlargement of its degree of dispersion (Zhang et al. 2009).

The occupation CuCr₂O₄ by PANI in the PANI@CuCr₂O₄ nanocomposite might be confirmed through establishing FTIR analyses. Figure 2 exhibits FTIR spectra data of PANI, neat CuCr₂O₄ as well as PANI@CuCr₂O₄ specimens. It is clear that the FTIR spectrum of neat CuCr₂O₄ exhibits a strong absorption peak at 522 cm⁻¹, this peak is associated with the stretching mode of the Cu–O bond (Zhao et al. 2017). Whereas, FTIR spectrum of PANI displays numerous absorption peaks located at 1584, 1496, 1415, 1300 cm⁻¹, 1104 and 617 cm⁻¹. Evidently, existence of quinoid and benzenoid stretching rings could be verified via the appearance of the peaks located at 1584, 1496 and 1415 cm⁻¹. Whereas, stretching vibration mode of C–N corresponding to benzenoid unit might be documented through

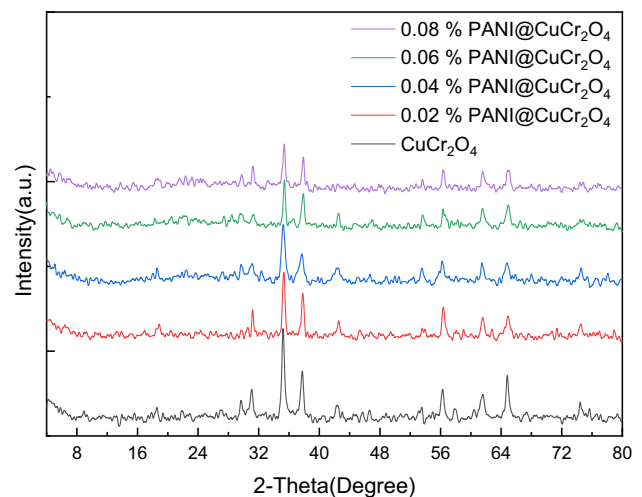


Fig. 1 XRD patterns of CuCr₂O₄ and PANI@CuCr₂O₄ samples

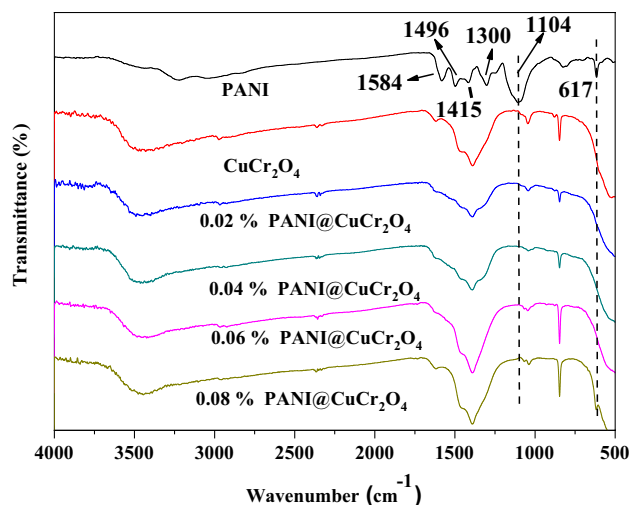


Fig. 2 FT-IR spectra of pure CuCr_2O_4 , PANI and $\text{PANI@CuCr}_2\text{O}_4$ samples

the emerging of the band located at 1300 cm^{-1} . Furthermore, the bands found at 1104 cm^{-1} and 617 cm^{-1} could be associated with C–H bending vibration mode (Zhang et al. 2009; Tanwar et al. 2017). On the other hand, FTIR spectrum of $\text{PANI@CuCr}_2\text{O}_4$ nanocomposite displays two distinct bands at 1104 and 617 cm^{-1} in addition to extra peaks similar to those of pure CuCr_2O_4 photocatalyst. The appearance of distinct absorption peak at 1104 cm^{-1} is associated with the stretching vibration mode of CAN in the benzenoid unit in PANI, whereas, the absorption peak located at 617 cm^{-1} could be correlated to the bending vibration mode of CAH. These findings confirm strongly the habitation of PANI in the fabricated $\text{PANI@CuCr}_2\text{O}_4$ nanocomposite. Obviously, the occurrence of extra peaks in FTIR spectrum of $\text{PANI@CuCr}_2\text{O}_4$ similar to those of pure CuCr_2O_4 affirms the inclusion of PANI to CuCr_2O_4 to fabricate $\text{PANI@CuCr}_2\text{O}_4$ does not alter the skeleton of CuCr_2O_4 .

XPS spectra of 0.06% $\text{PANI@CuCr}_2\text{O}_4$ nanocomposite are displayed in Fig. 3. Figure 3a confirms that $\text{PANI@CuCr}_2\text{O}_4$ nanocomposite specimen enclose Cu, Cr, O, C and N elements within its structure. Whereas, Fig. 3b displays two characteristic spectral peaks located at 935.2 and 954.0 eV and might be correlated to the $\text{Cu}2p$ high-resolution. In fact, $\text{Cu}2p_{3/2}$ and $\text{Cu}2p_{1/2}$ could be verified via the appearance of these peaks (at 935.2 and 954.0 eV, respectively). This finding reflects the oxidation state of Cu^{2+} in 0.06% $\text{PANI@CuCr}_2\text{O}_4$ nanocomposite. On the other hand, Fig. 3c displays two distinct spectral peaks located at 574.5 and 583.9 eV that could be associated with $\text{Cr}2p_{3/2}$ and $\text{Cr}2p_{1/2}$, respectively. This observation confirms the oxidation state of Cr^{3+} in 0.06% $\text{PANI@CuCr}_2\text{O}_4$ nanocomposite. Furthermore, the confirmation of O 1s existence could be achieved via the peak located

at 532.5 eV that reflects the oxidation state of O^{2-} in 0.06% $\text{PANI@CuCr}_2\text{O}_4$ nanocomposite (Fig. 3d). Finally, the presence of polyaniline in the fabricated nanocomposite could be confirmed via the appearance of the peaks located at 400 and 284.7 eV for N 1s and C 1s (Fig. 3e, f, respectively).

Figure 4 exhibits TEM images of pure CuCr_2O_4 as well as $\text{PANI@CuCr}_2\text{O}_4$ specimens. It is elucidated from the data of Fig. 4 that the dominated shape in all illustrated morphologies is the nanospherical morphology. Furthermore, it is noticed that the inclusion of PANI to CuCr_2O_4 has a negative effect on CuCr_2O_4 particle size (Fig. 4b–e). On the other hand, it is noticed that inclusion of different doses of PANI to CuCr_2O_4 , to fabricate various $\text{PANI@CuCr}_2\text{O}_4$ specimens, has no obvious consequence on the morphological structures of the diverse $\text{PANI@CuCr}_2\text{O}_4$ nanocomposites. The tiny dose of PANI explains the absence of the morphology corresponding to PANI in the TEM images of the fabricated $\text{PANI@CuCr}_2\text{O}_4$ nanocomposites.

Figure 5 exhibits HRTEM images for 0.06% $\text{PANI@CuCr}_2\text{O}_4$ specimen. It is concluded from the presence of lattice spacing at 0.476 nm, which characterizes the plane of (101) of CuCr_2O_4 , that the major phases in $\text{PANI@CuCr}_2\text{O}_4$ specimen are CuCr_2O_4 . On the other hand, the very low dose of PANI included in the $\text{PANI@CuCr}_2\text{O}_4$ specimen explains the absence of the lattice spacing corresponding to PANI.

Table 1 depicts the BET values for pure CuCr_2O_4 as well as the diverse $\text{PANI@CuCr}_2\text{O}_4$ nanocomposites. It is clear from the data tabulated in Table 1 that the specific surface areas of pure CuCr_2O_4 , 0.02% $\text{PANI@CuCr}_2\text{O}_4$, 0.04% $\text{PANI@CuCr}_2\text{O}_4$, 0.06% $\text{PANI@CuCr}_2\text{O}_4$ and 0.08% $\text{PANI@CuCr}_2\text{O}_4$ specimens are in the sequence of 100.00, 98.00, 95.00, 93.00 and 90.00 m^2/g . The lower specific surface areas of the specimens accommodating PANI compared to that of the pure CuCr_2O_4 clarifies that inclusion of PANI to CuCr_2O_4 has a negative effect on the specific surface areas corresponding to CuCr_2O_4 .

Figure 6 shows the UV–Vis spectra of the pure CuCr_2O_4 and $\text{PANI@CuCr}_2\text{O}_4$ specimens. It is obvious from the data of Fig. 6 that the absorption zones for the pure CuCr_2O_4 , 0.02% $\text{PANI@CuCr}_2\text{O}_4$, 0.04% $\text{PANI@CuCr}_2\text{O}_4$, 0.06% $\text{PANI@CuCr}_2\text{O}_4$ and 0.08% $\text{PANI@CuCr}_2\text{O}_4$ specimens are corresponding to visible light. Evidently, the bandgap magnitudes of the diverse fabricated specimens could be resolved from their UV–Vis spectral curves (Table 2). The bandgap magnitudes are found to be 2.12, 2.00, 1.92, 1.73 and 1.72 eV corresponding to the pure CuCr_2O_4 , 0.02% $\text{PANI@CuCr}_2\text{O}_4$, 0.04% $\text{PANI@CuCr}_2\text{O}_4$, 0.06% $\text{PANI@CuCr}_2\text{O}_4$ and 0.08% $\text{PANI@CuCr}_2\text{O}_4$ specimens, respectively. Hence, it could be concluded that band gap magnitude of the CuCr_2O_4 specimen is declined when PANI is included in the CuCr_2O_4 to form $\text{PANI@CuCr}_2\text{O}_4$ specimens. In general, decline of bandgap energy brings about

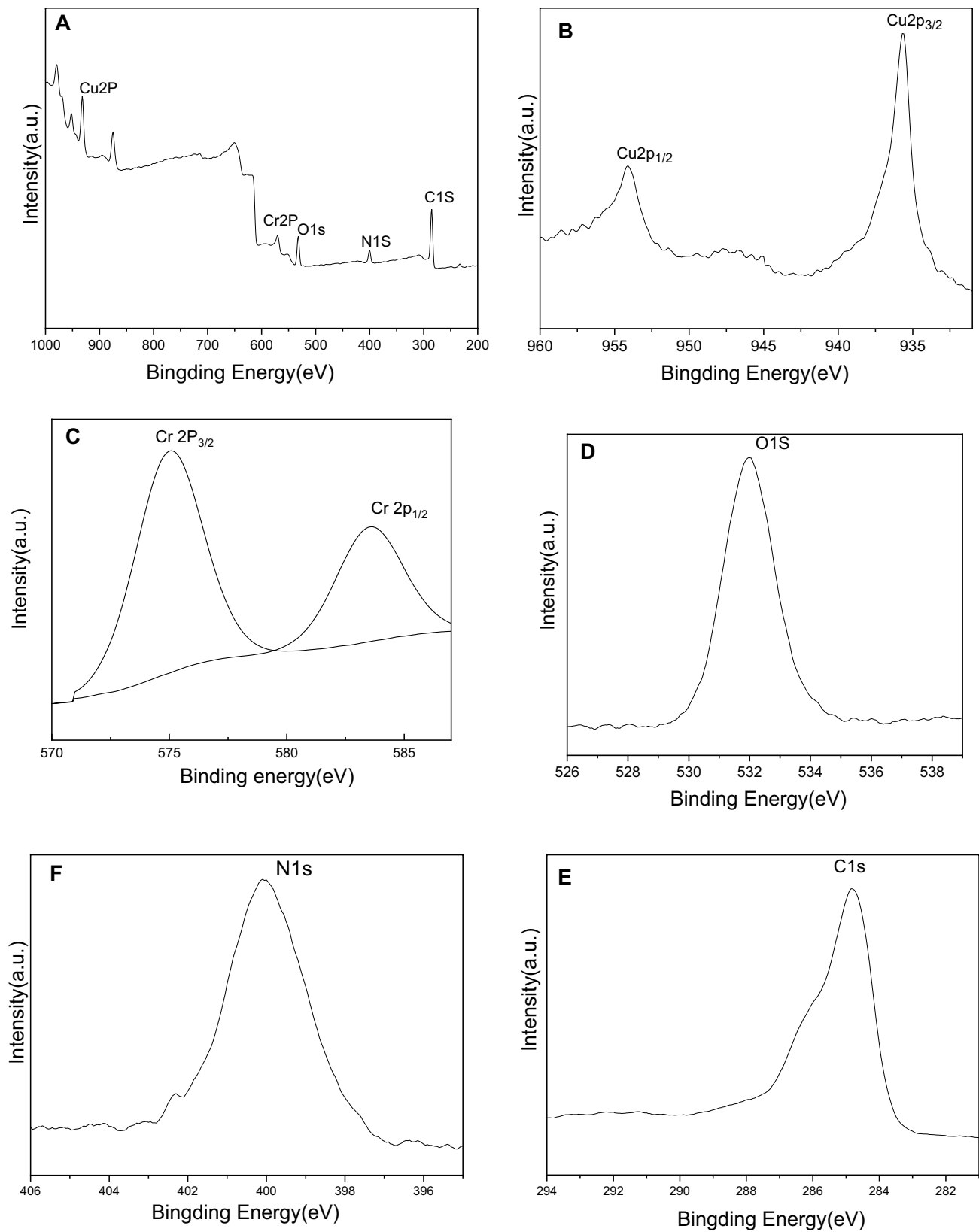


Fig. 3 XPS spectra for survey scan spectra (a), high-resolution spectra of Cu₂P (b), Cr₂p (c), O_{1s} (d), N_{1s} (e) and C_{1s} (f) of 0.06% PANI@CuCr₂O₄ sample

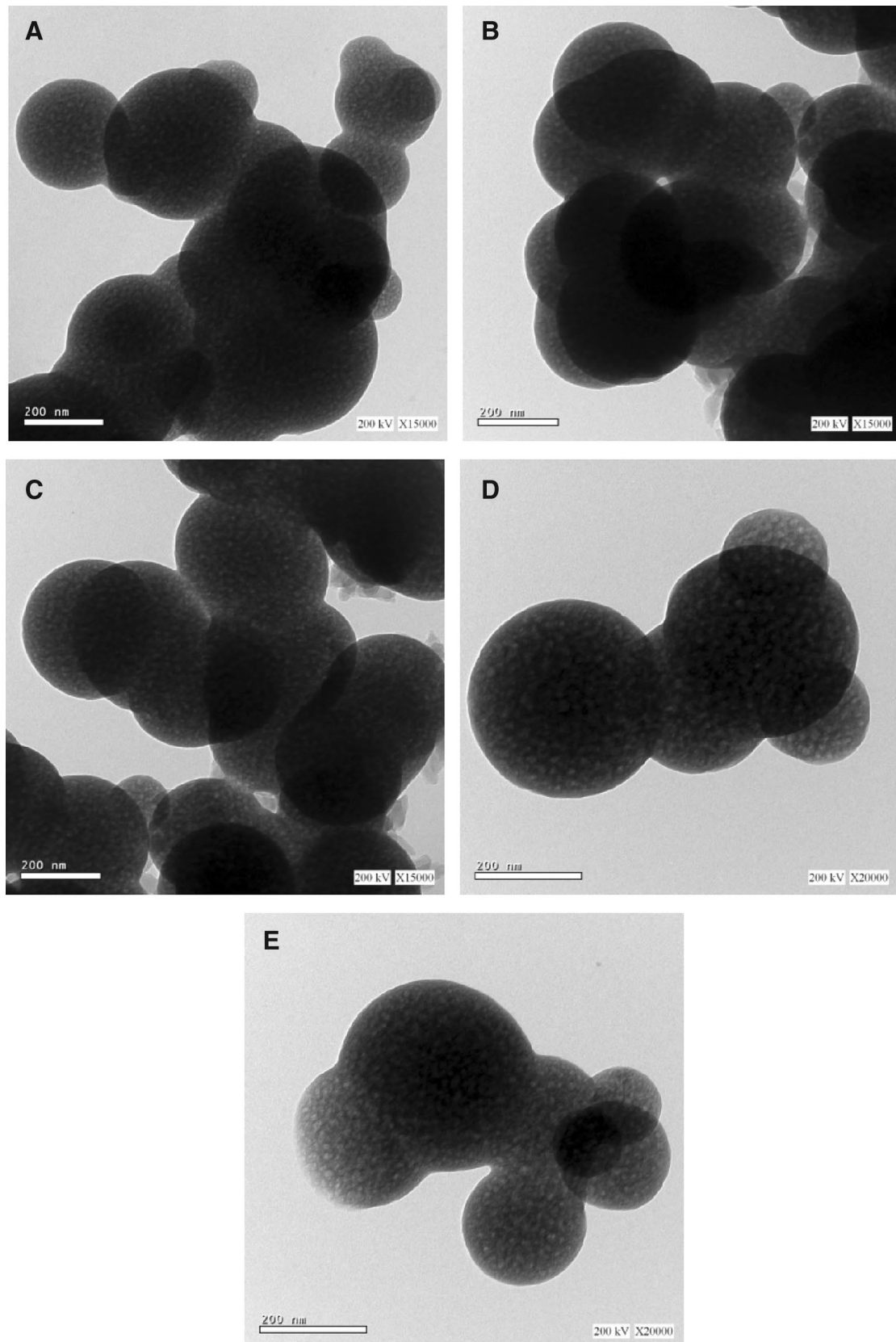


Fig. 4 TEM images of CuCr_2O_4 (a) 0.02% PANI@ CuCr_2O_4 (b) 0.04% PANI@ CuCr_2O_4 (c) 0.06% PANI@ CuCr_2O_4 (d) and 0.08% PANI@ CuCr_2O_4 (e) samples

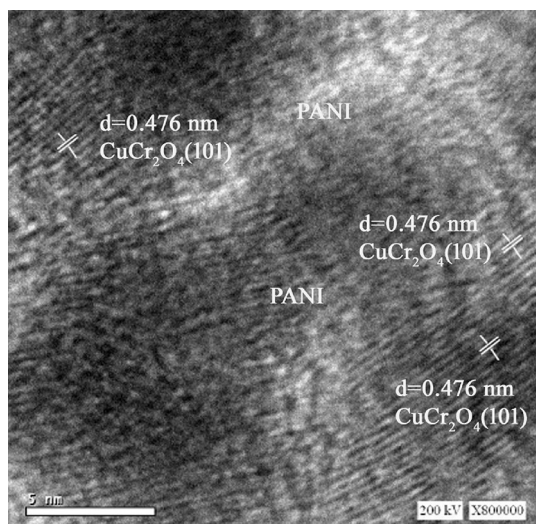


Fig. 5 HRTEM image of 0.06% PANI@CuCr₂O₄ sample

Table 1 BET surface areas of CuCr₂O₄ and PANI@CuCr₂O₄ samples

Samples	BET surface area, m ² /g
CuCr ₂ O ₄	100.00
0.02% PANI@ CuCr ₂ O ₄	98.00
0.04% PANI@ CuCr ₂ O ₄	95.00
0.06% PANI@ CuCr ₂ O ₄	93.00
0.08% PANI@ CuCr ₂ O ₄	90.00

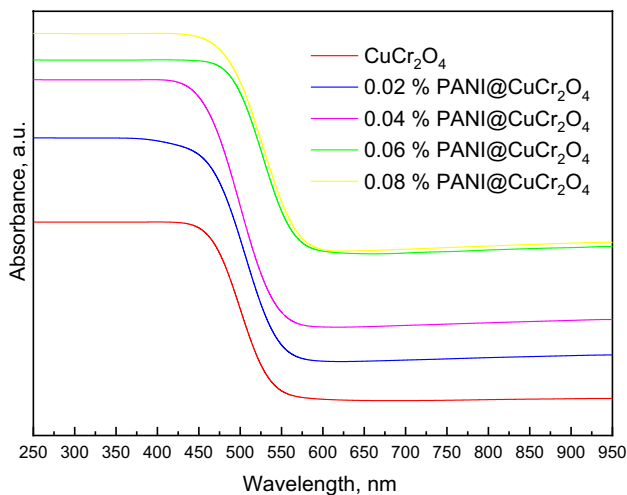


Fig. 6 UV–Vis spectra of the CuCr₂O₄ and PANI@CuCr₂O₄ samples

an enhancement in the photocatalytic reactivity of the fabricated PANI@CuCr₂O₄ nanocomposites.

Table 2 Band gap energies of CuCr₂O₄ and PANI@CuCr₂O₄ samples

Sample	Bandgap, eV
CuCr ₂ O ₄	2.12
0.02% PANI@CuCr ₂ O ₄	2.00
0.04% PANI@CuCr ₂ O ₄	1.92
0.06% PANI@CuCr ₂ O ₄	1.73
0.08% PANI@CuCr ₂ O ₄	1.72

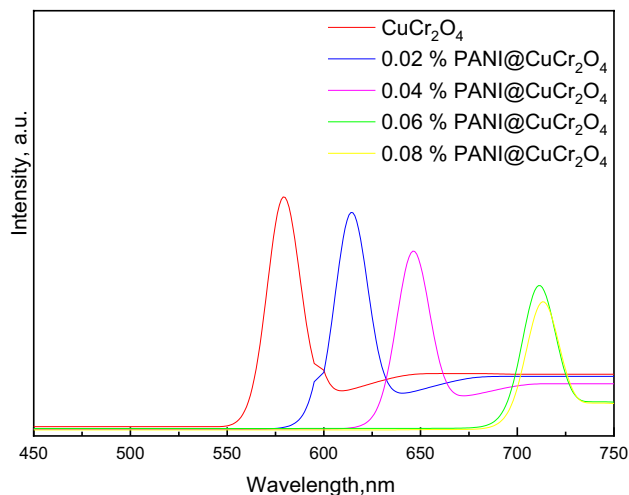


Fig. 7 PL spectra of the CuCr₂O₄ and PANI@CuCr₂O₄ samples

The PL spectra of pure CuCr₂O₄, as well as PANI@CuCr₂O₄ specimens, are interpreted in Fig. 7. The outcomes of Fig. 7 clarify that the CuCr₂O₄ specimen possesses high emission peak intensity announcing that the reconsolidation speed of the photo-generated charge transporters of the pure CuCr₂O₄ specimen is high. Whereas, the intensities of emission peaks for the diverse PANI@CuCr₂O₄ nanocomposites are small when correlated to that of the pure CuCr₂O₄ specimen. It is noticed that the intensities of the different peaks are in the order of; CuCr₂O₄ > 0.02% PANI@CuCr₂O₄ > 0.04% PANI@CuCr₂O₄ > 0.06% PANI@CuCr₂O₄ > 0.08% PANI@CuCr₂O₄. Accordingly, 0.06% PANI@CuCr₂O₄ specimen possesses the lowest emission peak intensity compared to those of other specimens. Besides, the reconsolidation speed of the photo-generated transporters is very small for the same specimen (0.06% PANI@CuCr₂O₄ sample) that brings about an enhancement of its photocatalytic efficacy.

Transient photocurrent responses of the fabricated CuCr₂O₄ and PANI@CuCr₂O₄ specimens are displayed in Fig. 8. The attained responses reflect that CuCr₂O₄ specimen possesses low photocurrent intensity. This finding suggests that the recombination speed of the photo-generated charge carriers for the CuCr₂O₄ specimen is high. On the

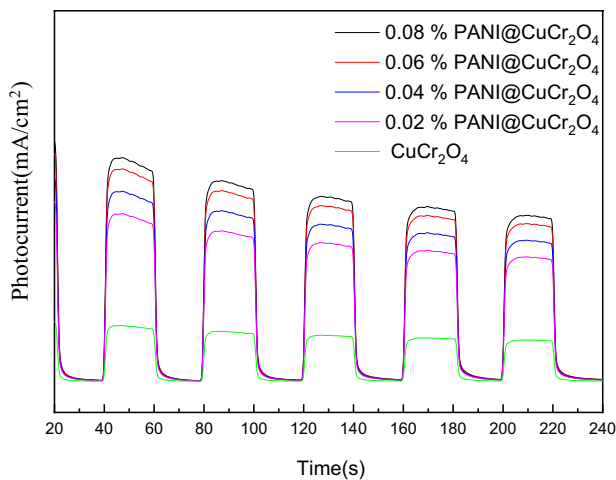


Fig. 8 Transient photocurrent responses of CuCr_2O_4 and $\text{PANI@CuCr}_2\text{O}_4$ samples

contrary, the photocurrent transient responses for the diversity $\text{PANI@CuCr}_2\text{O}_4$ specimens are large when correlated to those of pure CuCr_2O_4 specimens. Furthermore, the transient photocurrent responses corresponding to the diverse fabricated nanocomposites are arranged in the following regulation; $\text{CuCr}_2\text{O}_4 < 0.02\% \text{ PANI@CuCr}_2\text{O}_4 < 0.04\% \text{ PANI@CuCr}_2\text{O}_4 < 0.06\% \text{ PANI@CuCr}_2\text{O}_4 < 0.08\% \text{ PANI@CuCr}_2\text{O}_4$. Hence, it could be terminated that 0.06% $\text{PANI@CuCr}_2\text{O}_4$ specimen possesses the greatest photocurrent response and in a similar way, the greatest photocatalytic efficacy.

Photocatalytic achievement investigation

Destruction of acridine orange (AO) dye has been inspected on the diversity fabricated $\text{PANI@CuCr}_2\text{O}_4$ nanocomposites so to assess their photocatalytic achievement (Fig. 9). The photocatalytic destruction of acridine orange dye was implemented beneath Vis light irradiation. Figure 9 elucidates that when the photocatalytic destruction of acridine orange dye is conducted over CuCr_2O_4 specimen, the destruction speed of the dye is found to be about 60% after 1 h under the consequence of Vis light irradiation. Whereas, the inclusion of 0.02% PANI to CuCr_2O_4 in the fabrication of 0.02% $\text{PANI@CuCr}_2\text{O}_4$ nanocomposite leads to an enhancement in the photocatalytic destruction speed of the dye to 90% after 1 h. Additionally, when the novel nanocomposites (0.04% $\text{PANI@CuCr}_2\text{O}_4$, 0.06% $\text{PANI@CuCr}_2\text{O}_4$, and 0.08% $\text{PANI@CuCr}_2\text{O}_4$) have been endorsed, the destruction speeds of acridine orange dye have been promoted up to 100% after diverse reaction times (60, 50 and 50 min, respectively) beneath Vis light irradiation. The attained data elucidate that 0.06% $\text{PANI@CuCr}_2\text{O}_4$ nanocomposite possesses the greatest photocatalytic efficiencies as compared

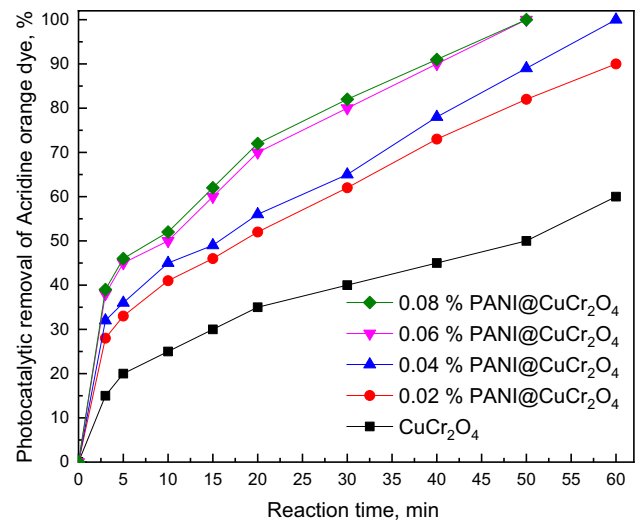


Fig. 9 Photocatalytic activities of CuCr_2O_4 and $\text{PANI@CuCr}_2\text{O}_4$ samples for degradation of acridine orange dye

to those of other fabricated specimens (CuCr_2O_4 , 0.02% $\text{PANI@CuCr}_2\text{O}_4$, 0.04% $\text{PANI@CuCr}_2\text{O}_4$, and 0.08% $\text{PANI@CuCr}_2\text{O}_4$ specimens even if short exposure time is applied (50 min).

Figure 10 elucidates the consequence of photo-catalyst dose on acridine orange dye photocatalytic destruction. It is noticed from the data of Fig. 10 that enlarging nanocomposite (0.06% $\text{PANI@CuCr}_2\text{O}_4$) dose from 0.5 to 1.0 g/L brings about an enhancement in the photocatalytic activity of 0.06% $\text{PANI@CuCr}_2\text{O}_4$ photo-catalyst from 80 to 90% after 60 min. on the other hand, the time needed to complete the photocatalytic destruction of the dye is declined from 50 to 40 min if the catalyst does is boosted

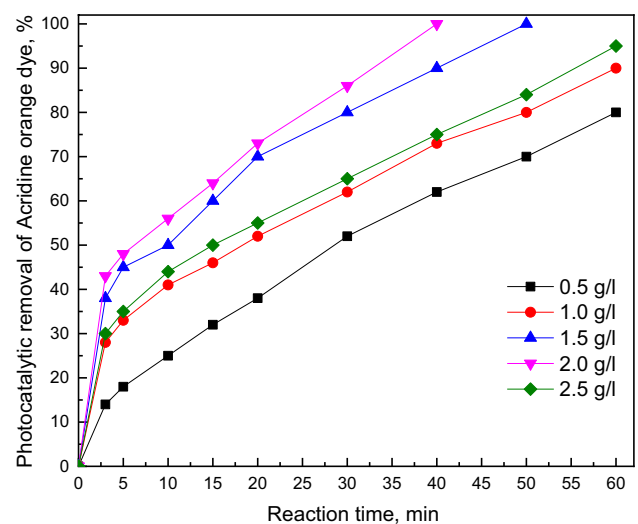


Fig. 10 Effect of dose of 0.06% $\text{PANI@CuCr}_2\text{O}_4$ photocatalyst for degradation of acridine orange dye

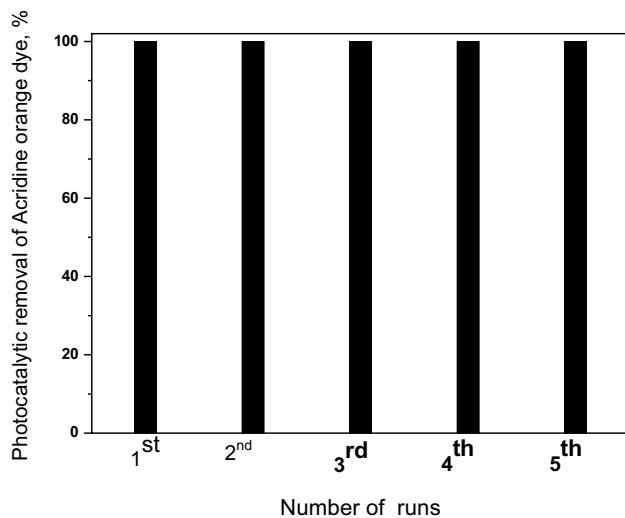


Fig. 11 Stability of 0.06% PANI@ CuCr₂O₄ photocatalyst towards the degradation of acridine orange dye after its application up to five times

from 1.5 to 2.0 g/L. It is obvious that enlarging of the catalyst dose (from 1.5 to 2.0 g/L) leads to a reduction in the time needed to complete the reaction (from 50 to 40 min) clarifying the enhancement in the photocatalytic efficiency, which might be associated with the upgrading of the feasible active centers. On contrary, utilization of higher dose of the fabricated photocatalyst (higher than 2.0 g/L) reduces the photocatalytic performance (down to 95%) at 1 h. This finding could be associated with the hindrance of Vis light dissipation to the surface of the photo-catalyst that retards acridine orange dye destruction.

Figure 11 exhibits the stability of 0.06% PANI@ CuCr₂O₄ nanocomposite towards the photocatalytic destruction of acridine orange dye upon its utilization up to five cycles. The observation of Fig. 11 affirms the greater stability of 0.06% PANI@CuCr₂O₄ nanocomposite upon its handling up to five times.

Conclusions

The outcomes of this investigation could be summarized as follows:

1. PANI@CuCr₂O₄ nanocomposite with the homogenous nanospherical design was successfully fabricated.
2. PANI@CuCr₂O₄ nanocomposite has been identified via FTIR, XPS, BET, XRD, TEM, and UV–Vis and PL analyses.
3. PANI@ CuCr₂O₄ nanocomposite could be utilized for acridine orange dye photocatalytic destruction beneath Vis light irradiation.

4. The photocatalytic performance of 0.06% PANI@ CuCr₂O₄ non-composite reached 100% towards the destruction of acridine orange dye after 40 min of Vis light exposure via utilization of 2.0 g/L of the photocatalyst.
5. 0.06% PANI@CuCr₂O₄ nanocomposite could be reutilized up to five times preserving its stability.

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