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RESEARCH PAPER

Effect of Sulfur and Nitrogen co-Doped Graphene Quantum Dots on Co_3O_4 Nanoparticles as Solar Induced Photocatalyst

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ABSTRACT

The photocatalyst process is considered the most promising method for the removal of water contamination. For excellent chemical and structural properties of Co_3O_4 nanoparticles, various Co_3O_4-based nanostructures can be applied as a photocatalyst. In this work, carbon quantum dots is prepared via an eco-friendly process and linked to Co_3O_4 effectively. X-ray diffraction pattern (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV-visible absorption spectroscopy and Fourier transform infrared spectroscopy (FT-IR). The photocatalyst process reveals that prepared nanocomposites can be degraded methylene blue under solar irradiation strongly. Results showed that methylene blue and methyl orange are degraded via 64% and 56% efficiency after 70 minutes of irradiation under visible irradiation using Co_3O_4 nanoparticles respectively. The photocatalytic performance of Co_3O_4 nanoparticles was improved via linking SN-GQDs and formation SN-GQDs/ Co_3O_4 nanocomposites. UV-Vis analysis revealed that charge transfer from Co_3O_4 to SN-GQDs and prevent charge recombination in Co_3O_4 which leads to better photocatalytic efficiency. This study introduces SN-GQDs/ Co_3O_4 nanocomposites as a novel and green photocatalyst agent.

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INTRODUCTION

Energy consumption is one of the critical challenges of humanity [1]. Industrialism has imposed some harmful effects including environmental and energy-based drawbacks. The mentioned challenges are crucial for human life and play a key role in the economy, policy, and national security. Till now, many efforts have been focused on the balancing of these drawbacks [2, 3]. One of the most prominent methods which is developed is the photocatalytic process. A photocatalyst is a material that absorbs light and converts it

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to a higher energy level before passing it on to a reacting product to degrade different organic pollutants [4-6]. So, the photocatalyst uses solar energy as a renewable energy source to solve the environmental issue. The photocatalytic process is the intersection of energy and environment [7, 8]. The emergence of nanoscience leads to utilizing nanoscience and nanotechnology to overcome energy and environment-based challenges. Till now, various nanostructures have been applied for overcoming these challenges [9-12].

GQDs have recently become the subject of study due to their interesting luminescence properties that are size-dependent. This distinguishes it from other carbon derivatives. GQDs can be defined as very tiny size graphene fragments which cause quantum confinement in GQDs [13-15]. This characteristic makes GQDs biocompatible, photostable, high quantum efficiency, and chemically inert [16]. Next to this, GQDs can be synthesized via a simple method and low-cost precursors [17]. These excellent properties lead to the application of GQDs in the photocatalysis-based application. GQDs suffer from various limitations such as a strong tendency of aggregation, and the difficulty of recovery and reusability. To overcome these problems, other nanomaterials can be used alongside GQDs [14, 18, 19]. Co_3O_4-based nanostructures are a good candidate for the improvement of the photocatalytic activity of GQDs. Cobalt oxide is widely used as magnetic material, catalyst and photocatalyst, antibacterial agent, and drug delivery. The use of Co_3O_4 causes easily magnetically separation from the reaction system. Since the physical and chemical properties of Co_3O_4 nanomaterials are tunable, they can be synthesized in any size and shape depending on the application field [20-22].

Chun-Hui Shen and et al. prepared Co_3O_4/CeO_2 nanocomposites by a simple chemical reaction, followed by annealing in a muffle furnace. They applied prepared nanocomposites to activate peroxymonosulfate (PMS) for ciprofloxacin (CIP) degradation. They reported that the 5 wt% Co_3O_4/CeO_2/PMS showed the highest degradation efficiency of CIP (87.8%) under visible light irradiation. The prepared Co_3O_4/CeO_2/PMS system still provided a sufficient catalytic activity in presence of different anions [23].

In another work, Co_3O_4/red phosphorus (Co_3O_4/RP) photocatalyst was prepared via a hydrothermal and mechanically grinding route. The findings revealed that Co_3O_4 nanocrystals were mounted on the RP's surface. When compared to pure RP, the addition of Co_3O_4 to the RP improved light absorption. It is found that under visible light, 94.5% of malachite green (MG) can be photodegraded within 20 min via 10% Co_3O_4/RP composite, while only 17.3% and 59.9% of MG can be photodegraded via pure Co_3O_4 and RP [24].

In this work, novel Co_3O_4/SN-GQDs nanocomposites were synthesized via a simple and facile hydrothermal method. The prepared products were characterized with XRD, FTIR, SEM, TEM, and UV-Vis analysis. Then, the prepared nanomaterials were applied as a photocatalyst for the degradation of organic pollutants under visible irradiation.

MATERIALS AND METHODS

Chemical and reagents

Cobalt nitrate (Co $(NO_3)_2.6H_2O$), Polyvinylpyrrolidone (PVP), sodium hydroxide (NaOH), citric acid, and L-cysteine were purchased from Merck and all the chemicals were used as received without further purifications.

Synthesis of SN-GQDs

SN-GQDs was prepared according to a previously published paper [25]. In brief, citric acid and L-cysteine, 1:1 molar ratio, were dissolved in 10 mL distilled water and heated for 6 hours at 90 °C in an oil bath. Then, the obtained viscous gel was transferred to stainless autoclave and heated to 180 °C for 6 h. The obtained product was diluted with 200ml distilled water and centrifuged at 12000 rpm for 30 min. The obtained solution was kept at 4°C for further tests.

Preparation of Co_3O_4 nanoparticles

In a typical procedure, 2 mmol (0.58g) of Co $(NO_3)_2.6H_2O$ and 0.5g PVP were dissolved in 20 ml distilled water. Then, NaOH (2M) was added dropwise to the Co-containing solution. Then, the solution was transferred to stainless autoclave and heated at 120 ˚C for 20 hours. The prepared product was centrifuged at 12000 rpm for 30 min. The collected solid was washed with ethanol and water for several times. Finally, the product was dried at 60 ˚C for overnight.

Preparation of Co_3O_4/SN-GQDs nanoparticles

First, 0.3g as-prepared Co_3O_4 was dispersed in 20 ml prepared SN-GQDs solution under sonication

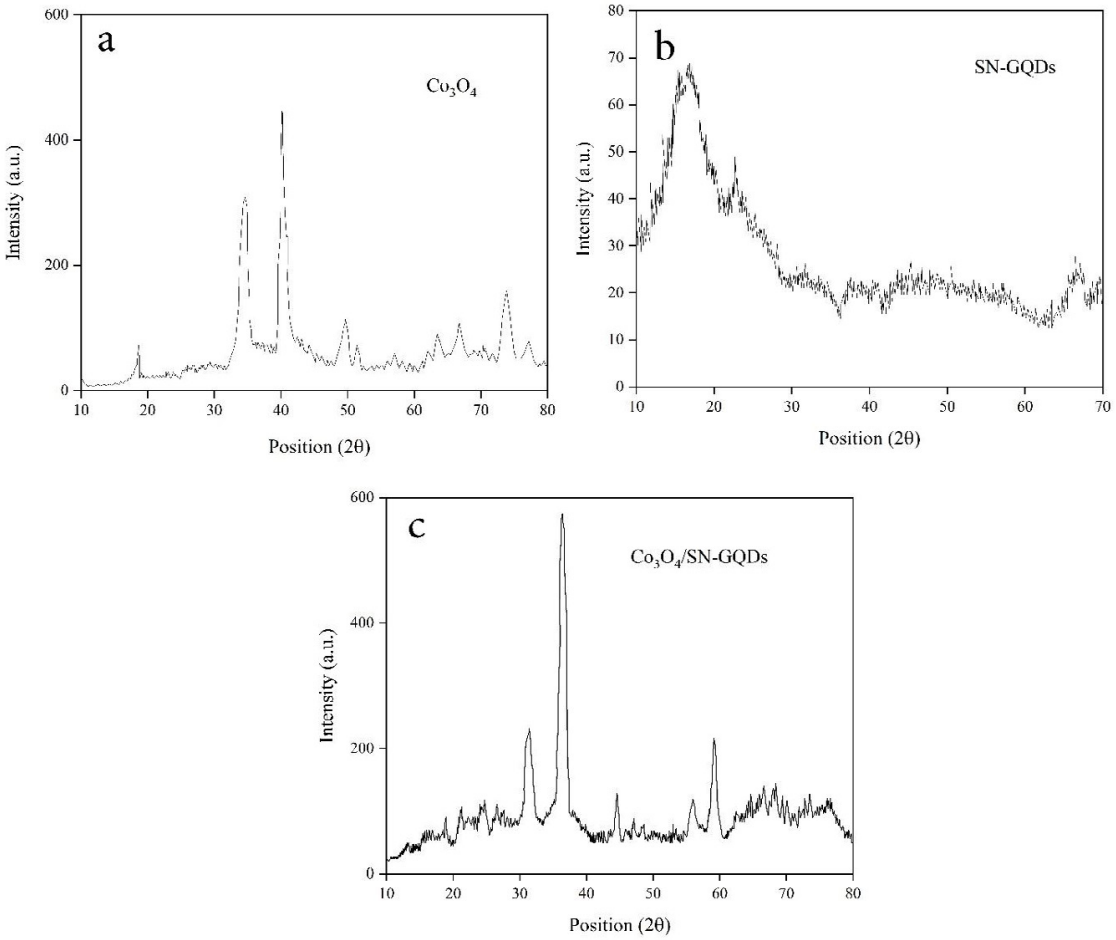

Fig. 1. XRD pattern of prepared a) Co_3O_4 nanoparticles b) SN-GQDs and c) Co_3O_4/SN-GQDs nanocomposites

for 45 min. Then, the mixture was stirred at ambient condition for 24 hours. The prepared nanocomposites was collected via centrifuge (12000 rpm) and dried at 50 ˚C for overnight.

Characterization

Using Ni-filtered Cu K radiation, the XRD patterns were reported using a Rigaku D-max C III X-ray diffractometer (Rigaku Corporation, Shibuya-ku, Japan) (λ = 1.5418 Å). SEM images were obtained using an LEO instrument model 1455VP. Transmission electron microscope (TEM) images were obtained on a Philips EM208S transmission electron microscope with an accelerating voltage of 100 kV. UV–vis diffuse reflectance spectroscopy analysis (UV–vis) was carried out using Shimadzu UV-vis scanning spectrometer. Fourier transform infrared (FT-IR) spectra were recorded using a Nicolet 6700 FT-IR spectrophotometer at room temperature.

Photocatalytic test

The photocatalytic efficiency of Co_3O_4 nanoparticles and Co_3O_4/SN-GQDs nanocomposites were investigated by degrading methylene blue and methyl orange under visible light irradiation. Until photodegradation, Co_3O_4 nanoparticles and Co_3O_4/SN-GQDs nanocomposites (0.01g) and methylene blue and methyl orange solution (10 ppm) were stirred for 30 minutes in the dark to achieve adsorption-desorption equilibrium. At regular intervals, the suspension (2 mL) was removed from the system and isolated. The dye concentration was determined with aid of a UV-vis spectrophotometer.

RESULTS AND DISCUSSION

XRD analysis was utilized for the characterization of crystallinity. Fig. 1 displays XRD analysis of prepared Co_3O_4 nanoparticles, SN-GQDs, and Co_3O_4/SN-GQDs nanocomposites.

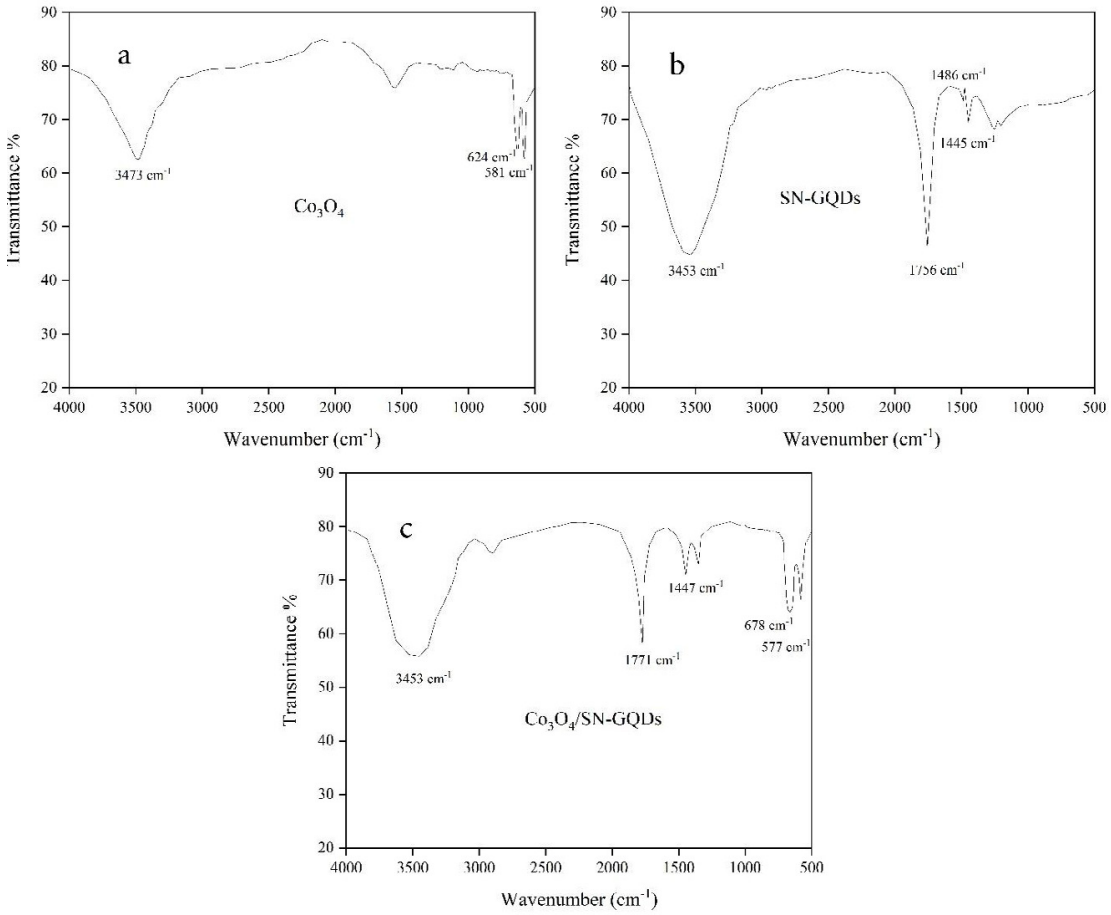

Fig. 2. FTIR spectrum of prepared a) Co_3O_4 nanoparticles b) SN-GQDs and c) Co_3O_4/SN-GQDs nanocomposites

According to the data obtained from the Xpert high score software, the prepared sample has an XRD pattern with JCPDS No.80-0075, space group: P63mc, confirming the successful synthesis of cubic phase Co_3O_4 nanoparticles. The XRD results were also confirmed the formation of Co_3O_4 without impurity. The crystalline size was calculated 27 nm via Scherrer equation [26]:

$$Dc=K\lambda/\beta Cos\theta \quad (1)$$

where β is the width of the observed diffraction peak at its half maximum intensity (FWHM), K is the shape factor, which takes a value of about 0.9, and λ is the X-ray wavelength (CuKα radiation, equals to 0.154 nm). Fig. 1b shows the XRD pattern of prepared SN-GQDs. The broad peak at 2θ=24˚ is attributed to the graphitic structure of SN-GQDs. The greater d-spacing value of the SN-GQDs suggests that prepared SN-GQDs still contain oxygen-containing functional groups. This may be linked to GQDs' size and edge effects. The nanoscale size of the GQDs with just a few layers of graphene sheets is due to the broad diffraction peak. Fig. 3b presents the XRD pattern of Co_3O_4/SN-GQDs nanocomposites. The compassion of XRD results confirmed the formation of Co_3O_4/SN-GQDs nanocomposites with any impurity.

Fig. 2 shows The FT-IR spectra of prepared Co_3O_4 nanoparticles, SN-GQDs, and Co_3O_4/SN-GQDs nanocomposites. The two characteristic absorption peaks at 581 cm^{-1} and 624 cm^{-1} are attributed to Co-O bond. The presence of these peaks confirms the bond formation of Co^{3+}-O (581 cm^{-1}) and Co^{2+}-O (624 cm^{-1}). In SN-GQDs, a strong absorption peak at 1756 $cm^{-1}$is assigned to the surface-adsorbed COOH functional group. Also, the different appeared peaks at 1000-1500 cm^{-1} are related to C-C and C-O stretching mode. The FTIR spectra of Co_3O_4/SN-GQDs nanocomposites also confirm the linking of SN-GQDs to Co_3O_4 nanoparticles.

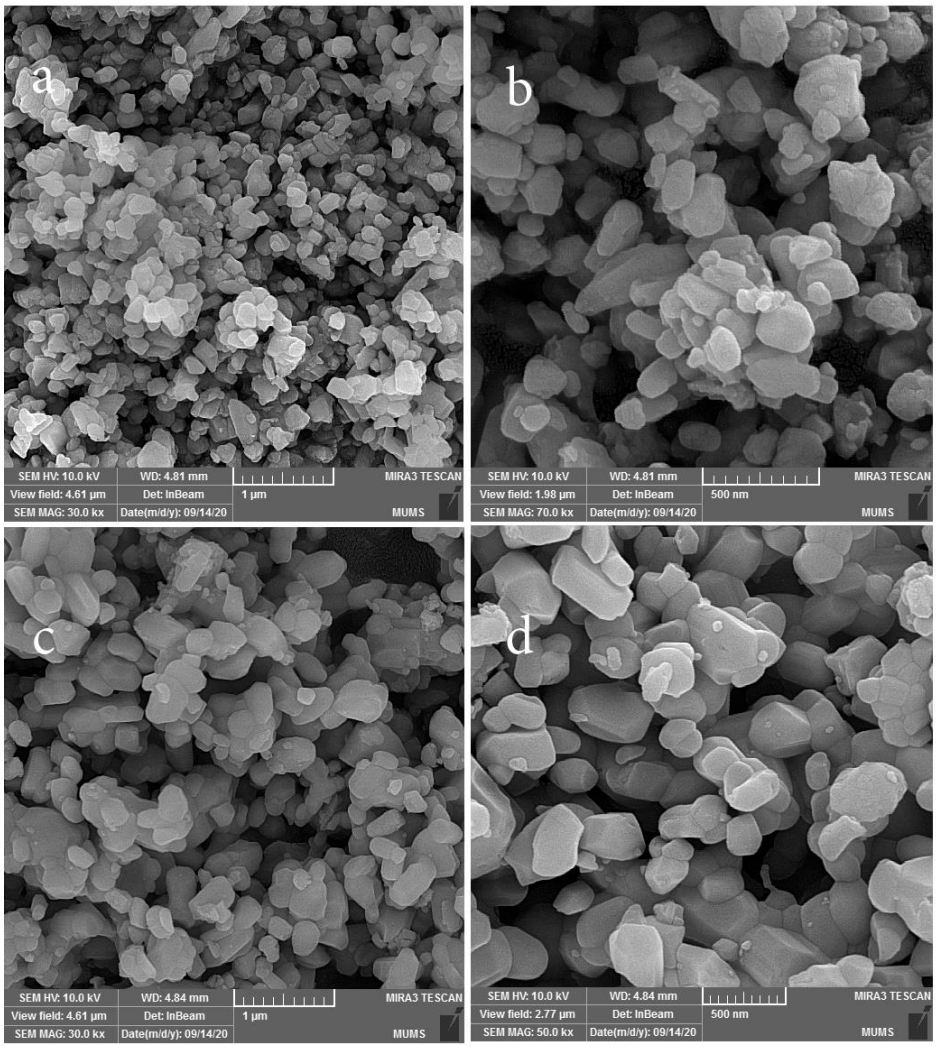

Fig. 3. SEM images of a,b) Co_3O_4 nanoparticles c,d) Co_3O_4/SN-GQDs nanocomposites at two magnifications

Scanning electron microscope (SEM) was applied to investigate the shape, size, and texture of prepared products. For better investigation, the SEM image is presented in two magnifications for each sample (Fig. 3). Fig. 3a and Fig. 3b which is related to SEM images of prepared Co_3O_4 nanoparticles confirms homogenous nanoparticles with an average 95 nm. For Co_3O_4/SN-GQDs nanocomposites (Fig. 3c, and Fig. 3d), it is clear that small size SN-GQDs are formed with greater Co_3O_4 nanoparticles. Transmission electron microscopy (TEM) was applied for in-depth morphological examination of Co_3O_4 nanoparticles, and Co_3O_4/SN-GQDs nanocomposites. Fig. 4a, and Fig. 4b show TEM images of Co_3O_4/SN-GQDs. The obtained results from TEM images is in good agreement with SEM images. As well as shown, the small size SN-GQDs are formed beside Co_3O_4 nanoparticles. It can be concluded from SEM and TEM images that homogenous Co_3O_4 nanoparticles and Co_3O_4/SN-GQDs nanocomposites are formed with nanoscale shape and size.

The UV-Vis diffuse reflectance spectroscopy was applied for the investigation of optical properties of products. Fig. 5a shows two absorption bands in the 423 nm and 586 nm which is due to O^{2-}- Co^{2+} and O^{2-}-Co^{2+}, respectively. Via introducing SN-GQDs it is clear that absorption band is shifted to higher wavelength (visible region) (Fig. 5b). This blue shift lead to application of prepared nanocomposites in photocatalytic process.

Organic pollutants are one of the most problematic concerns. The photocatalytic removal of these contaminants has been found

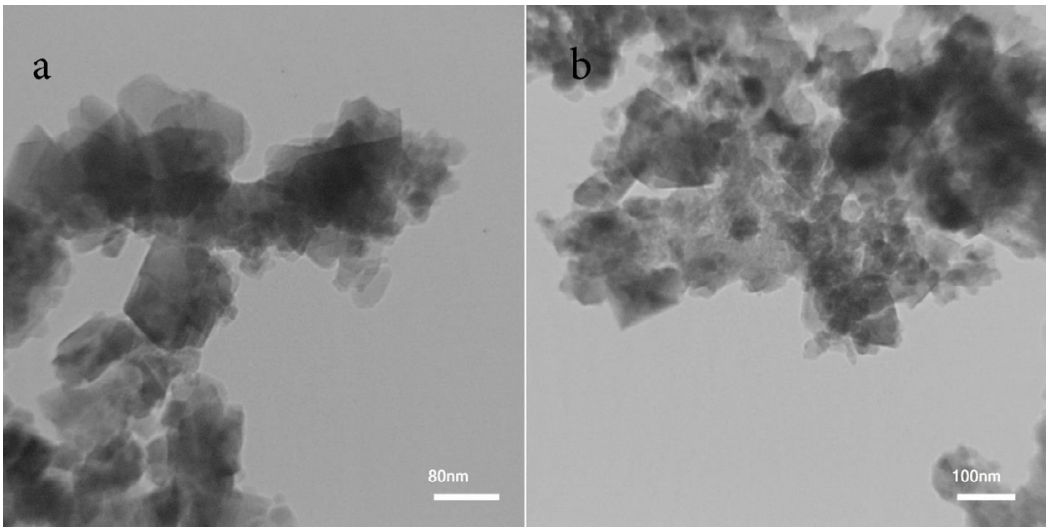

Fig. 4. TEM images of prepared Co_3O_4/SN-GQDs nanocomposites

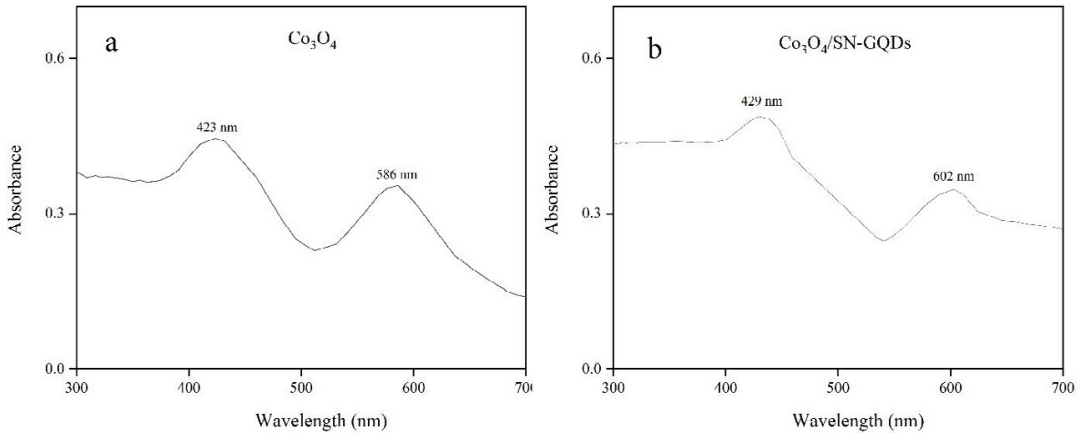

Fig. 5. UV-Vis analysis of prepared a) Co_3O_4 nanoparticles b) Co_3O_4/SN-GQDs nanocomposites

more attention in the recent decade. Fig. 6 and Fig. 7 show the photocatalytic performance of prepared Co_3O_4 nanoparticles, and Co_3O_4/SN-GQDs nanocomposites for degradation of methylene blue and methyl orange under visible light respectively. The photocatalytic efficiency was calculated via:

Photocatalytic efiiciency (%) = $(C_0\text{-}C_t/ C_0) \times 100$ (2)

Where C_0 (mgL^{-1}) is the initial concentration of methylene blue in solution, and C_t (mgL^{-1}) is the concentration of methylene blue and methyl orange at any irradiation time t (min). It is found that 63% of methylene blue was degraded after 70 minutes via using Co_3O_4 nanoparticles. The photocatalytic efficiency was raised to 88% after 70 minutes via Co_3O_4/SN-GQDs nanocomposites. For methyl orange, the photocatalytic efficiency was measured 81% and 56% for Co_3O_4 and Co_3O_4/SN-GQDs respectively. The better photocatalytic performance of Co_3O_4/SN-GQDs may be related to the better charge-separation process in Co_3O_4/SN-GQDs nanocomposites. UV-Vis analysis revealed that charge transfer from Co_3O_4 to SN-GQDs and prevents charge recombination in Co_3O_4. This led to the formation of OH radicals on the surface of Co_3O_4/SN-GQDs nanocomposites and facilitates the photocatalytic process.

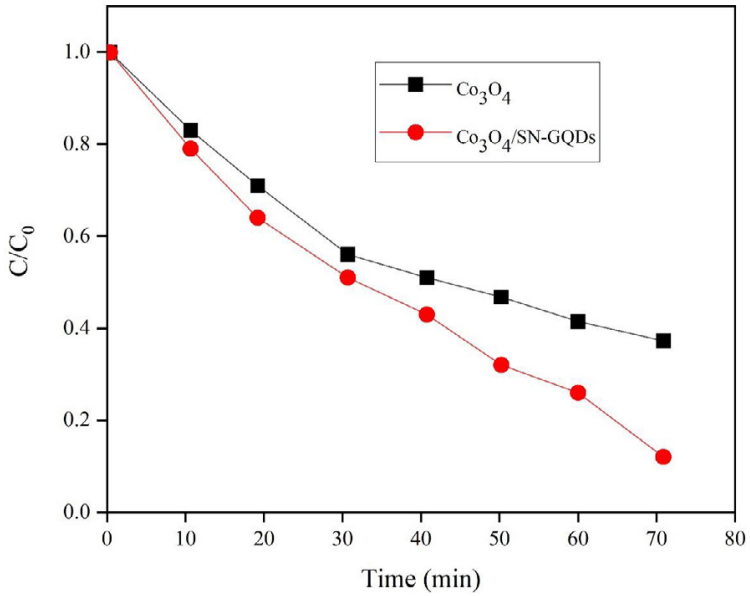

Fig. 6. Photocatalytic performance of prepared Co_3O_4 nanoparticles and Co_3O_4/SN-GQDs nanocomposites against methylene blue

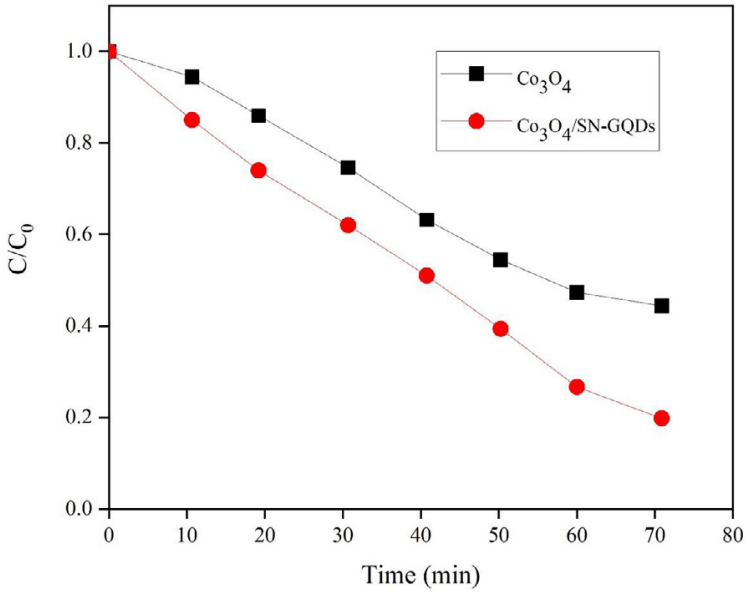

Fig. 7. Photocatalytic performance of prepared Co_3O_4 nanoparticles and Co_3O_4/SN-GQDs nanocomposites against methyl orange

CONCLUSION

In conclusion, Co_3O_4 nanoparticles, and SN-QDs were prepared via the facile hydrothermal method. Then, Co_3O_4/SN-GQDs nanocomposites were prepared via the ultrasonic-assisted method. The prepared nanocomposites were characterized via XRD, FTIR, SEM, TEM, and UV-Vis analysis comprehensively. The UV-Vis analysis of samples led to the application of prepared nanomaterials as photocatalysts for the degradation of organic pollutants. The prepared Co_3O_4 nanoparticles and Co_3O_4/SN-GQDs nanocomposites were applied for the photodegradation of methylene blue and methyl orange under visible light. The results revealed that Co_3O_4 nanoparticles can degrade 64% and 56% of methylene blue and methyl orange after 70 minutes under visible light respectively. The photocatalytic efficiency was raised to 88%

and 81% for Co_3O_4/SN-GQDs nanocomposites case against methylene blue and methyl orange respectively. This improvement can be attributed to a better charge-separation process in Co_3O_4/SN-GQDs nanocomposites.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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