Journal of Contemporary Research in Chemistry (2016) 1(1): 42-50

ORIGINAL PAPER

Fabrication of SnO_2/CQDs composite for photocatalytic degradation of malachite green dye

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ABSTRACT In the present study, an attempt had been made to design and fabricate the SnO_2/CQDs composite. Initially, SnO_2 nanoparticles were prepared by co-precipitation method. X-ray diffraction (XRD) results have revealed the formation of pure single phase tetragonal SnO_2 nanoparticles. Carbon quantum dots (CQDs) have been prepared by microwave assisted method. The formation of SnO_2/CQDs composite has been confirmed by fourier transformed infrared (FTIR) spectroscopy. The slight shift in peak position of Sn-O-Sn bond has revealed the formation of SnO_2/CQDs composite. Scanning electron microscopy (SEM) of the samples has indicated the formation of SnO_2 nanoparticles and dispersion of SnO_2 nanoparticles into CQDs matrix. Further, SnO_2 nanoparticles and its composite with CQDs were employed as photocatalysts in the degradation of Malachite green (MG) dye under open sun light irradiation. The excellent feature of the study is that for both the photocatalysts, only in 10 minutes complete degradation of dye has been achieved. Photocatalytic results have revealed that SnO_2/CQDs photocatalyst possesses better photocatalytic activity than that of pure SnO_2 nanoparticles.

Keywords: Carbon quantum dots, Degradation, Fabrication, Photocatalytic activity, SnO_2 nanoparticles, SnO_2/CQDs composite

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To cite this article as: Javed, R., Nawaz, F., Sohail, M., & Ahmad, I. (2016). Fabrication of SnO_2/CQDs composite for photocatalytic degradation of malachite green dye. *Journal of Contemporary Research in Chemistry*, *1*(1), 42-50.

INTRODUCTION

Tin oxide is considered to be a wide band gap an n-type semiconductor. Its excellent optical, electronic and chemical properties makes it possible to be used for several applications, such as electrode luminescence, gas sensor and anode material for lithium ion batteries (Gnanam & Rajendran, 2010). One of the interesting applications of SnO_2 nanoparticles is its potential use in photocatalysis. Its catalytic property is greatly affected by changing its surface morphology and different surface features may offer different catalytic properties. Therefore, it is desirable to tune the surface morphological features of SnO_2 either by changing the synthesis conditions or by its surface functionalization through composite formation with other materials like carbon nanotubes (Kim et al., 2015), TiO_2 nanoparticles (Scarisoreanu et al., 2017), graphen (Wang et al., 2015) etc.

Another excellent candidate for photocatalysis, which is attracting deep interest, is carbon nanostructured material due to its distinctive and novel features. The intense and adjustable luminescence of these materials make them unique from other materials. Further, the quantum effect in carbon based materials is vital for various technological applications (Iijima, 1991; Bethune et al., 1993; Kang et al., 2003; Kang et al., 2005). Today, photoluminescent carbon nanomaterial is the main focus area of the researchers. Different synthetic routes have been adopted by the researchers to fabricate the carbon based nanomaterials, e.g., laser ablation, electrochemical, thermal, vapor deposition, proton-beam, microwave assisted synthesis and bottom-up methods (Yu et al., 2005; Bottini et al., 2006; Sun et al., 2006; Cao et al., 2007; Zhou et al., 2007). However, the size of graphite nanoparticles is very small (ca. 2 nm) but they present intense blue photoluminescence (Zheng et al., 2009). Among carbon nanostructured materials, carbon quantum dots (CQDs) have particle size below 10 nm and the confinement of their excitons is in all the three dimensions. It has been observed that CQDs can be used as efficient catalysts

for the degradation of organic dyes under the visible light. They can also be employed in photocatalysis along with other materials like TiO_2 and SiO_2 for the degradation of dyes like methyl blue (Li et al., 2010).

Although, both SnO_2 nanoparticles and CQDs possess the good photocatalytic properties but, still there is need of improvement in their properties. One way to enhance their photocatalytic properties is surface functionalization of SnO_2 nanoparticles through composite formation with CQDs. In this article, we have reported a composite consisting of SnO_2 nanoparticles and CQDs to exploit the photocatalytic properties of both for degradation of malachite green (MG) dye. With the best of our knowledge we are using first time CQDs with SnO_2 nanoparticles in the form of composite material as a photocatalyst for degradation of MG dye.

MATERIALS AND METHODS

Chemicals

The chemicals employed are citric acid with 99.5% purity (BDH Chemicals), ethylenediamine with 99% purity (Sigma-Aldrich), tin (II) chloride with 99.99% purity (Merck), sodium hydroxide with 98% purity (Sigma-Aldrich), ethanol with 99.5% purity (Sigma-Aldrich) and malachite green with 90% purity (Merck). No further treatment of chemicals was performed and they were used as received.

Preparation of SnO_2 nanoparticles

The solution of tin chloride ($SnCl_2$) having molarity 0.1 mol/dm^3 was prepared by adding 1.89 g of $SnCl_2$ in 100 mL distilled water. On the other hand, 0.2 mol/dm^3 solution of sodium hydroxide was also prepared by dissolving 2 g of it in 250 mL of doubly distilled water. The solution of tin chloride was stirred on hot plat at room temperature. Then the solution of NaOH was poured drop wise into the beaker containing solution of $SnCl_2$ till the pH reached to 10.5 and at that pH, white precipitates were appeared in the solution. Then reaction mixture was agitated for a period of three hours. Then filtration was done to separate out the precipitates. The repeated washings of precipitates were performed with the doubly distilled water and ethanol respectively. Finally precipitates were dried in oven at 373 K and annealed at 773 K for two hours in muffle furnace.

Preparation of carbon quantum dots

The solution of citric acid with molarity of 0.5 mol/dm^3 was made by adding its 2.6 g in 25 mL doubly distilled water. After that, 10 mL solution of citric acid was added into a beaker already containing 0.5 mL ethylene diamine. Then beaker was placed in the microwave oven and was irradiated with irradiation power of 700 watt for 2-3 minutes. After that, beaker was removed from microwave oven and CQDs were collected.

Synthesis of SnO_2/CQDs composite

The SnO_2/CQDs composites were synthesized by adding 0.05 g of SnO_2 nanoparticles and 20 µL CQDs into 100 mL beaker containing 25 mL of ethanol. Afterward the stirring of solution on magnetic hot plate was performed at 80 ^oC for a period of 30 minutes. After that filtration was performed, then precipitates were washed with distilled water and finally with ethanol to remove the impurities. Then, collected SnO_2/CQDs composites were dried in oven.

Structural characterization of samples

X-ray diffraction (XRD) analysis of SnO_2 nanoparticles was performed by X-Ray diffractometer (PANalytical X' Pert PRO 3040/60) equipped with Cu K_α x-rays source at 45 kV and 40 mA. Scanning electron microscopy (SEM) of the SnO_2 nanoparticles and SnO_2/CQDs composite was carried out by microscope model JEOL JSM-840. Fourier transformed infrared (FTIR) spectroscopic analysis of SnO_2 nanoparticles, CQDs and SnO_2/CQDs composites was carried out by Perkin Elmer FTIR spectrum-2000 spectrometer.

Photocatalysis

To compare the photocatalytic performance of SnO_2 nanoparticles with SnO_2/CQDs composite, an industrial dye, Malachite green (MG) was chosen for photocatalytic degradation. For this purpose, 10 mg of SnO_2 nanoparticles were added in 200 mL solution ($1x10^{-4}$ M) of MG. Then, solution was subjected to the open sunlight irradiation on an orbital shaker with continuous shaking. After that, 5 mL solution was withdrawn from the reaction mixture and immediately centrifuged to remove the nanoparticles. And finally, UV/Visible spectrum of that solution was recorded by UV-1100 spectrophotometer. The same was repeated after regular interval of 10 minutes up to 60 minutes. The similar procedure was adopted for SnO_2/CQDs composite.

RESULTS AND DISCUSSION

X-ray diffraction studies of SnO_2 nanoparticles

The XRD pattern of SnO_2 nanoparticles annealed at 773K is presented in the Fig. 1. The diffraction peaks observed at 2θ values of 26.74, 33.89, 52.04 and 65.25 correspond to planes with hkl values of 110, 101, 211, and 301, respectively and these diffraction peaks were well matched with a standard pattern; JCPDS code No. 21-1250. This kind of diffraction pattern is characteristic of tetragonal phase of SnO_2 nanoparticles. The magnitude of average crystallite size "*D*" has been determined by calculating the width of diffraction peaks at half of the maximum height employing Debye-Scherer equation (Ahmad, Shah, Ashiq, & Khan, 2016; Chandramouleeswaran et al., 2007).

$$D = \frac{0.94\lambda}{\beta cos\theta} \quad (1)$$

Where λ is the wavelength of radiation (1.5418 A°) employed in XRD analysis, β is peak broadening (full width at half of the maximum height) and θ is an angle in radian. Crystallite size for SnO_2 nanoparticles has been calculated from all the diffraction peaks and its average value is 26.13 nm.

SEM studies

SEM is an excellent tool to explore the surface morphology of nanomaterials and to study the surface characteristics, SEM studies of SnO_2 nanoparticles and SnO_2/CQDs composite have been carried out. SEM images of SnO_2 nanoparticles and SnO_2/CQDs composite are displayed in Fig. 2 (A and B). It is clear from the SEM results that SnO_2 nanoparticles exhibit their rod like shapes and have random distribution throughout. Further, dispersion of SnO_2 nanoparticles in matrix of CQDs is visible in Fig. 2 (B). It is evident from both the SEM micrographs that particle sizes of both SnO_2 nanoparticles and SnO_2/CQDs composite are almost same and no substantial change has been observed in this regard even after CQDs coverage.

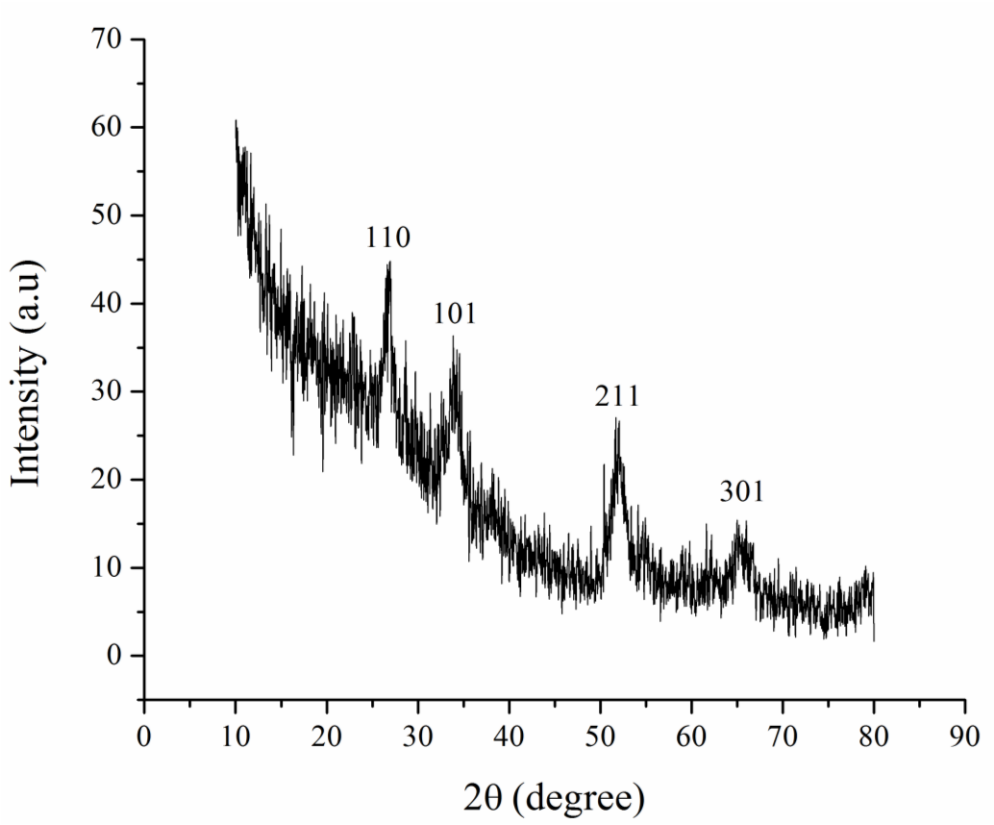

Fig. 1 XRD pattern of SnO_2 nanoparticles annealed at 773 K

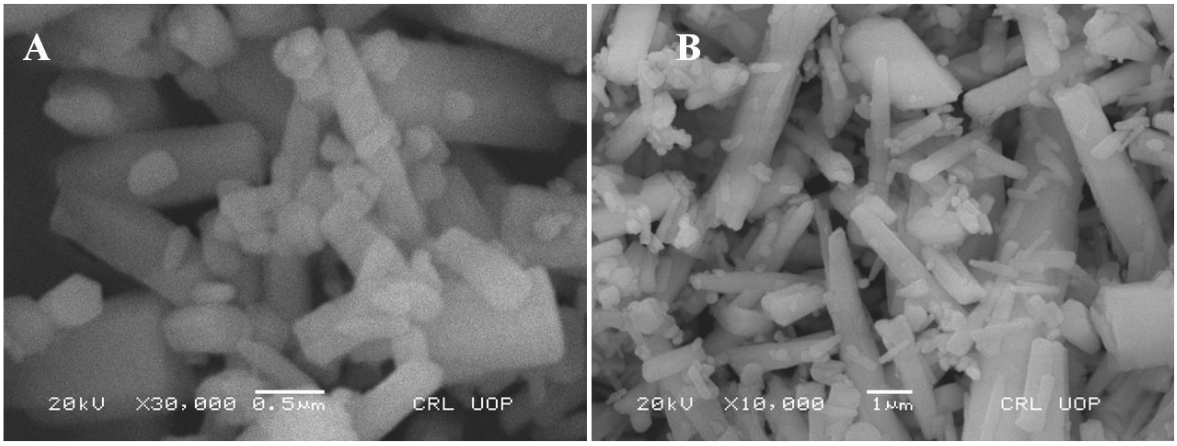

Fig. 2 SEM micrographs of (A) SnO_2 nanoparticles and (B) SnO_2/CQDs composite

FTIR studies

FTIR spectroscopy is an essential technique employed for the identification of the major functional groups in different compounds (Silverstein et al., 2014). FTIR studies were performed to confirm the composite formation of SnO_2 nanoparticles with CQDs. FTIR spectrum of CQDs is shown in Fig. 3. The characteristic absorption peaks of ethylene diamine-CQDs were observed for carbonyl group υ (C=O) (~1732 cm^{-1}), amine group υ (N–H) (3264 cm^{-1}) and δ (N-H) (1662 cm^{-1}) and cyanide group υ (C–N) (~1580 cm^{-1}) (Zhai et al., 2012). This characteristic absorption pattern of FTIR shows the development of CQDs (Dong et al., 2015).

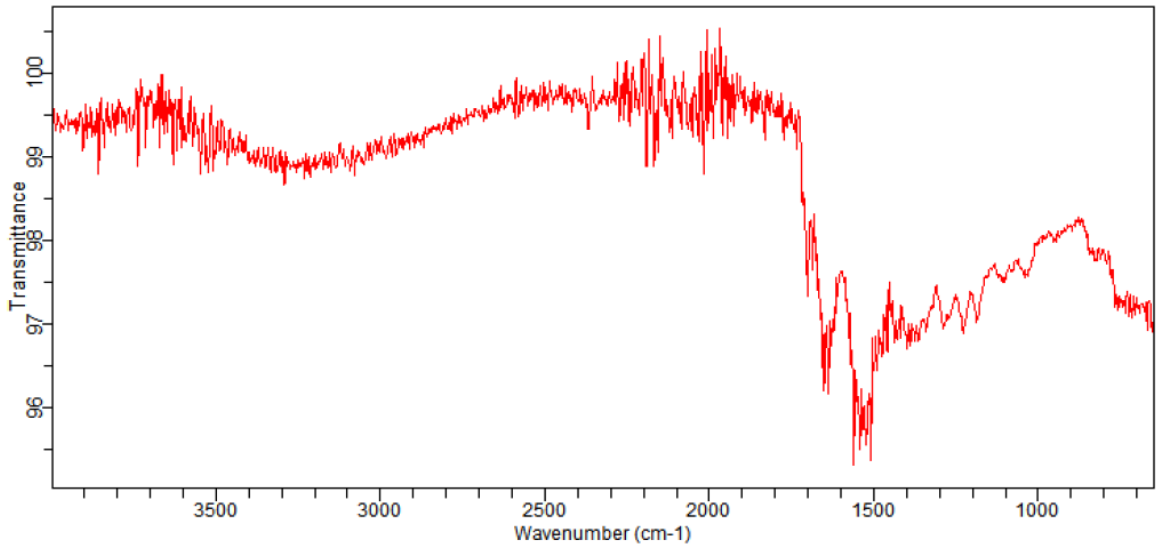

Fig. 3 FTIR spectrum of CQDs recorded at room temperature

Fig. 4 represents the FTIR spectrum of SnO_2 nanoparticles recorded at 298 K. The spectrum of SnO_2 nanoparticles is important from 2000-600 cm^{-1} range. The FTIR spectrum depicts the fundamental absorption peaks at about 1720, 1420, 1048, and 660 cm^{-1}. The peak observed at 1720 cm^{-1} is due to adsorbed water molecules on the surface of SnO_2 nanoparticles and is attributed to bending vibrations of H-O-H bond (Bouhekka & Bürgi, 2012). The lattice vibrations correspond to the region 1480-1090 cm^{-1} due to the decrease in the intensity that leads to overtones and the combinations of the water molecules which are adsorbed on the surface of SnO_2 sample. The peak centred at region of 680-600cm^{-1} is due to the stretching mode of Sn-O-Sn (Yang et al., 2004), hence showing the formation of SnO_2.

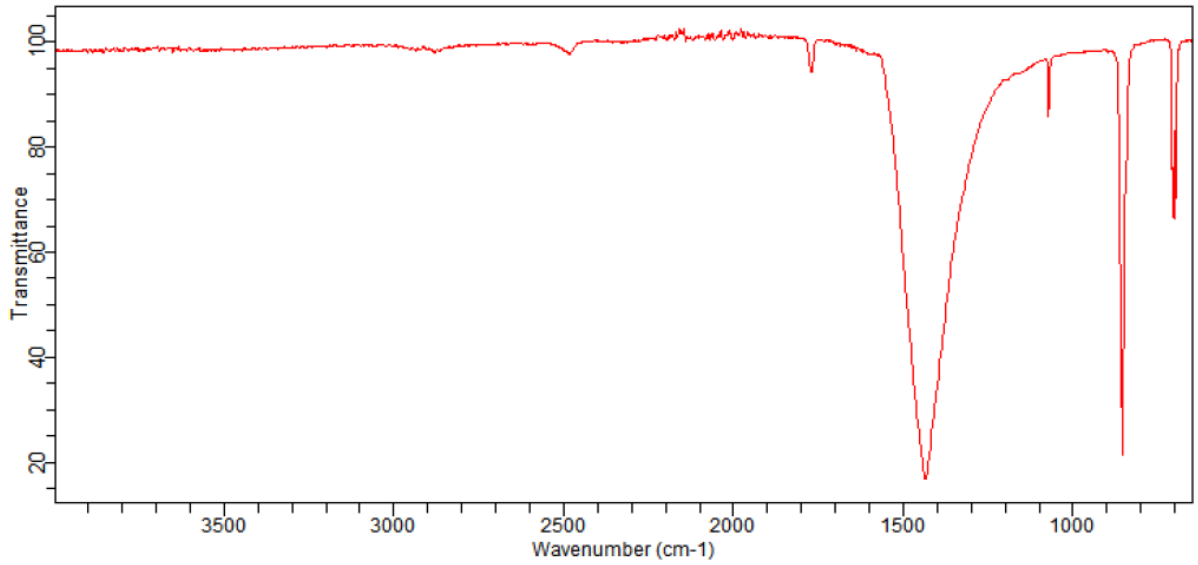

Fig. 4 FTIR spectrum of SnO_2 nanoparticles annealed at 773 K

Fig. 5 shows the FTIR spectrum of SnO_2 nanoparticles/CQDs composite. The slight peak shift of Sn-O-Sn bond reveals the formation of SnO_2/CQDs composite.

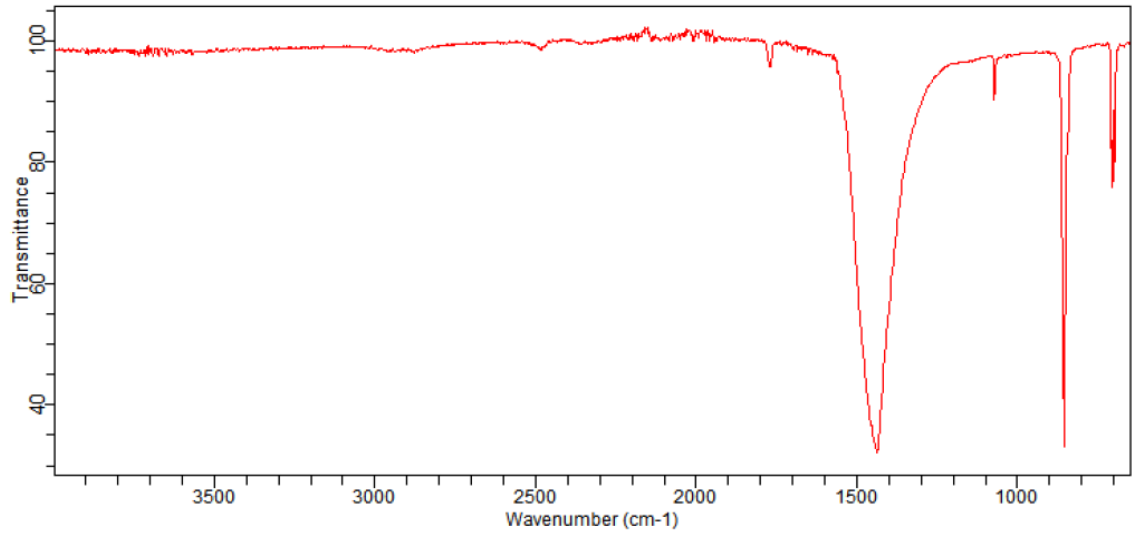

Fig. 5 FTIR spectrum of SnO_2/CQDs composite recorded at room temperature

Photocatalytic activity of SnO_2 nanoparticles and its composite with CQDs

To evaluate the photocatalytic performance of the prepared SnO_2 nanoparticles, 10 mg of it and its composite in separate experiments have been added into beakers already containing 200 mL of 10^{-4} M aqueous solutions of MG. Then, these solutions were stirred on orbital shaker in open sun light. In the presence of sunlight, different photochemical reactions happen on the surface of SnO_2 or SnO_2/CQDs photocatalyst. It is well known fact that surface area of catalyst plays a key role in its performance. Therefore, increased surface area results in better catalytic performance and hence, resulting greater degradation of the dye. Hence, nanoparticles of SnO_2 and its composite with CQDs have been chosen for the degradation of MG. UV/Visible spectra of solutions of MG dye were recorded after regular interval of time to study the progress of the photocatalytic degradation reactions.

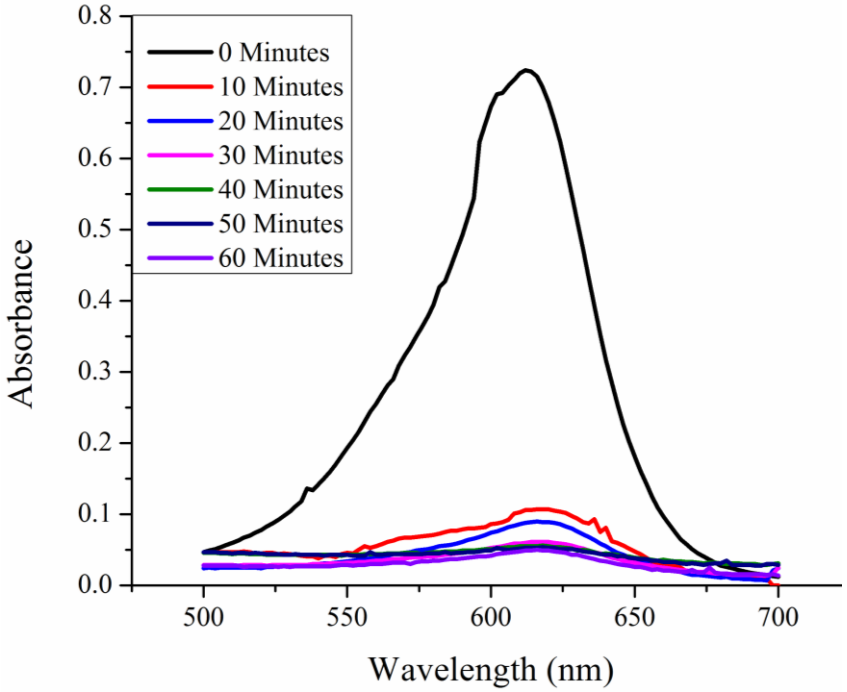

Fig. 6 UV/Visible absorption spectra of MG in the presence of SnO_2 nanoparticles under sunlight irradiation recorded at different times

Fig. 6 and 7 show the UV/Visible spectra of MG dye solutions at different exposure times of solar irradiation in the presence of SnO_2 nanoparticles and SnO_2/CQDs composite, respectively. The UV/Visible spectrum of MG exhibits a λ_{max} at about 612 nm. Gradually intensity of this peak decreases which reveal the degradation of MG dye (Kansal et al., 2009). When time period of 60 minutes is elapsed, for SnO_2 nanoparticles as well as SnO_2/CQDs, the solutions become almost transparent.

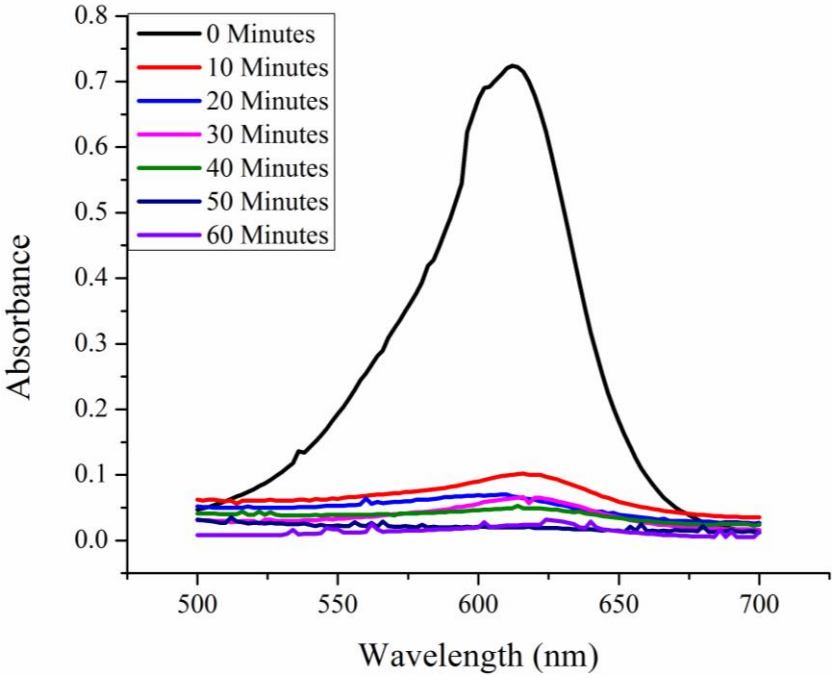

Fig. 7 UV/Visible absorption spectra of MG in the presence of SnO_2/CQDs composite under sunlight irradiation recorded at different times

Further, comparison in terms of fraction of MG retained in the solution at various times is displayed in Fig. 8. which clearly demonstrates that the photocatalytic performance of SnO_2/CQDs composite in terms of degradation of MG is better than the pure SnO_2 nanoparticles and it can be attributed to the combinational effect of SnO_2 nanoparticles and CQDs (Muthulingam et al., 2015). The overall action mechanism of photoctalsyst is summarized in the following reactions (Muthulingam et al., 2015).

$$SnO_2/CQDs + hv \longrightarrow e^-(CQDs) + h^+(SnO_2) \quad (1)$$

$$e^- + O_2 \longrightarrow O_2^- \quad (2)$$

$$h^+ + OH \longrightarrow OH^- \quad (3)$$

$$O_2^{-\bullet} + H_2O \longrightarrow HO_2 + OH^- \quad (4)$$

$$HO_2^{\bullet} + H_2O \longrightarrow H_2O_2 + OH^{\bullet} \quad (5)$$

$$H_2O_2 \longrightarrow 2OH^{\bullet} \quad (6)$$

$$OH^{\bullet} + dye \longrightarrow CO_2 + H_2O \quad (7)$$

$$HO_2^{\bullet} + dye \longrightarrow CO_2 + H_2O \quad (8)$$

$$O_2^{\bullet} + dye \longrightarrow CO_2 + H_2O \quad (9)$$

High energy radicals generated in reaction (3), (4), (5) and (6) are responsible for the degradation of larger molecules like MG (Bourlinos et al., 2008).

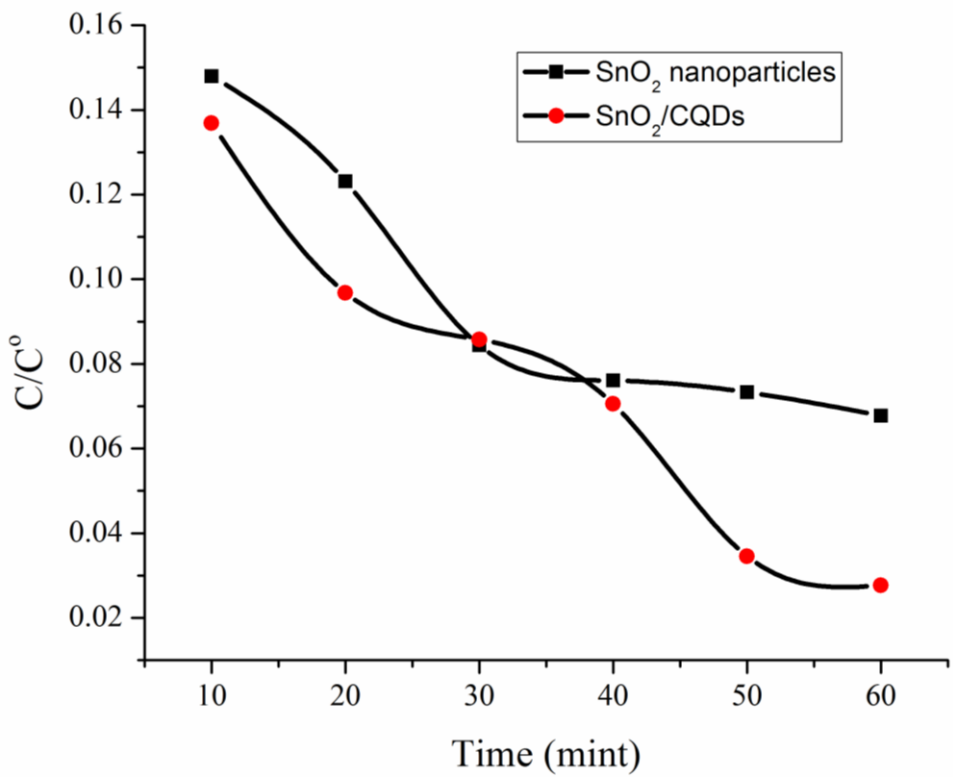

Fig. 8 Comparison of photocatalytic degradation of MG in the presence of SnO_2 nanoparticles and SnO_2/CQDs composite

CONCLUSION

The tetragonal phase of SnO_2 nanoparticles has been achieved by co-precipitation method. The fabrication of SnO_2/CQDs composite has also been successfully performed. The SnO_2/CQDs photocatalyst has demonstrated a better catalytic performance than that of pure SnO_2 nanoparticles towards photocatalytic degradation of MG dye. Thus, this kind of photocatalyst may be a better photocatalyst for detoxification of different organic dyes present in industrial effluents under open sunlight irradiation, instead of employing a specific light source.

Author Contribution Statement All the authors have contributed to prepare this manuscript. Further, manuscript has been read and approved by all the authors.

Conflict of Interest Authors declare that they have no conflict of interest.

Acknowledgement Authors would like to thank Mr. Anwaar Ul Haq, Research Associate at Department of Chemistry, University of Sargodha, Women Campus, Faisalabad, Pakistan, due to his valuable cooperation during experimental studies.

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