Visible light efficient and photo stable nanostructure of GO/CuO/m-TiO₂ ternary composite

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Abstract
Various combinations of mesoporous-titania (m-TiO₂) in binary composites of GO/m-TiO₂, CuO/m-TiO₂ and ternary composite of GO/CuO/m-TiO₂ with 4.0 wt% CuO and 10.0 wt% GO were prepared. XRD manifests mesoporous nature with anatase phase of m-TiO₂. In binary and ternary composites, the peak of GO is shifted due to presence of Cu and Ti. In GO/CuO/m-TiO₂ ternary composite, GO sheets appeared as irregular and flaky sheets showing successful distribution of clew like CuO and m-TiO₂. UV-vis DRS indicated that all photo catalysts showed strong response in visible region. The N₂ sorption desorption isotherms indicated meso-porous nature and high surface area of ternary composite. The synergistic effect of C–Cu–Ti and C–O–Ti linkages is studied by FTIR and Raman analyses. Ternary CuO/GO/m-TiO₂ composite demonstrates the highest degradation of methyl orange (MO) reduction and phenol oxidation simultaneously under visible light. The free electrons are scavenged by MO and reduced it while the holes oxidized the phenol.

1. Introduction

Energy crises and environmental pollutions are becoming more rigorous issues due to the rapid growth of industries and population [1]. Organic dyes are extensively utilized in a number of industries. Most dyes are toxic and detrimental. Their direct ejection into water as a harmful organic pollutants can adversely deteriorate the environment [2, 3]. Purification of waste water containing organic pollutants, dyes and aromatic compounds through photo catalysis are more addressable area of research [4]. TiO₂ based photo catalysts are promising material and gaining considerable attention owing to their good chemical stability, non-toxicity, biological inertness and cost efficiency for production of clean energy and degradation of organic pollutants into carbon dioxide and H₂O [5]. But most of semi conductor based photo catalysts like ZnO, SnO₂ and TiO₂ [6–8] are only responsive to UV light (4%–5%) due to possessing the large band gap energy value which suppresses their photocatalytic effect under visible irradiation [9]. To overcome this drawback, coupling of TiO₂ with narrow band gap metal oxides and expand their applications in visible region which makes the foremost and imperative fraction (47%) of solar spectrum.

CuO is a transition metal oxide which has been broadly exploited for the degradation of waste materials in visible light. It has narrow band gap energy value, naturally profuse, low cost and high chemical stability [10–13]. The coupling of CuO with TiO₂ tuned the optical and electronic properties of TiO₂ on account of enhancement in photocatalytic oxidation rate by collecting the photo generated electrons through metal oxide and augment the production of free OH /O₂⁻ radicals [14]. This combination makes a promising, environmental friendly and viable candidate which exhibits the sturdy photocatalytic activity under visible light [15]. Wu et al. fabricated the CuO nanotube decorated with TiO₂ nanoparticles which was utilized for better photocatalytic activity [16]. Lei et al. synthesized the CuO-modified TiO₂ photo catalysts by impregnation method. Photocatalytic degradation...
of poly brominated diphenyl ethers were performed by TiO2 and CuO/TiO2 photo catalysts but the rapid degradation of 2, 2', 4,4'-tetra bromo diphenyl ether was conducted by CuO/TiO2 photo catalysts [17]. Shamaila et al. prepared mesoporous TiO2 by sol-gel process and incorporated Cu into mesoporous TiO2 by wet chemical impregnation method. The interfacial Ti-O-Cu linkages improved photocatalytic activity in degradation of MO and 2, 4-DCP [18].

Carbon based nanomaterials including carbon nanotubes, graphene oxide (GO) and reduced graphene oxide (RGO) have been extensively used in many applications like photo catalysis, super capacitors, lithium-ion batteries, solar cells and chemical sensors [19–23] due to possessing the unique and fascinating properties. GO is a two-dimensional single sheet of oxidized carbonaceous material. Oxygen functionalities make it possible to dispense in water and other organic materials [24–29]. GO has the characteristics of high surface area, fast electron mobility, π–π conjugation, electrical, thermal conductivities and periphery bearing oxygen functionalities. It acts as an efficient photosensitizer when its surface is adapted with metal oxides in photo degradation of organic waste materials [30, 31]. GO behaves as good transporter owing to unpaired π electrons which proficiently suppress rate of recombination of free charge carriers. The band gap reduction of GO based metal oxides hybrid structure leading to augmentation in photocatalytic activities [32, 33]. Yong fang et al. prepared ternary composites of R-GO/meso-TiO2/Au-NPs through hydrothermal treatment. Elevation in degradation rate of MB by ternary composite of R-GO/meso-TiO2/Au was 8.2 times higher than that of P25 under visible light [4]. Zheng et al. fabricated the Pt@TiO2/GO ternary composite by hydrolysis and poly condensation methods. Diao et al. have reported the simultaneous removal of Cr (VI) and Phenol from aqueous solutions with degradation of 99.30% and 71.50%, respectively by bentonite-supported zero-valent iron persulfate nano-system [34]. Páez et al. have studied the H2O2 assisted α–Fe2O3–Bi2WO6 system demonstrated higher photocatalytic efficiency to degrade both MO and Phenol with 100 and 95% under UV-illumination than pristine Bi2WO6 or α–Fe2O3 [35]. Shamaila et al. studied bismuth-modified ordered mesoporous TiO2 for simultaneous phenol oxidation and chromium reduction under visible irradiation [36].

In the present work, GO was fabricated by modified Hummers method. Mesoporous TiO2 and clew like CuO nanomaterials were prepared by hydrothermal treatment, respectively. 4.0 wt% CuO and 10.0 wt% GO nano-sheets on the surface of m-TiO2 were introduced to produce GO/m-TiO2, CuO/m-TiO2, and GO/CuO/m-TiO2 nanocomposite structure by simple and facile route of chemical impregnation method. The synergistic effect of nanocomposites for simultaneous photocatalytic degradation of MO reduction and phenol oxidation under visible light is observed. GO modifies the properties of binary and ternary composite nanomaterials. The formation of C–Cu–Ti, C–Cu–Ti and C–O–Ti linkages with high surface area of GO/CuO/m-TiO2 nanocomposite is helpful in enhancement of photocatalytic degradation of organic pollutants under visible light. GO sheets play the crucial function in photo-electron excitation and then transfer to TiO2 and CuO due to its photo-absorptive nature on exposure of light source and reduce the rate of recombination of free charge carriers. The ternary composite of GO/CuO/m-TiO2 shows much superior photocatalytic activity as compared to single and hetero structure (binary composites) based on m-TiO2 owing to high surface area, electron transfer, synergistic effect and low band gap value.

2. Experimental section

2.1. Materials
Graphite powder (C), Sodium nitrate (NaNO3), Sulfuric acid (H2SO4, 98%), Nitric Acid (HNO3), Potassium permanganate (KMnO4), Hydrochloric acid (HCl), Hydrogen peroxide (H2O2, 30%), Pluronic P123, TBT (C16H36O4Ti), Copper nitrate Cu(NO3)2, Sodium hydroxide (NaOH) and Ethanol (C2H5OH). All chemicals were analytical grade and purchased from Sigma Aldrich. Double distilled water was used throughout the experimental process.

2.2. Synthesis of GO
GO sheets were synthesized all the way through modified Hummers’ method [37]. 3.0 g of graphite powder and 1.5 g of NaNO3 dissolved in 80 mL of H2SO4 (98%) to expand the graphite powder under magnetic stirring for 1 h at room temperature. Then solution was placed in ice bath keeping the temperature below 4 °C. 9.0 g KMnO4 was added slowly in solution by keeping the temperature constant under continuous stirring. The greenish purple colored hybrid solution was obtained. The mixture was transferred to water bath keeping temperature at 35–40 °C and stirred continuously for 2 h. The thick paste of dark brown colored was diluted by slow addition of 200 mL distilled water. Then temperature was increased up to 98 °C under magnetic stirring for 15 min. 300 mL more water was added. 30 mL H2O2 (30%) slowly introduced into solution to dissolve manganese species. Ther resultant color of product changed into orange brown colloidal solution of GO, centrifuged (6000 rpm min–1) and rinsed with 10% HCl solution. In order to remove residual acids and un-exfoliated particles, GO slurry was
washed with distilled water throughout to adjust the pH between 6 and 7. Final product was dried in oven at 60 °C for 48 h to obtain GO sheets. The synthesis of GO is given in Scheme 1.

2.3. Synthesis of catalysts
For the preparation of mesoporous TiO2, 10.0 g Pluronic P123 as soft template was dissolved into 50 mL of 99% ethanol under mild magnetic stirring until fully dissolved. 20 mL TBT as TiO2 precursor dissolved into 100 mL mixture of ethanol and distilled water drop wise under vigorous stirring to control the hydrolysis process. A milky solution was formed. A few drops of concentrated HCl were added for maintaining pH level between 3 and 4. The solution containing P123 was added drop wise into above solution. The homogenization of mixture was occurred under sonication of 30 min. Then transferred into a Teflon-lined stainless-steel autoclave (100 mL capacity) and heated at 150 °C for 8 h. After cooling it naturally at room temperature, white colored precipitate was collected by centrifugation (4000 rpm, 10 min) and washed with distilled water for several times. Then dried it overnight at 60 °C and calcined at 500 °C for 3 h.

Cu(NO3)2 is used as a precursor for CuO nanomaterials. 0.25 M solution of Cu(NO3)2 was dissolved in 85 mL of distilled water under magnetic stirring for 1 h. In another beaker, 1M solution of NaOH was dissolved in 85 mL of distilled water under mild magnetic stirring for 1 h. NaOH solution was mixed into above solution at room temperature (pH = 10). The homogenization of solution was made under sonication for 30 min. The mixture was transferred into stainless-steel autoclave (100 mL capacity) and heated at 60 °C for 8 h. For washing, above steps are repeated to obtain CuO nanomaterials. The black colored precipitate was annealed at 350 °C for 3 h.

In order to form the binary composites of GO/m-TiO2 and CuO/m-TiO2 and ternary composite of GO/CuO/m-TiO2, 10.0 wt% GO and 4.0 wt% CuO was incorporated in m-TiO2 by chemical wet impregnation method.

2.4. Characterization
The crystalline structure of the prepared samples was determined by a Rigaku D/MAX 2550 x-ray diffractometer. X-ray diffraction patterns of all samples were collected in the range of 5°–80° (2θ) using (Cu Kα1 radiation, λ = 1.5406 Å), operated at 40 kV and 100 mA. The crystalline size was determined by applying the Scherrer equation. \[ D = \frac{k\lambda}{\beta \cos \theta} \] where \( \beta \) is the half height width of the diffraction peak, \( K = 0.89 \) is a coefficient, \( \theta \) is the diffraction angle and \( \lambda \) is the X-ray wavelength corresponding to the CuKα irradiation. Scanning electron microscopic images and energy dispersive x-ray spectra were observed by MIRA 3 TESCAN instrument. The morphology of m-TiO2 and ternary composite was determined by JEOL JEM1010 transmission electron microscope operating at 80 kV. FT-IR spectrometer of manufacturing model Nicolet 740 equipped...
3.1. XRD profile

In order to verify the crystal phases, purity and crystalline size of synthesized nanomaterials, XRD analysis is performed. Figure 1 shows XRD patterns of pure samples of m-TiO₂, GO and CuO and binary composites of GO/m-TiO₂, CuO/m-TiO₂ and ternary composite of GO/CuO/m-TiO₂ nanomaterials. The other diffraction peaks correspond to (101), (004), (112), (200) and (105) index planes indicate the anatase phase of TiO₂ [38, 39]. In addition to the above peaks, a small intensity peak at 2θ = 17.9° manifests the porous nature of TiO₂ [18]. In XRD pattern of GO (figure 1(b)), a small characteristic peak at 26.1° (002) appears due to graphite as a starting material. After the oxidation process and interaction of acidic groups with graphitic layer, this peak is shifted to higher angle region. A sharp peak is appeared at ~11.3° (001) of GO correspond to larger interlayer distance of 7.8 Å due to possessing the oxygen functionalities as compared to graphite which is noted as 3.4 Å [40–42]. The diffraction peaks of CuO (figure 1(c)) at 2θ = 32.8°, 35.6°, 38.8°, 48.7° and 58.4° correspond to (110) (002), (111), (202) and (202) planes of monoclinic phase of CuO [43]. The XRD spectra of binary composites of GO/m-TiO₂ and CuO/m-TiO₂ and ternary composite of GO/CuO/m-TiO₂ are indicated in figures 1(d)–(f), respectively. In composites, the peak of GO is slightly shifted into higher angle region due to Cu–C–Ti linkage. No diffraction peak of CuO is observed in CuO/m-TiO₂ and GO/CuO/m-TiO₂ composite due to its small concentration or elevated dispersion. In binary and ternary composite samples, all characteristics peaks of TiO₂ reflect the anatase phase. It is also noted that small angle peak of anatase TiO₂ in composite samples is slightly

![Figure 1. XRD diffraction patterns of single, binary and ternary composites, (a) m-TiO₂, (b) GO, (c) CuO, (d) GO/m-TiO₂, (e) CuO/m-TiO₂, (f) GO/CuO/m-TiO₂.](image-url)

with beam splitter of KBr along with TGS detector was used for obtaining spectra of the samples. UV visible spectroscopy was performed using Scan UV-vis-NIR spectrophotometer equipped with an integrated sphere assembly, using BaSO₄ as a reflectance sample. Raman spectrum of GO/CuO/m-TiO₂ nanocomposite was recorded by uRAMBOSS Dangoo Optron Co. Ltd Raman spectrometer at room temperature with excitation wavelength of 532.0 nm. Nitrogen adsorption and desorption isotherms were obtained at 77 K with a Micromeritics 2010 ASAP system.

2.5. Photocatalytic activity

The textile industry effluents contain azo dyes and organics. MO is an azo dye which is very stable due to –N=N– linkage. Similarly the phenol is very toxic and carcinogenic chemical. It is demanding to degrade it under visible light. The photo catalytic activity was performed in a 100 mL quartz photochemical reactor with 1000 W Xenon lamp. The photocatalytic activity of the prepared samples is examined by using the initial concentration of 20 mg L⁻¹ of each MO and phenol in same solution simultaneously under visible light source for 5 h. All photo catalysts (0.05 g) were dispersed in 50 mL of MO and phenol mixed solution and kept at constant magnetic stirring under darkness to obtain adsorption-desorption equilibrium for 30 min. After regular intervals of time, the suspended solutions were withdrawn and centrifuged to examine the degradation of MO and phenol. The absorption of 4.0 mL of each irradiated MO and phenol photo catalyst solution was determined at 464 and 270 nm, respectively. In binary and ternary composite samples, all characteristics peaks of TiO₂ correspond to larger interlayer distance of 7.8 Å due to possessing the oxygen functionalities as compared to graphite which is noted as 3.4 Å

3. Results and discussion

3.1. XRD profile

In order to verify the crystal phases, purity and crystalline size of synthesized nanomaterials, XRD analysis is performed. Figure 1 shows XRD patterns of pure samples of m-TiO₂, GO and CuO and binary composites of GO/m-TiO₂, CuO/m-TiO₂ and ternary composite of GO/CuO/m-TiO₂ nanomaterials. The other diffraction peaks correspond to (101), (004), (112), (200) and (105) index planes indicate the anatase phase of TiO₂ [38, 39]. In addition to the above peaks, a small intensity peak at 2θ = 5.0° manifests the porous nature of TiO₂ [18]. In XRD pattern of GO (figure 1(b)), a small characteristic peak at 26.1° (002) appears due to graphite as a starting material. After the oxidation process and interaction of acidic groups with graphitic layer, this peak is shifted to the lower angle region. A sharp peak is appeared at ~11.3° (001) of GO correspond to larger interlayer distance of 7.8 Å due to possessing the oxygen functionalities as compared to graphite which is noted as 3.4 Å [40–42]. The diffraction peaks of CuO (figure 1(c)) at 2θ = 32.8°, 35.6°, 38.8°, 48.7° and 58.4° correspond to (110) (002), (111), (202) and (202) planes of monoclinic phase of CuO [43]. The XRD spectra of binary composites of GO/m-TiO₂ and CuO/m-TiO₂ and ternary composite of GO/CuO/m-TiO₂ are indicated in figures 1(d)–(f), respectively. In composites, the peak of GO is slightly shifted into higher angle region due to Cu–C–Ti linkage. No diffraction peak of CuO is observed in CuO/m-TiO₂ and GO/CuO/m-TiO₂ composite due to its small concentration or elevated dispersion. In binary and ternary composite samples, all characteristics peaks of TiO₂ reflect the anatase phase. It is also noted that small angle peak of anatase TiO₂ in composite samples is slightly

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shifted to higher angle indicating distorted d-spacing of host TiO2 material. The small pores are compacting into larger pores and pore channels are totally covered by foreign materials also confirmed by BET analysis [36]. The average crystalline size of all synthesized samples is calculated by Scherer’s equation as shown in table 1. The decline trend in crystalline size in composite structures is assigned that average distance covered by photo generated charge carriers to reach on the surface of catalyst at reaction site becomes smaller. At reactive sites, they suffered in oxidation and reduction process which alternatively responsible in enhancement of photocatalytic activity by lowering the rate of recombination process in binary and ternary structures as compared to single one.

### Table 1. Average crystalline size and band gap values of synthesized nanomaterials.

| Nanomaterials | Average FWHM (°) | Average particle size (nm) | Band gap (eV) |
|---------------|-----------------|---------------------------|--------------|
| m-TiO2        | 0.8680          | 9                         | 3.14         |
| GO            | 0.7478          | 11                        | 2.50-3.50    |
| CuO           | 0.3545          | 23                        | 2.51         |
| GO/m-TiO2     | 0.6363          | 13                        | 2.70         |
| CuO/m-TiO2    | 0.2084          | 39                        | 2.80         |
| GO/CuO/m-TiO2 | 0.7680          | 10                        | 2.60         |

#### Figure 2. SEM images of single, binary and ternary composites, (a) m-TiO2, (b) GO, (c) CuO, (d) GO/m-TiO2, (e) CuO/m-TiO2, (f) GO/CuO/m-TiO2 materials.

3.2. SEM analysis

SEM images of synthesized nanostructures of pure samples of m-TiO2, CuO, GO, binary composites of GO/m-TiO2, CuO/m-TiO2 and ternary composites of GO/CuO/m-TiO2 are depicted in figure 2. SEM photographs of m-TiO2 prepared by using P123 are shown in figure 2(a). It is clearly seen that during hydrothermal treatment, re-precipitation of m-TiO2 nanomaterial leads to formation of aggregated and irregular shaped primary particles. It is observed that granular texture of prepared sample is similar to porous structure of TiO2 [39]. The morphology of GO is shown in figure 2(b). It is clearly observed that GO has an ultrathin, flexible and sheet like texture. The edges of GO are folded, wavy and wrinkled which reflect the occurrence of H2O molecules, hydroxyl or carboxyl groups. GO possesses many aggregated closely associated conducting sheets which are soluble in water. CuO particles with vertical elongated terminal edges at pH = 10 are observed by SEM image (figure 2(c)). It reveals that formation of agglomerated clew like CuO nanoparticles
by hydrogen bonding due to the presence of elevated amount of OH\textsuperscript{−} species in the nanomaterial\cite{44}.

Figure 2(d) demonstrates the morphology of GO/m-TiO\textsubscript{2} binary composite. The roughness of GO surface is indicative that whole GO sheets are covered with small porous like irregular agglomerated TiO\textsubscript{2} nanoparticles. In CuO/m-TiO\textsubscript{2} binary structure (figure 2(e)) shows that CuO nanomaterial has irregular clew like morphology and unevenly distributed on the surface of m-TiO\textsubscript{2} nanomaterial. Figure 2(f) illustrates the GO/CuO/m-TiO\textsubscript{2} ternary composite. GO sheets appeared crumpled rough, irregular and flaky like texture in ternary composite form which shows that CuO and m-TiO\textsubscript{2} nanomaterials are successfully distributed on the whole surface of GO. Here, it is difficult to distinguish the morphological structure of CuO nanoparticles on the broken surface of GO due to their high dispersion, although GO/CuO/m-TiO\textsubscript{2} nanomaterial indicates an improved photocatalytic activity.

### 3.3. TEM analysis

TEM results represent the morphological composition of prepared mesoporous TiO\textsubscript{2} and GO/CuO/m-TiO\textsubscript{2} ternary composites in figure 3. TEM image of m-TiO\textsubscript{2} (figure 3(a)) indicates the irregular and small porous morphology with average particle size ~8–9 nm corresponding to domain size (ca. 9 nm) obtained from Scherer’s equation in XRD pattern. In GO/CuO/m-TiO\textsubscript{2} ternary composites (figures 3(b) and (c)) at different magnification, clearly seen the dispersion of elongated clew like CuO nanomaterial and agglomerated irregular porous shaped TiO\textsubscript{2} on the entire transparent surface of the GO sheet which are also confirmed by SEM photographs. The distribution of metal oxides on GO sheet is promising for photocatalytic activity.

### 3.4. EDX spectra

Figure 4 represents EDX spectra of GO, binary composites of GO/m-TiO\textsubscript{2}, CuO/m-TiO\textsubscript{2} and ternary composites of GO/CuO/m-TiO\textsubscript{2}. The weight percentage of Ti, O, C and Cu elements in the synthesized nanomaterials are given in table 2. Figure 4(a) exhibits that EDX spectra of GO contains carbon and oxygen indicating high purity of material. Figure 4(b) represents that GO/m-TiO\textsubscript{2} consist of C, O and Ti elements in samples without any other impurity. In GO sheets, weight % of C and O elements are 59.46 and 40.54, respectively. In GO/m-TiO\textsubscript{2} nanocomposites, weight % of C, O and Ti elements are 15.82, 41.79 and 42.39 respectively. EDX spectra of binary composite of CuO/m-TiO\textsubscript{2}, and ternary composite of GO/CuO/m-TiO\textsubscript{2} are depicted in figures 4(c) and (d), respectively which showed complete dispersion of CuO on m-TiO\textsubscript{2} and GO sheets in nano-composites. In all above cases, no extra peaks for other elements as impurities are observed.

### 3.5. Nitrogen sorption studies

The textural properties of the synthesized photo catalysts were examined through N\textsubscript{2} adsorption-desorption behaviors. N\textsubscript{2} adsorption desorption isotherms of m-TiO\textsubscript{2}, GO/m-TiO\textsubscript{2} and GO/CuO/m-TiO\textsubscript{2} are presented in figure 5(A). All isotherms are of characteristic type IV which indicate capillary condensation of adsorbent in the mesopores. It is worth seen that the isotherms are obtained at relative pressure range of 0.4–0.8 with a sloppy adsorption and sharp steep desorption branch. All the hysteresis loops represents H\textsubscript{2} type according to the IUPAC classification systems associated with narrow pore sizes. Figure 5(B) shows Barrett–Joyner–Halenda (BJH) pore-size distribution curves of photo catalysts. The BET surface area and BJH pore sizes results of photo catalysts are summarized in table 3. Higher BET surface area of TiO\textsubscript{2} nanoparticles presents sufficient space for infiltration of GO and CuO nanomaterials. Due to the high surface area, light is more proficiently harvested in...
multiple scattering. The small surface area of GO/CuO/m-TiO₂ nanocomposite is noted which shows that GO and CuO properly cover the pore channels of TiO₂ nanomaterial. This nano system could enhance the photocatalytic degradation of organic pollutants under visible irradiation.

3.6. UV-vis spectra and optical band gap values
UV-vis spectra of pure m-TiO₂, GO, CuO and binary composites of GO/m-TiO₂, CuO/m-TiO₂, and ternary composite of GO/CuO/m-TiO₂ photo catalysts are shown in figure 6. The spectrum of GO (figure 6(A)) indicates a strong characteristics absorption peak at 229 nm which arises from the aromatic C=C bonds of GO attributing to π → π* transitions. A small shoulder about 308 nm is observed which is ascribed to the n → π* transition due to C=O. UV-vis spectra of m-TiO₂, CuO, GO/m-TiO₂, CuO/m-TiO₂ and GO/CuO/m-TiO₂ nanocomposite materials are represented in figure 6(B) (a)–(c). It is worth noting that the band edges of the spectra of all photo catalysts show strong response near to the visible region. In CuO spectrum (figure 6(B), (b)), absorption edge is attributed to the transition from O (2p) to Cu (3d) orbital. The band gap energy value (figure 7) of samples is achieved by Tauc relation with a linear extrapolation by using the following relation;

\[
\alpha h \nu^{1/2} = A (h \nu - E_g)
\]

Where \( h \) is Planck’s constant, \( \nu \) is the photon’s frequency, \( \alpha \) is the absorption coefficient, \( E_g \) is the band gap and \( A \) is a proportionality constant. The value of the exponent denotes the indirect allowed electronic transition [45].
The calculated optical band gap value of CuO is 2.51 eV. The modification in the band gap of m-TiO$_2$ by incorporation of carbonaceous species and CuO considerably affects the optical properties of m-TiO$_2$ as shown in figure 6(B)(c) and (d). The absorption edges of GO/m-TiO$_2$ and CuO/m-TiO$_2$ are observed at about 459 and 442 nm which exhibited the response in visible light region. The surface modification of m-TiO$_2$ by incorporation of GO through the O=C–OH bond originated from –COOH groups of GO, GO/m-TiO$_2$ and GO/CuO/m-TiO$_2$ nanocomposites exhibit optical band gap energies around 2.7 and 2.6 eV respectively. It is inferred from UV-vis (Tauc relation) spectra that the optical band gap energy value of GO/CuO/m-TiO$_2$ photo catalyst is lower than GO/m-TiO$_2$ which could be ascribed to the inherent light absorption capability of carbonaceous species and the electron transitions among m-TiO$_2$, CuO and GO sheets.
3.7. FTIR analysis

The bonding characteristics of different functional groups in m-TiO$_2$, GO, CuO and GO/CuO/m-TiO$_2$ nanomaterials are determined by FTIR spectroscopy (figure 8). All samples with broad absorption peaks in the range of 3100–3400 cm$^{-1}$ are attributed to the adsorbed water on the surface of photo catalysts. The absorption peak at 1600–1650 cm$^{-1}$ is attributed to the O–H stretching vibration due to adsorbed water molecules on all photo catalysts. In FTIR spectra of m-TiO$_2$ nanoparticles (figure 8(a)), the characteristic peaks at 843 cm$^{-1}$ and 564 cm$^{-1}$ correspond to the Ti–O and Ti–O–Ti stretching mode of vibration, respectively which confirms the formation of m-TiO$_2$ nanoparticles. In FTIR spectrum of CuO (figure 8(b)), absorption peak at 1370 cm$^{-1}$ is attributed to the existence of CO$_3^{2-}$ stretching vibration. This peak in FTIR spectrum indicates that starting material is mixed in open air environment. The signals at 1636 cm$^{-1}$ is attributed due to presence of hydroxyl group and adsorbed water molecules on the surface of photo catalyst. The frequency peaks below 900 cm$^{-1}$ are assigned to Cu–O bending vibration which confirms the manufacturing of monoclinic phase of CuO nanomaterial. The surface of GO is functionalized by various oxygen functional groups are observed in FTIR spectrum (figure 8(c)). A small absorption peak at 1751 cm$^{-1}$ is attributed to C=O stretching mode of vibration arises due to presence of carbonyl moieties at edge of GO nano-sheets. The characteristic absorption peaks at 1621 cm$^{-1}$ and 1410 cm$^{-1}$ are assigned to C=C bond due to skeletal vibration of graphitic structure and C–O by carboxyl group, respectively. The signals at 1070 cm$^{-1}$ are attributed to C–O–C stretching vibrations of the epoxy group of GO nano-sheets. In ternary composite of GO/CuO/m-TiO$_2$ (figure 8(d)), small shift in absorption peaks at 1637 cm$^{-1}$, 1396 cm$^{-1}$ and 1070 cm$^{-1}$ occurs due to C=C, C–O and C–O–C stretching vibrations. The existence of frequency peaks range at 1000–900 cm$^{-1}$ is attributed to Cu–O–Ti and C–O–Ti bending vibrations [46]. The signals at 519 cm$^{-1}$ are attributed to C–Cu–Ti stretching vibration which indicates
the formation of GO/CuO/m-TiO2 photo catalyst. It is noted that the signals corresponding to the stretching vibration of water and O–H are broader and stronger in GO/CuO/m-TiO2 photo catalyst. The functional groups of O–H play crucial function in the photocatalytic activity by trapping the hole generated under irradiation to form OH radicals which can reduce in electron-hole pair recombination and ultimately augment the photocatalytic process.

3.8. Raman study
The Raman spectra of ternary composite of GO/CuO/m-TiO2 photo catalyst are shown in figure 9. Raman bands of GO/CuO/m-TiO2 nanocomposite indicate the signals of the m-TiO2 at 156 cm−1 and 403 cm−1. Raman bands of anatase TiO2 are typically observed at 146.0, 196.0, 397.0, 516.0 and 638.0 cm−1 attributed to the E g, B 1g, A 1g, B 2g and E g vibrational modes, respectively [18]. The signals at range shift of 279 cm−1 and 600 cm−1 indicates the presence of CuO nanomaterial. The existence of carbon based material in prepared sample is confirmed by appearance of small intensity D (1350 cm−1) and G (1565 cm−1) bands corresponding to symmetrical feature of sp3 defects and in-plane stretching vibrations of sp2 C–C bonds, respectively [47]. The existence of characteristic signals of small intensity D (1361 cm−1) and G (1568 cm−1) bands showed little higher shift in comparison to pure GO indicating the synergistic effect of GO and CuO in mesoporous TiO2.

3.9. Photocatalytic activity
The photocatalytic activities of synthesized nanomaterial photo catalysts i.e m-TiO2, GO, CuO, CuO/m-TiO2, GO/m-TiO2 and GO/CuO/m-TiO2 over simultaneous reduction of MO and phenol oxidation under visible light are evaluated in figures 10(A) and (B), respectively. The highest decomposition rate of MO reduction and phenol oxidation is observed in ternary composite of GO/CuO/m-TiO2. Pure TiO2 shows very less degradation activity due to the large band gap values. In the absence of photo catalyst, no noticeable degradation of MO (photo-fading) and phenol is observed. The photocatalytic degradation process of MO and phenol follow pseudo first order kinetics;

\[
\ln \left( \frac{C_0}{C} \right) = k_{app}t
\]

Where \(C_0\) is the initial concentration at \(t = 0\), \(C\) is the concentration of solute remaining in the solution, \(t\) is the time of irradiation and \(k_{app}\) is degradation rate constant. The degradation rate constant for the decomposition of MO and phenol for synthesized different photo catalysts is calculated. It is noticed that GO/CuO/m-TiO2 ternary composite has the highest value of \(k_{app}\) as compared to other photo catalysts as shown in figures 11(A) and (B) respectively. The calculated rate constant values of different samples are given in table 4.

Being a photo catalyst, CuO could absorb light in UV-vis region due to possessing the small band gap value. But its less photo catalytic activity is noted which could be attributed to its low charge transportation rate which enhance the chances of charge recombination rate. A rapid photo catalysis is observed when surface of m-TiO2 is modified with CuO and GO to form the binary and tri-junctions. In case of CuO/m-TiO2 heterojunction, photo catalytic reduction of MO and oxidation of phenol is noted as ∼64% and ∼55%, respectively. The enhancement in catalytic degradation of mixed organic species is due to the generation of reduced form of CuO which leads to formation of oxygen vacancies. These vacancies acts as the electron donor by binding the photo generated electrons and fruitful in the formation of holes and hydroxyl radicals (OH−). These free hydroxyl radicals provoke mineralization of the mixed organic species. m-TiO2 has large surface area and provides sufficient
active sites for the CuO content on its surface and generates the Cu–O–Ti linkage. This linkage shows the good photocatalytic activity under visible illumination. In case of GO/m-TiO$_2$ heterojunction system, a better photocatalytic activity in case of MO reduction and phenol oxidation i.e. $\sim$85 and $\sim$76% is noted. In this coupled system, the reduction potential of GO ($-0.75$ V versus NHE) is upper than the reduction potential of TiO$_2$ ($-0.2$ V versus NHE), which can play an imperative role in reduction of m-TiO$_2$ and create the oxygen vacancies. The oxidation potential of GO (1.5 V versus NHE) is much lower than that of TiO$_2$ (3V versus NHE), the electrons shuttle from the surface of TiO$_2$ towards GO. The results are matched well with the report [48]. Murcia et al. have observed in Pt-TiO$_2$ catalyst that Pt significantly increases the TiO$_2$ photo deposition, photo reactivity

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**Table 4.** Kinetics parameter of GO/CuO/m-TiO$_2$ photo catalyst with MO reduction and phenol oxidation.

|          | MO  | Phenol |
|----------|-----|--------|
| $K_{app}$ (h$^{-1}$) |     |        |
| m-TiO$_2$ | 0.022 | 0.012  |
| CuO      | 0.140 | 0.076  |
| GO/m-TiO$_2$ | 0.370 | 0.280  |
| CuO/m-TiO$_2$ | 0.200 | 0.160  |
| GO/CuO/m-TiO$_2$ | 0.570 | 0.440  |

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**Figure 10.** The degradation of organic pollutants; MO reduction (A) phenol oxidation (B) under visible light over (a) m-TiO$_2$, (b) CuO, (c) GO/m-TiO$_2$, (d) CuO/m-TiO$_2$, (e) GO/CuO/m-TiO$_2$ nanocomposites.

**Figure 11.** Kinetic parameters of MO reduction (A) phenol oxidation (B) under visible light over (a) m-TiO$_2$, (b) CuO, (c) GO/m-TiO$_2$, (d) CuO/m-TiO$_2$, (e) GO/CuO/m-TiO$_2$ nanocomposites.
toward phenol and MO via interaction of azo group with surface Ti$^{4+}$ [49]. Istratie et al. have tested that magnetic iron oxide/carbon nano system as adsorbents for the removal of MO and phenol from aqueous solutions and observed 1.7 times greater adsorption of MO than that of phenol [50]. GO acts as an electron acceptor. The impregnation of GO to m-TiO$_2$ creates the interfacial C–O–Ti linkages. Most of organic pollutants have aromatic compounds that create π–π stacking with the delocalized electrons of GO and enhance adsorption affinity on the surface of GO. The adsorption of organic species with the photo catalysts facilitate to overcome rate of recombination of photo generated charge carriers and improve photo degradation of organic species in visible region. In GO/CuO/m-TiO$_2$ tri-junction nanocomposite, the highest photocatalytic activity is observed for mixed organic species in photocatalytic test. GO/CuO/m-TiO$_2$ composite demonstrates the reduction of MO to hydrazine derivative and phenol solution was observed ~93% and ~90%, respectively. GO acts as photo-electron acceptor when light source is irradiated due to presence of oxygen-containing functional groups like hydroxyl, epoxy and carboxyl groups at the edge of sheet. These functional groups may facilitate the electron transfer process among m-TiO$_2$, CuO and GO sheets and reduce probability of charge recombination process. In GO/CuO/m-TiO$_2$ ternary composite, mesoporous texture is helpful in improving the photocatalytic degradation rate of organic pollutants by providing a large interacting surface area. In order to determine the stability of photo catalyst, GO/CuO/m-TiO$_2$ nanocomposite was exploited four times in degradation of MO and phenol with diminutive dropped efficiency as shown in figure 12. This result indicates that GO/CuO/m-TiO$_2$ nanocomposite has high stability under visible light source and cost effective. Further stability of GO/CuO/m-TiO$_2$ nanocomposite is also confirmed by XRD pattern, SEM image and EDX analysis (figure 13). XRD profile still exhibits reflected diffraction peaks corresponding to GO and TiO$_2$. SEM photographs and EDX analysis indicate the original morphology and composition of GO/CuO/m-TiO$_2$ nanocomposite after four repeated cycles of photocatalytic tests. These results confirmed the stability of photocatalyst in photocatalytic reaction.

3.10. Photocatalytic mechanism
Photocatalytic mechanism demonstrates the redox properties of GO/CuO/m-TiO$_2$ nanocomposite in case of simultaneous photo reduction of MO and phenol oxidation as illustrated in scheme 2. It has been found that GO sheets possess the different oxidation levels. The indirect band value of GO is calculated in range of 2.5–3.5 eV. The conduction band edge of GO is located at ~0.75 V and valence band has minimum value at 1.5 V (versus NHE) [48]. GO plays the crucial function in photo–electron excitation and carrying to m-TiO$_2$ and CuO due to its photo-absorptive nature on exposure of light source. Upon irradiation of visible light, electrons and holes are produced on the surface of GO/CuO/m-TiO$_2$ catalyst. GO acts as both photo-sensitizer and electrons acceptor. GO transfers the electrons to the conduction band of m-TiO$_2$ and CuO. Photo-induced electrons of m-TiO$_2$ could switch to the valence band of CuO. MO is reduced to hydrazine derivatives by scavenging photo-generated electrons on the surface of conduct band of CuO. The photo-generated holes on valence band of CuO could be transferred to the TiO$_2$ and GO surface to contribute in oxidation reactions of phenol [51]. GO/CuO/m-TiO$_2$ ternary composite can produce high amount of free electrons and holes which in turn degrade the mixed organic pollutants. In the photo-degradation reaction, GO produces electrons and transfer
them to m-TiO₂ and CuO under visible-light. This is helpful in the reduction of recombination rate of electron-hole pairs. Essential steps involved in oxidation reduction reaction of GO/CuO/m-TiO₂ nanomaterial and organic species are represented by chemical equations given below:

$$\begin{align*}
\text{GO/CuO/m} & \rightarrow \text{TiO}_2 + h\nu \rightarrow \text{GO/CuO/mTiO}_2(h^+ + e^-) \\
\text{GO/CuO/mTiO}_2(h^+ + e^-) & \rightarrow \text{GO/CuO/mTiO}_2 \\
h^+ + \text{H}_2\text{O} & \rightarrow \text{H}^+ + \text{O}_2 + \text{OH} \\
\text{MO} + h^+ + e^- & \rightarrow \text{MOH}_2 \\
\text{OH} + \text{phenol} & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \\
h^+ + \text{phenol} & \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\end{align*}$$

4. Conclusions

GO sheets were fabricated by modified Hummer method. CuO and mesoporous TiO₂ nanomaterials are synthesized by hydrothermal treatment. The binary composites of GO/m-TiO₂ and CuO/m-TiO₂ and ternary composite of GO/CuO/m-TiO₂ with 4.0% CuO and 10.0% GO are prepared by wet chemical impregnation method. XRD pattern confirms the diffraction peaks of TiO₂, GO and CuO nanomaterials. The dispersion of
elongated clew like CuO nanomaterials and agglomerated irregular shaped porous d TiO₂ on the entire surface of the GO sheet are confirmed by SEM and TEM photographs. UV-vis spectra indicate that all nanocomposites show strong response in the visible region. FTIR studies indicate C–Cu–Ti and C–O–Ti linkages which confirm the formation of GO/CuO/m-TiO₂ tri-junction. Large surface area of nanocomposite with small pore size is helpful in enhancement of photocatalytic degradation of mixed organic species under visible light. In Raman spectrum, the existence of characteristics signals related to TiO₂, CuO and GO indicates that GO/CuO/m-TiO₂ nanomaterial is successfully synthesized. The highest rate of simultaneous MO reduction and phenol oxidation is noted by GO/CuO/m-TiO₂. On visible light irradiation, the C–Cu–Ti linkage of GO/CuO/m-TiO₂ photo catalyst enhance adsorption of organic species and pollutants. On the absorption of photon, the electrons are excited from GO sheets and shifted towards the m-TiO₂ and CuO. Electrons of GO and reduced form of CuO leads to formation of oxygen vacancies which facilitate to overcome rate of recombination of photo-generated charge carriers by producing the high amount of free electrons and holes pairs. The free electrons are helpful in the reduction of MO while holes are responsible to oxidize the phenol into simple compounds. The high catalytic activity is due to both the unique combination and high surface area, reduced electron-hole recombination and low band gap. The ternary nanocomposite of GO/CuO/m-TiO₂ is cost effective and highly photostable.

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References

[1] Feng J, Hou Y, Wang X, Quan W, Zhang J, Wang Y and Li L 2016 In-depth study on adsorption and photocatalytic performance of novel reduced graphene oxide–Zn Fe₂O₆-polyamine composites J. of Alloys Comp. 681 157–66
[2] Sajjad S, Bano T and Leghari S A K 2017 Efficient visible light magnetic modified iron oxide photo catalysts Ceram. Int. 43 14672–7
[3] Kann N 2012 Applications of the Nicholas reaction in the synthesis of natural products Current Org. Chem. 16 3223–34
[4] Yang Y, Ma Z, Xu L, Wang H and Fu N 2016 Preparation of reduced graphene oxide/meso-TiO₂/AuNPs ternary composites and their visible-light-induced photocatalytic degradation of methylene blue Appl. Surface Science 369 576–83
[5] Ye Z, Seter J R, Centelles F, Cabot P L, Brillas E and Síres I 2019 Photocatalysis–Fenton as post-treatment for electro coagulated benzophenone-3-loaded synthetic and urban wastewater J. Clean. Prod. 208 1393–402
[6] Adamu H, Duvey P and Anderson J A 2016 Probing the role of thermally reduced graphene oxide in enhancing performance of TiO₂ in photocatalytic phenol removal from aqueous environments Chem. Eng. J. 284 380–8
[7] Ma J Z, He H and Liu F D 2015 Effect of Fe on the photocatalytic removal of NOx over visible light responsive Fe/TiO₂ catalysts Appl. Catal. B: Environ. 179 21–8
[8] Lin C J, Liao S J, Kao L C and Liou S Y H 2015 Photo electrocatalytic activity of a hydrothermally grown branched ZnO nanorod–array capacitor electrodes made from porous CuO nanobelts and single-walled carbon nanotubes ACS Nano 9 2013–9
[9] Wu X Y, Yin S, Xue D F, Komarneni S and Sato T 2015 A CsₓWO₃/ZnO nanocomposite as a smart coating for photocatalytic environmental cleanup and heat insulation Nanoscale 7 17048–54
[10] Zhao X, Wang P, Yan Z and Ren N 2015 Room temperature photoluminescence properties of CuO nanowire arrays Opt. Mater. 42 544–7
[11] Wang B, Wu X L, Shu C Y, Guo Y G and Wang C R 2010 Synthesis of CuO/graphene nanocomposite as a high-performance anode material for lithium-ion batteries J. Mater. Chem. 20 10681–4
[12] Zhang X, Shi W, Zhu J, Kharistia D J, Zhou W, Lalia B S, Hing H H and Yan Q 2011 High-power and high-energy-density flexible pseudo capacitor electrodes made from porous CuO nanobelts and single-wall carbon nanotubes ACS Nano 5 2013–9
[13] Zhao X, Wang P and Li B 2010 CuO/ZnO core/shell hetero structure nanowire arrays: synthesis, optical property, and energy application Chem. Commun. 46 6768–70
[14] Chiang K, Amal R and Tran T 2002 Photocatalytic degradation of cyanide using titanium dioxide modified with copper oxide Adv. Environ. Res. 6 471–85
[15] Kargar A, Jing Y, Kim S J, Riley C T, Pan X and Wang D 2013 ZnO/CuO heterojunction branched nanowires for photo electrochemical hydrogen generation ACS Nano 7 11112–20
[16] Wu Z, Zhu Y, Li C and Wei Y 2011 A novel CuO–TiO₂ composite photo catalyst and its degradation of methyl orange under UV irradiation J. Adv. Mater. Res. 295 1129–32
[17] Lei M, Wang N, Zhu L, Zhou Q, Niea G and Tang H 2016 Photocatalytic reductive degradation of polybrominated diphenylethers on CuO/TiO₂ nanocomposites: a mechanism based on the switching of photocatalytic reduction potential being controlled by the valence state of copper Appl. Cat. B: Environ. 182 414–23
Mater. Res. Express 6 (2019) 125087

[18] Sajjad S, Leghari S A K and Zhang J 2013 Copper impregnated ionic liquid assisted mesoporous TiO$_2$ visible light photo catalyst RSC Adv. 3 12678–87
[19] Yoo E J, Okata T, Akita T, Kohyama M, Nakamura J and Homma I 2009 Enhanced electrocatalytic activity of Pt sub nanoclusters on graphene nanosheet surface Nano Lett. 8 2326–30
[20] Wang X, Zhi L and Millen K 2008 Transparent, conductive graphene electrodes for dye-sensitized solar cells Nano Lett. 8 2323–7
[21] Zhang J, Liu X Q, Zhou H, Yan X F, Liu Y J and Yuan A H 2014 Pt-doped graphene oxide/ML-101 nanocomposites exhibiting enhanced hydrogen uptake at ambient temperature RSC Adv. 4 28908–13
[22] Yang H X and Li L 2014 Tin–indium/graphene with enhanced initial columbic efficiency and rate performance for lithium ion batteries J. Alloy Compd. 584 76–80
[23] Cheng Z G, Li Q, Li Z J, Zhou Q Y and Fang Y 2010 Suspended graphene sensors with improved signal and reduced noise Nano Lett. 10 1864–8
[24] Berger C et al 2006 Electronic confinement and coherence in patterned epitaxial graphene Science 312 1191–6
[25] Zhang J H, Wan S, Yan B, Wang L B and Qian Y T 2013 Graphene encapsulated Fe$_3$O$_4$ nanospindles as a superior anode material for lithium-ion batteries J. Nanoscience and Nanotechnol. 13 4364–9
[26] Stankovich S, Dikin D A, Dommett G H B, Kohlhaas K M, Zimney E J, Stach E A, Piner R D, Nguyen S T and Ruoff R S 2006 Graphene-based composite materials Nature 442 282–6
[27] Aleksandrzak M, Kukulka W and Mijowska E 2017 Graphitic carbon nitride: recent progress RSC Adv. 7 22467–73
[28] Chen D, Feng H and Liu J 2012 Graphene oxide: preparation, functionalization, and electrochemical applications J. Chem. Rev. 112 6027–53
[29] Dreyer D R, Park S, Bieilawski C W and Ruoff R S 2010 The chemistry of graphene oxide Chem. Soc. Rev. 39 228–40
[30] Zhao G, Wen T, Chen C and Wang X 2012 Synthesis of graphene based nanomaterials and their application in energy related and environmental related areas RSC Adv. 2 9286–303
[31] Zhang H and Wu H 2013 Graphene-based nanocomposites: preparation, functionalization, and energy and environmental applications Energy Environ. Sci. 6 3483–507
[32] Gu L, Wang J, Cheng H, Zhao Y, Liu L and Han X 2013 One-step preparation of graphene-supported anatase TiO$_2$, with exposed $\{001\}$ facets and mechanism of enhanced photocatalytic properties ACS Appl. Mater. Interfaces 5 3085–93
[33] Lee J S, You K H and Park C B 2012 Highly photostable, low band gap TiO$_2$ nanoparticles wrapped by graphene Adv. Mater. 24 1084–8
[34] Diao Z H, Xu X R, Jiang D, Kong L J, Sun Y X, Hu Y X and Chen H 2016 Bentonite-supported nanoscale zero-valent iron/persulfate system for the simultaneous removal of Cr (VI) and phenol from aqueous solutions Chem. Eng. J. 302 213–22
[35] Pérez J C, Navio J A, Hidalgo M C, Bouziani A and Azouzou M E 2017 Mixed $\alpha$-Fe$_2$O$_3$/Bi$_2$WO$_6$ oxides for photoassisted hetero-Fenton degradation of Methyl Orange and Phenol J. Photoch. Photobio. A 332 521–33
[36] Sajjad S, Leghari S A, Chen F and Zhang J 2010 Bismuth doped ordered mesoporous TiO$_2$: visible-light catalyst for simultaneous degradation of phenol and chromium Chem. A Eur. J. 16 13795–804
[37] Kong D, Zhao M, Li S, Huang F, Song J, Yuan Y, Shen Y and Xie A 2016 Synthesis of TiO$_2$/r-GO nanocomposites with enhanced photoelectrochemical performance and photocatalytic activity Nano Energy 11 1650007–1650015
[38] Liu L, Liu S, Bai H and Sun D D 2012 Concurrent filtration and solar photocatalytic disinfection/degradation using high performance Ag/TiO$_2$ nanofiber membrane Water Res. 46 1101–12
[39] Sajjad S, Leghari S A K, Chen F and Zhang J 2010 Synthesis and characterization of mesoporous–TiO$_2$, with enhanced photocatalytic activity for the degradation of chloro-phenol Mater. Res. Bull. 45 1375–82
[40] Zhang X, Sun Z, Xu B, Yue S, Tao Y, Zhan W and Liu B 2011 Mechanically strong and highly conductive graphene aerogel and its use as electrodes for electrochemical power sources J. Mater. Chem. 21 6494–7
[41] Xu Y, Sheng K, Li C and Shi G 2010 Self-assembled graphene hydrogel via a one-step hydrothermal process ACS Nano 4 4324–30
[42] Zhang L and Shi G 2011 Preparation of highly conductive graphene hydrogels for fabricating supercapacitors with High rate capability J. Phys. Chem. C 115 17205–12
[43] Duan Y, Liu X, Han L, Aashina S, Xu D, Cao Y, Yao Y and Che S 2014 Optically active chiral CuO ‘nanoflowers’ J. Am. Chem. Soc. 136 7193–6
[44] Dey K K, Kumar A, Shanker R, Dhawan A, Wan M, Yadav R R and Srivastava A K 2012 Growth morphologies, phase formation, optical & biological responses of nanostructures of CuO and their application as cooling fluid in high energy density devices RSC Adv. 2 1387–403
[45] Viezbicke B D, Patel S, Davis B E and Birnie D P 2015 Evaluation of the Tauc method for optical absorption edge determination: ZnO thin films as a model system Phys. Status Solidi b 252 1700–10
[46] Wang P, Zhan S, Xia Y, Ma S, Zhou Q and Li Y 2017 The fundamental role and mechanism of reduced graphene oxide in r-GO/Pt-TiO$_2$ nanocomposite for high performance photocatalytic water splitting Appl. Catal. B Environ. 207 335–46
[47] Sajjad S, Khan M, Leghari S A K, Ryma N A and Farooqui S A 2019 Potential viable WO$_3$/GO composite photocatalyst Int. J. Ceram. Tech. 16 1216–27
[48] Yeh T F, Chan F F, Hsieh C T and Teng H 2011 Graphite oxide with different oxygenated levels for hydrogen and oxygen production from water under illumination: the band positions of graphite oxide J. Phy. Chem. C 115 22387–97
[49] Murcia J J, Hidalgo M C, Navio J A, Araña J and Rodrigues J M D 2014 Correlation study between photo-degradation and surface adsorption properties of phenol and methyl orange on TiO$_2$ Vs platinum-supported TiO$_2$ Appl. Catal. B Environ. 150 107–15
[50] Istrate R, Stoia M, Păcuraru C and Locovici C 2016 Single and simultaneous adsorption of methyl orange and phenol onto magnetic iron oxide/carbon nanocomposites Arab. J. Chem. (https://doi.org/10.1016/j.arabjc.2015.12.012)
[51] Zhao J, Yu H, Li H, Sun L, Zhang K and Yang H 2015 Visible-light photocatalytic activity of graphene oxide–wrapped Bi$_2$WO$_6$ hierarchical microspheres Appl. Surf. Sci. 344 101–6

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