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Original Research Paper

Synthesis of a borosilicate zeolite/graphene quantum dot nanocomposite and investigation of its antibacterial properties

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Abstract: In recent years, Graphene quantum Dots (GQDs) have emerged as promising nanomaterials in various industrial and environmental applications due to their unique physicochemical properties, such as ultrasmall dimensions, excellent electrical conductivity, strong fluorescence and high biocompatibility. However, the common challenge of particle agglomeration often hinders their effective application. Supporting nanoparticles on a suitable substrate can effectively prevent their agglomeration. In this research work, borosilicate zeolite with ZSM-5 structure, graphene quantum dots (GQDs) and GQDs/ZSM-5-type borosilicate composite were prepared using hydrothermal, and pyrolysis methods. The resulting materials were characterized using by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and field emission scanning electron microscopy (FE-SEM) analyses.
Furthermore, the antibacterial performance of the synthesized nanocomposite was evaluated against the Gram-negative bacterium Escherichia coli. The results revealed that the GQDs/ZSM-5 hybrid effectively suppressed bacterial proliferation, leading to a significant reduction in the growth rate of E. coli. Accordingly highlighting the potential of this novel nanoconstruct for environmental applications.

Keywords: Borosilicate zeolite, ZSM-5, Graphene quantum Dots, Nanocomposite, Antibacterial properties.

Introduction

The unique porous architecture of zeolites, high ion-exchange capacity, extensive surface area, and robust thermal and chemical stability, has made them valuable in a wide range of applications [1-4]. The physicochemical properties of zeolites can be finely tuned through isomorphic substitution within the framework (e.g., substituting aluminum with heteroatoms like boron). This process yield novel zeolite variants that preserve the parent structural topology while offering enhanced functionality for emerging technological applications [5-8]. Borosilicate zeolites are produced via substituting aluminum atoms in the zeolite framework with boron, and they used as effective supports for the synthesis of various nanocomposites [8].

In the context of environmental applications, Carbon-based nanostructures, such as carbon quantum dots and graphene, have attracted significant attention owing to their unique chemical and electrical properties and their ability to be functionalized with inorganic nanomaterials. Graphene quantum dots (GQDs), which are graphene nanosheets with thicknesses below 10 nm, exhibit superior dispersion in aqueous media compared to bulk graphene. When these nanostructures are integrated with a zeolite matrix, hybrid with increased surface area are obtained that leads to improved adsorption performance, active surface area, and mechanical robustness [9-13]. In addition, Zeolites, an important class of porous materials, used as supports for the immobilization of photocatalysts. Their porous structure enables uniform distribution of active sites, thereby increasing the overall catalytic efficiency [14]. Zeolites can also suppress the recombination of photogenerated electron–hole pairs due to their intrinsic electron-donor and electron-acceptor properties [15]. The growth and proliferation of bacteria in any field causes harm that necessitates the need for antibacterial substances. Antibacterial materials are chemical substances that act against bacteria and stop the influence of many various types of bacteria. An antibacterial agent is a chemical substance that destroys microorganisms—particularly bacteria—or inhibits their growth. Therefore, antibacterial properties have received much attention in various fields today.

Organo-mineral compounds are among the materials that have been used in this field.

Although numerous studies have investigated the antibacterial effects of nanoparticles [16-19].

Relatively fewer investigations have examined the efficacy of GQDs on bacteria. Therefore, considering the unique characteristics of GQDs, the present study focused on evaluating the antibacterial properties against this nanocomposite.

Experimental

Materials:

Silicic acid ($SiO_2.xH_2O$), borax ($Na_2B_4O_7.10H_2O$), tetrapropylammonium bromide (TPABr, $C_{12}H_{28}N.Br$), and Broth powder were purchased from Merck Company. Sodium hydroxide (NaOH), sulfuric acid (H_2SO_4, 98 %), and Citric acid monohydrate ($C_6H_8O_7.H_2O$), were obtained from Dr. Mojallali chemical industries complex (Iran). All chemicals were used without further purification.

Characterization apparatus:

The crystallographic properties of the samples were examined using X-ray diffraction (XRD) on a Tongda TD-3700 diffractometer equipped with Cu Kα radiation (λ = 1.5406 Å), operating over a 2θ range of 4–70° at ambient temperature. Fourier-transform infrared (FT-IR) spectra were acquired on a Bruker Tensor 27 spectrometer in the range of 400–4000 cm^{-1} using KBr pellets. Morphological features were investigated by field-emission scanning electron microscopy (FE-SEM, Tescan MIRA3, 15 kV) analysis.

Preparation of borosilicate zeolite:

The ZSM-type borosilicate zeolite was synthesized via a hydrothermal procedure as formerly reported [8]. In a typical synthesis, 0.320 g of NaOH was dissolved in 5 mL of distilled water. Then, 1.106 g of silicic acid and 0.606 g of tetrapropylammonium bromide were added to the solution, followed by vigorous stirring until a homogeneous gel was obtained. This gel was then slowly introduced into an aqueous borax solution (0.096 g in 7 mL distilled water) under continuous stirring. The pH of the resulting mixture was adjusted to 11 using diluted H_2SO_4, and stirring was maintained for an additional 90 min. The final gel was transferred into a 100 mL Teflon-lined stainless-steel autoclave and subjected to hydrothermal crystallization at 160 °C for 44 h. The solid product was recovered by filtration and washed with distilled water until neutral pH was achieved. The resulting powder was dried at 60 °C overnight and subsequently calcined at 500 °C for 3 h. The resultant competent was denoted as Na[B]ZSM-5.

Preparation of GQDs:

Graphene quantum dots were synthesized via pyrolysis of citric acid following a previously reported procedure [13]. Briefly, 2 g of citric acid were placed in a crucible and heated at 200 °C for 30 min. After heating, a light orange product was obtained, indicating the formation of GQDs (Figure 1). The resulting suspension was then neutralized by the dropwise addition of sodium hydroxide solution 0.25 mol L^{-1} under vigorous stirring until pH 7 was reached. Eventually, the solvent was vaporized and the product was dried at 100 °C for 24 h.

Fig. 1. Appearance of citric acid pyrolysis

Preparation of nanocomposite:

At first, 0.1g of citric acid (corresponding to the GQDs: borosilicate zeolite weight ratio of 1:1) were mixed with the 0.1 g of calcined borosilicate zeolite and dispersed in water. The suspension was sonicated for 2 h and then the pyrolysis of citric acid was carried out according to the procedure used for the synthesis of GQDs to achieve the GQDs/ borosilicate zeolite composite. The resultant composite was denoted as P-GQDs/Na[B]ZSM-5 (1:1).

Investigation of antibacterial properties:

The antibacterial properties of the prepared composite were evaluated using the Broth Micro dilution method, following the standards established by the Clinical and Laboratory Standards Institute (CLSI).

The broth micro dilution technique use to determine the Minimum Inhibitory Concentration (MIC) of an antibacterial agent against a specific microorganism.

At first, Bacterial and media Suspension was prepared by dissolving 4.7 g of the broth medium in 200 mL of deionized water. Then, 15 mL of this prepared broth solution was dispensed into each 96-well micro plate (in a 12×80 configuration). All glassware, plastic ware, and the prepared broth solution were sterilized via autoclaving. The bacterial suspension concentration was adjusted to an optical density (OD) of 0.6 μg/mL using a UV-Vis spectrophotometer set at a wavelength of 600nm. Sterilized broth solution (2mL) was transferred into sterile vials, followed by the addition of 0.02 g of the adsorbent composite samples to each vial. These vials, containing the bacteria (E.coli in this study) and the samples, were placed in a shaking incubator under visible light for 1 h. The MIC determination was carried out using the micro dilution assay in the 96-well micro plates. 20 μL of the mixture from the vials (containing E. coli and the samples) was spread evenly across the surface of prepared agar plates. In the final step, the inoculated plates were incubated at 37◦C for 24 h.

Results and discussion

FT-IR spectra

FT-IR spectra was employed to characterize the chemical structure of prepared materials (borosilicate zeolite, GQDs and P-GQDs/Na[B]ZSM-5 (1:1)) as shown in Figure 2a–c. The FT-IR spectrum of borosilicate zeolite (Fig. 2a) shows a characteristic band at 551 cm^{-1} which is assigned to the vibrations of 5-membered double rings and confirms the formation of ZSM-5 structure.

Moreover, the connection of boron into zeolite framework is approved by the appearance of a doublet band at 1000–1100 cm^{-1} corresponded to the internal asymmetric stretching vibrations of O−T−O (where T = Si or B).

The bands at 450 and 798 cm^{-1} are attributed to the bending vibration and external symmetric stretching vibrations of T−O−T, respectively [20].

For GQDs (Fig. 2b), characteristic absorption bands assignable to the C− H bending vibration, C− OH stretching vibration, symmetric stretching vibration of carboxyl groups, and aromatic C = C vibration can be observed at 841, 1075, 1393, and 1572 cm^{-1}, respectively [21].

The FT-IR spectra of the nanocomposite (Figure 2c) is similar to those of pure Na[B]ZSM-5, except for two peaks at wavenumbers around 1400 cm^{-1} and 1585 cm^{-1}, corresponding to the symmetric stretching vibration of carboxyl groups and the aromatic C=C vibration, which appeared due to the presence of GQDs.

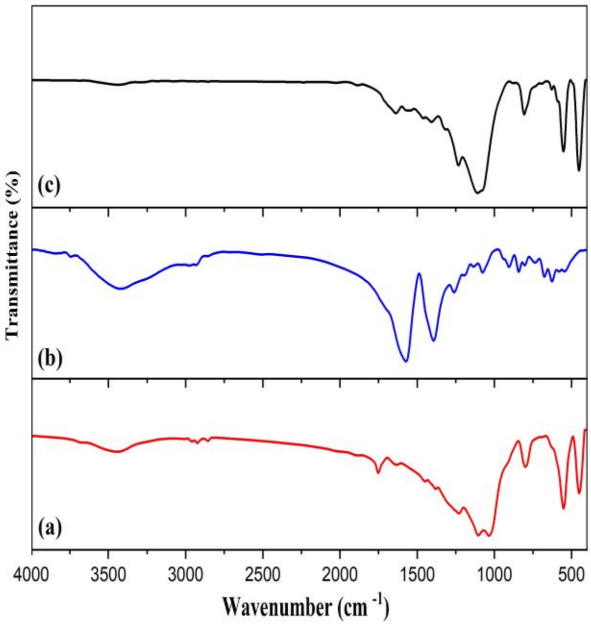


Fig. 2. FT-IR spectrum of Na[B]ZSM-5 (a), GQDs (b), and P-GQDs/Na[B]ZSM-5 (1:1) (c).

X-ray Diffraction (XRD) Analysis

The XRD pattern of the synthesized composite is shown in Fig. 3 a. For comparison, the XRD patterns of the individual components—borosilicate zeolite and GQDs—are also included in (Fig. 3 a) and (Fig. 3 b).

As presented in Fig. 3a, the borosilicate zeolite exhibits the characteristic diffraction peaks of the ZSM-5 framework in the 2θ ranges of 7–10° and 23–25°, confirming the formation of a pure single-phase zeolite [22].

The XRD pattern of GQDs (Fig. 3b) displays a wide diffraction centered at 2θ ≈ 20–40°, which corresponds to the (002) plane typical of carbonaceous materials [23]. The broadening of this peak showed the presence of very small crystallites in the GQDs. Also, the absence of additional peaks further confirms the high purity of the synthesized GQDs.

Overall, the X-ray diffraction pattern of P-GQDs/Na[B]ZSM-5 (1:1) as seen in Figure (3.a) appears similar to that of pure Na[B]ZSM-5. However, the broadening of the peaks in the composite, especially around θ2≈22-32°, can be attributed to the presence of GQDs nanoparticles. The characteristic diffraction peaks of Na[B]ZSM-5 are reduced in the nanocomposite, which is probably influenced by the GQDs nanoparticles. (For comparison, the peak intensities in both samples are shown with the arrow direction).

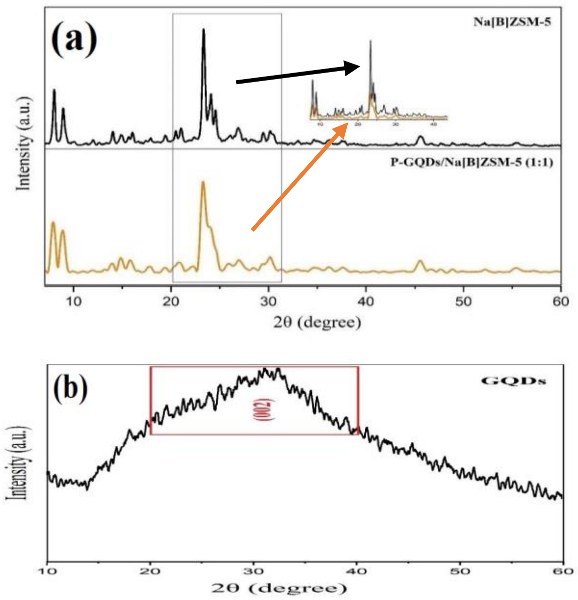


Fig 3. XRD patterns for of Na[B]ZSM-5 and P-GQDs/Na[B]ZSM-5 (1:1) (a), GQDs (b).

SEM Analysis

The morphology of the synthesized materials was examined using the field emission scanning electron microscopy (FE-SEM). FE-SEM images of borosilicate zeolite (Fig. 4a) exhibit the micron-sized spheres.

The Graphene quantum dots have spherical morphology with small dimensions in consistent with XRD results. Also, the small size of GQDs is confirmed by their blue emission under UV light (inset in Fig. 4b). As the diameter of quantum dots decreases, their energy gap increases. Therefore, the light emitted from this sample shifts toward shorter wavelengths. So, as the size of quantum dots decreases, their emitted light shifts from red to blue [24, 25].

The FE-SEM images of nanocomposite is presented in Fig. 4. c, d. In examining the FE-SEM images of the P-GQDs/Na[B]ZSM-5 1:1 composite presented in Figure (4. c.d), the morphology of the samples is spherical like that of pure Na[B]ZSM-5, but the smooth surface of this sample in the nanocomposite has become relatively rough with the presence of quantum dots. In this way, the most of the nanoparticles are connected to each other and form a smooth layer on the surface of the borosilicate zeolite.

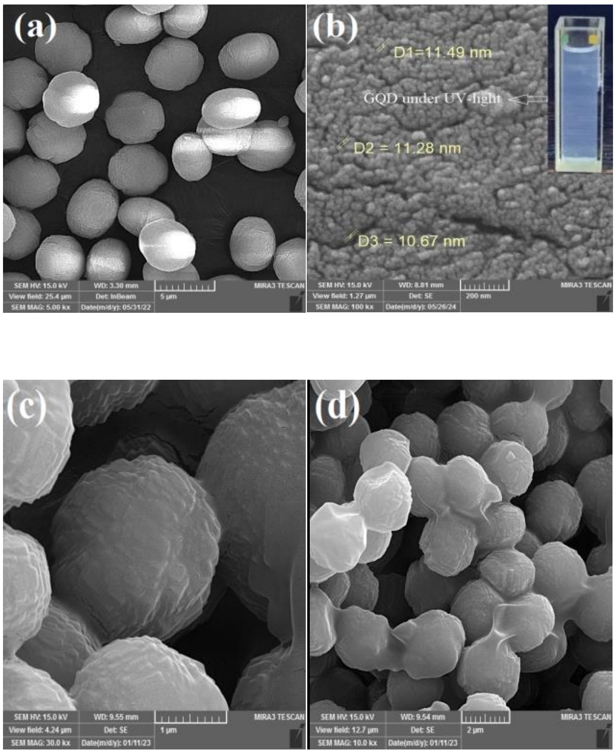


Fig 4. FESEM morphology for Na[B]ZSM-5 (a), GQDs (b), and P-GQDs/Na[B]ZSM-5 (1:1) (c. d).

Evaluation of antibacterial activity of prepared samples

The antibacterial activity of the investigated samples was determined by the broth micro dilution method, as detailed in the Experimental section, with three repetitions. Correctly adjustment the concentration of the bacteria is a crucial step for achieving reliable and desirable results in this experiment. The presence of a small and countable number of bacteria in the plates indicates that the test sample has an inhibitory effect on the growth of the desired microorganism (Escherichia coli bacteria). In contrast, the large number of these bacteria in the plates indicates that the tested sample is not able to inhibit the growth of microorganisms and therefore lacks antibacterial properties. The obtained images (Figure 5) show that based on experimental observations, the samples used in the experiment have this property and were capable of inhibiting E. coli growth. As shown in the figure, graphene quantum dots (GQDs) and the P-GQDs/Na[B]ZSM-5 (1:1) composite showed pronounced antibacterial activity.

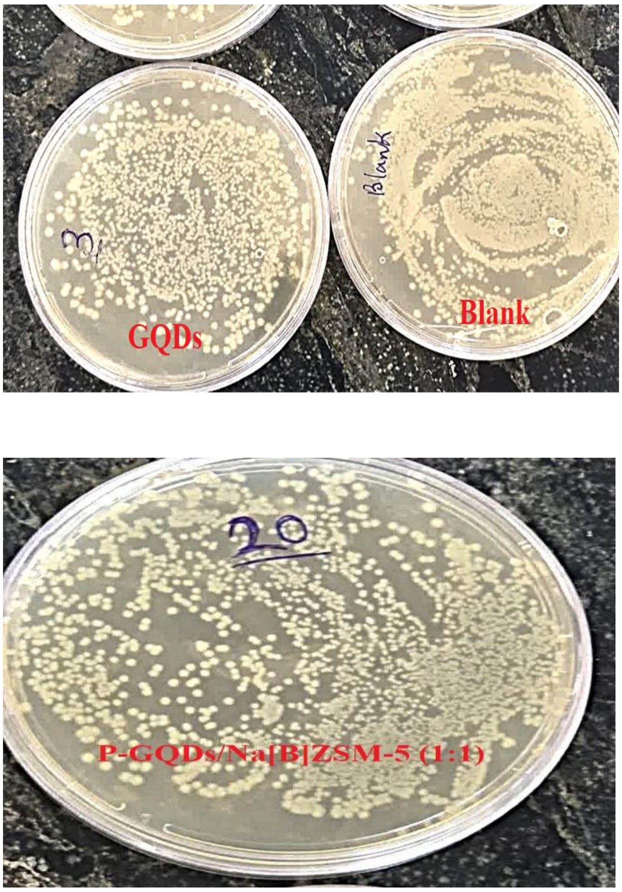
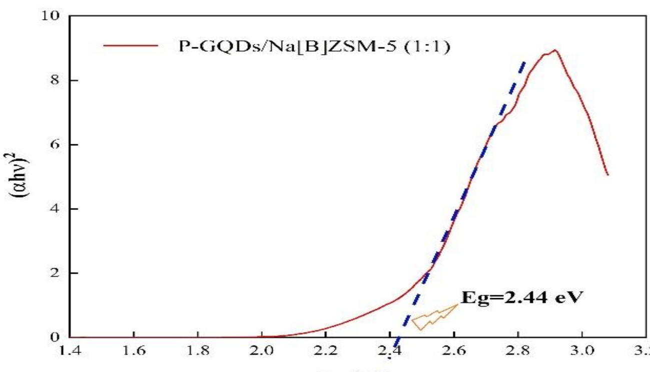


Fig 5. Observations on the antibacterial properties of the samples

This mechanism can be explained as follows: In nanoparticles containing graphene quantum dots, electron-hole pairs are produced by light irradiation. The hole (h^+) reacts with (OH^-) on the surface of the nanoparticles and produces hydroxyl radical (OH°).

These free and active radicals destroy and kill the microorganism cells. The Tauc plots for these two samples are presented in Figure 6.



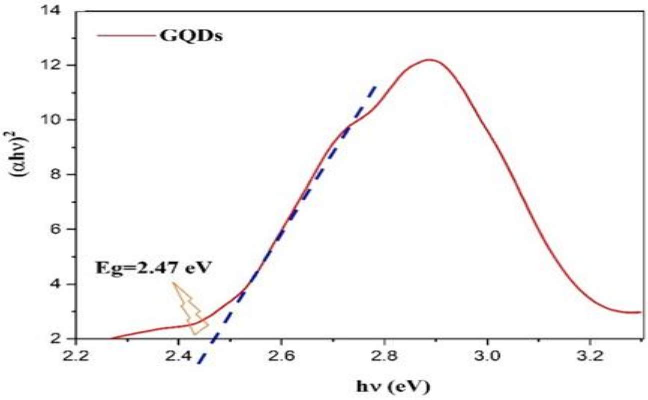


Fig 6. Tauc plots related to samples

In photocatalysts containing GQDs, the Tauc plot plays a crucial role in explaining the photocatalytic mechanism, since the band-gap value extracted from this plot determines the ability material's to absorb light and form electron-hole pairs.

Based on the Eg obtained, the materials are able to absorb visible light and initiate the electron transfer from the valence band to the conduction band, which leads to the generation of photoactivated holes.

These holes react with surface hydroxide ions and generate highly reactive hydroxyl radicals, species responsible for the destruction of the cellular structure of microorganisms.

Thus, the determination of the Eg through the Tauc plot not only characterizes the optical properties of the material, but is also related to the activation and efficiency of the photocatalytic reaction pathway, allowing for a detailed analysis of the antibacterial efficiency of the photocatalyst [26, 27].

Conclusion

In this study, a novel GQDs/ZSM-5-type borosilicate nanocomposite was successfully synthesized through combined hydrothermal and pyrolysis techniques. The obtained samples were comprehensively characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), and field-emission scanning electron microscopy (FE-SEM). The synthesized nanocomposite exhibited remarkable antibacterial activity against the Gram-negative bacterium Escherichia coli, effectively reducing bacterial growth. The results show that immobilizing GQDs onto a borosilicate zeolite framework not only prevents particle agglomeration but also enhances their performance. Overall, these results demonstrate that the developed nanocomposite represents a promising candidate for both environmental remediation and antibacterial applications.

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