Fluorescent semiconductor quantum dots (QDs) have attracted widespread attention because of their unique electronic properties, tunable optical properties and good stability. Among QDs, CNQDs hold promise for extensive application in bioimaging, biosensing, ion detection, substance testing, drug delivery, biomedical applications, electrocatalysis and photocatalysis owing to their outstanding optical properties. CNQDs are usually employed as photosensitizers to form nanoheterojunction photocatalytic materials, and are combined with various traditional wide-gap photocatalysts to enhance the efficiency of solar light for photocatalytic performances. Moreover, CNQDs can be coupled with photocatalysts to further extend the spectral responsive range of the photocatalytic system to the near infrared ray region. Several CNQDs-based photocatalyst materials have been developed, such as CNQDs/TiO$_2$, CNQDs/Bi$_2$WO$_6$, CNQDs/g-C$_3$N$_4$, CNQDs/h-BN, CNQDs/La$_2$O$_3$, CNQDs/GO–InVO$_4$, CNQDs/TiO$_2$, CNQDs/Bi$_2$WO$_6$, and BiOBr/rGO, which are promising materials for photocatalysis. The use of 3D aerogels of CNQDs/rGO-based materials as photocatalysts is nothing new. Hu et al. constructed CNQDs/GO–InVO$_4$ as excellent photocatalysts for NO removal. He et al. developed 3D ternary graphene/CQDs/g-C$_3$N$_4$ aerogels for methyl orange removal. However, none of them either intentionally or accidentally synthesized the CNQDs/rGO hybrid as a contrast sample.

Herein, we synthesized 3D aerogel photocatalysts by using CNQDs and rGO via a hydrothermal method. We tested the visible light photocatalytic performance of the as-prepared samples toward ciprofloxacin (CIP) and tetracycline (TC). We fabricated an intimate interfacial connection and a highly efficient heterojunction interaction between CNQDs and rGO. rGO supplied photoelectrons favorable for transferring channels, and separating the holes and electrons produced by CNQDs. The photocatalysts exhibited good stability and enhanced the photodegradation of CIP and TC under visible light irradiation. Finally, we proposed a possible photocatalytic mechanism by which these hybrid photocatalysts improve visible light photocatalytic performance.
2. Experimental

2.1 Preparation of photocatalysts

GO was obtained by oxidizing crystalline flake graphite powder following a Hummers’ method reported elsewhere. CNQDs were synthesized via a hydrothermal method as previously reported, and the details was shown in ESI.

rGO/CNQD composite aerogels were synthesized as follows (Scheme 1): different volumes of CNQDs solution was mixed with 10 mL GO (2 mg mL⁻¹) under ultrasonication for a few minutes, and then 80 µL of ethylenediamine was introduced. The mixed suspension was heated at 90 °C for 7 h without stirring to obtain a columnar hydrogel. After lyophilization, the rGO/CNQD 3D aerogel hybrids were obtained. The rGO/CNQD composite aerogels were denoted as rGO/CNQDs-x, where x represents the volume of CNQDs added during the preparation process. Pure graphene aerogels were following the same steps but without the addition of CNQDs.

2.2 Characterization of rGO/CNQDs aerogels

The morphology of the materials were studied via field emission scanning electron microscopy (FE-SEM, Hitachi TM4000). High-resolution transmission electron microscopy (HRTEM) images were observed using JEOL JEM 2100F. Crystallographic structure was measured via X-ray diffraction (XRD, Philips X’ Pert PRO, the Netherlands). The materials were characterized via Fourier transform infrared (FT-IR) spectroscopy by using a Spectrum One Autoima spectrometer. Brunauer–Emmett–Teller (BET) surface areas were measured using Micromeritics ASAP2460 system. Composite was analyzed via X-ray photoelectron spectroscopy (XPS, Thermo VG 250, USA). The CHI chemical properties of the aerogels were examined via photocurrent and electrochemical impedance spectroscopy (EIS). Electron spin resonance (ESR) spectra were recorded using a Bruker EMXnano spectrometers, which detected the signal of \( ^{1}O_2 \); 50 mM 5,5-dimethyl-1-pyrroline N-oxide (DMPO) solution was used as the paramagnetic species spin-trap agent (methanol dispersion for \( ^{1}O_2 \) trapping). Photoluminescence (PL) spectra were recorded using an RF-6000 fluorescence spectrophotometer, which detected the signal of 2-hydroxyterephthalic acid with terephthalic acid as the probe molecule.

2.3 Photocatalytic performance

The photocatalytic activity of the synthesized samples was evaluated using a 300 W xenon lamp (Beijing NBT Technology Co., Ltd, China) with a cut-off filter \( (\lambda = 420 \text{ nm}) \) at ambient temperature. The rGO/CNQDs were used to photodegrade CIP and TC in aqueous solution at a certain concentration. These reaction mixtures were then stirred in the dark for 30 min at room temperature to achieve absorption equilibrium. At given time intervals, 4.0 mL of the suspension was withdrawn during the photocatalytic process for analysis. The concentrations of CIP and TC were determined by measuring the absorption peak strength at 272 and 355 nm, respectively.

3. Results and discussion

3.1 Morphology and structure of the as-prepared aerogel hybrids

As illustrated in Fig. 1a, the rGO/CNQD-0.02 aerogel hybrid exhibited a two-dimensional laminated structure similar to graphene nanosheets with folds and wrinkles. The TEM image of CNQDs shown in Fig. 1b demonstrated that these quantum dots were evenly dispersed and had a diameter ranging from 2 nm to 6 nm (average diameter of 4.4 nm). In Fig. 1c, the rGO nanosheet remained as a 2D flat and thin structure. This structure are typically formed from only a few layers of graphene.

![Scheme 1](image)

Scheme 1 Schematic of the steps for synthesizing rGO/CNQDs aerogel hybrids.
sheets, and it is helpful for building the 3D model. The CNQDs were loaded on the surfaces of GO, and no aggregation was observed. As shown in Fig. 1d, the CNQDs were loaded on the surface of rGO, and the CNQDs were slightly crystallized. The lattice distance was measured as 0.32 nm in accordance with the (002) plane of g-C3N4.

As shown in Fig. 2a, in the FT-IR spectra of CNQDs, rGO, and rGO/CNQDs aerogel hybrids, the absorption bands at 3440, 2919, 1633, 1397, and 1048 cm\(^{-1}\) were ascribed to the stretching vibrations of O–H, C–H, C=O, and C–N and an antisymmetric stretching of C–O–C, respectively. The FT-IR spectra of the aerogel hybrids were evidently similar to those of the main peaks of pure rGO. The result suggested that no obvious structural change in rGO occurred after it combined with the CNQDs, and the CNQDs were successfully incorporated into rGO. The band at 2353 cm\(^{-1}\) was ascribed to gaseous CO\(_2\). The crystal structures of graphite, GO, rGO, and rGO/CNQDs aerogel hybrids were examined via XRD. Only a sharp diffraction peak appeared at around 10.2°, which corresponded to the (002) reflection for pure GO (Fig. 2b). Moreover, the emergence of the broad peak centered at \(2\theta = 24^\circ\) indicated the poor ordering of rGO and hybrids sheets along their stacking directions. No clear characteristic diffraction peaks of CNQDs were observed in the aerogel hybrid, and this result could be attributed to the relatively low amount of CNQDs.

On the basis of IUPAC classification, the N\(_2\) adsorption–desorption isotherm of the as-prepared samples was identified as type IV with an H3 type hysteresis loop (Fig. 2c). This isotherm indicated the presence of mesoporous characteristics and slit-like pores in rGO and aerogel hybrids. Barret–Joyner–Halenda analysis revealed that the mesopores in the aerogel hybrids were about 3 nm in diameter (Fig. 2d), which was less than the average diameter of CNQDs (4.4 nm). These micropores completely disappeared compared with those of rGO. The change in pore size distribution plots could be attributed to the fact that the CNQDs were not loaded on the surfaces of rGO. Aside from the \(\pi-\pi\) stacking and hydrogen-bonding interactions between CNQDs and GO, CNQDs could also be used as a reductant capable of reducing GO (Fig. S1†), resulting in a denser structure.

The CNQDs showed a strong photoluminescence emission peak at 440 nm, whereas the aerogel hybrids exhibited a weak photoluminescence emission peak (Fig. S2†). rGO played an important role in separating the photogenerated carriers generated on the surface of the CNQDs under illumination.

The surface chemical states and the elemental composition of the as-prepared samples were further characterized via XPS. The overall XPS spectra showed that C, N, and O elements without other impurities existed in rGO, CNQDs, and the aerogel hybrids (Fig. 3a). The N 1s spectrum of rGO presented two main peaks at 399.1 and 401.0 eV, which could be ascribed to pyridine N and pyrrolic N, respectively (Fig. 3b). Pyridinic-N, pyrrolic-N, and graphitic-N in the aerogel hybrids were the main components of pristine rGO and CNQDs. Compared with pure rGO, the emergence of pyrrolic N in the aerogel hybrids endowed them with excellent photocatalytic activity. Four
Fig. 3  XPS spectra of pristine CNQDs, rGO, and rGO/CNQDs-0.02: (a) survey. (b) C 1s, (c) N 1s, and (d) O 1s.

Fig. 4  (a) Visible light photocatalytic removal of aqueous CIP; (b) corresponding first-order kinetic simulation curves and (c) repeated photocatalytic experiments of rGO/CNQDs-0.02 for CIP removal within 4 cycle runs; (d) FT-IR spectra of rGO/CNQDs-0.02 before and after photocatalysis experiments.
distinct peaks appeared at 284.4, 285.5, and 287.8 eV, which corresponded to C=C/C=C, C=N, and COOH, respectively (Fig. 3c). The functional groups in the aerogel hybrids were clearly mainly derived from rGO and CNQDs, suggesting that the CNQDs were incorporated well with rGO. The O 1s spectrum showed two binding energies at 532.0 and 531.1 eV, which were assigned to C=O and C-O, respectively (Fig. 3d).

The photocatalytic performance of the as-prepared samples was evaluated by examining the photodegradation of CIP under visible light irradiation. The photodegradation rates of CIP aqueous solution under visible light irradiation without a photocatalyst or with CNQDs could be neglected (Fig. 4a). In 150 min, only 40% and 50% of CIP was removed by g-C₃N₄ and rGO, respectively. The visible light photocatalytic activities of the aerogel hybrids were substantially higher than those of pure rGO because of the positive effect of the CNQDs. Among the aerogel hybrids, rGO/CNQDs-0.01 displayed the best adsorption capability, whereas rGO/CNQDs-0.02 exhibited the highest visible light photocatalytic rate, and its reaction rate constant of CIP degradation (0.014 min⁻¹) was about 3.4 and 6.1 times higher than that of rGO and g-C₃N₄, respectively (Fig. 4b). Nevertheless, the photodegradation efficiency of the rGO/CNQDs-0.03 decreased slightly. Due to mesoporous structure, the rGO/CNQDs-0.02 have big surface areas with high catalytic activity, but too much CNQDs will result in more density structure for its reducibility, and inhibit the separation of photogenerated electrons and holes.

For further analysis of the photocatalytic reaction products, the CIP solution were filtered and then analyzed by the TOC test. Before and after the visible light irradiation, the TOC content were 27.9 and 9.5 mg L⁻¹ respectively, and the TOC removal rate was 65.9%.

The stability of rGO/CNQDs-0.02 was also measured by repeating the photodegradation experiments for four cycles. No considerable loss of photocatalytic activity occurred after four successive cycles, indicating that the aerogel hybrids possessed excellent stability (Fig. 4c). A comparison of the FTIR patterns of the rGO/CNQDs-0.02 aerogel hybrid before and after the four cycles of photocatalytic experiments did not reveal any change, implying that the aerogel hybrids possessed excellent reusability and stability without structural degradation during the photocatalytic reaction process (Fig. 4d).

The catalytic properties of rGO/CNQDs-0.02 as a response to visible light were further evaluated by testing the photodegradation of TC under visible light. The self-degradation of TC within 150 min under visible light irradiation was negligible (Fig. 5a). The hybrid catalysts exhibited excellent visible light activity compared with the pristine rGO and g-C₃N₄. These

![Fig. 5](a) Photocatalytic degradation of TC by the as-prepared samples under visible light (λ > 420 nm). (b) Cycle runs of rGO/CNQDs-0.02 for TC removal.

![Fig. 6](a) Effects of scavengers on the photocatalytic degradation of CIP with rGO/CNQDs-0.02 under visible light irradiation; (b) ESR spectra of DMPO–·O₂⁻ adducts.
results were consistent with those on CIP degradation. The photodegradation efficiencies of TC also exhibited no remarkable reduction after four successive cycles (Fig. 5b).

The role of the main reactive species involved in photocatalytic degradation in the presence of rGO/CNQDs-0.02 was examined via trapping tests (Fig. 6a). KI, isopropanol, and p-benzoquinone were adopted as the scavengers of hole (h⁺), hydroxyl radical (’OH), and super oxide radical (’O₂⁻). The introduction of KI into the CIP aqueous solution further enhanced the photodegradation efficiency (Fig. 6a). By contrast, isopropanol and p-benzoquinone inhibited the photodegradation efficiency, indicating that ’OH and ’O₂⁻ were the main reactive species in photocatalytic process of rGO/CNQDs-0.02.

The roles of the ’O₂⁻ in this photocatalysis process was determined further via the ESR. The weak signal of ’O₂⁻ was detected in the dark probably because and sample was not protected from light before the test was conducted (Fig. 6b). Under illumination, the obvious signal of DMPO–’O₂⁻ could be observed.

The ’OH can readily react with terephthalic acid in basic solution to generate 2-hydroxyterephthalic acid which emits a unique fluorescence signal centered at about 420 ± 6 nm under excitation at 315 nm. Moreover, the PL intensity of 2-hydroxyterephthalic acid is proportional to the amount of ’OH. The PL peak centered at about 420 nm obviously increased with the extension of irradiation time in the presence of the aerogel hybrids (Fig. S3†). This result implied that ’OH radicals were actually generated under visible light irradiation, and fluorescent intensity increased with irradiation time.

The results of scavenger test, ESR, and PL confirmed that ’O₂⁻ and ’OH existed in the rGO/CNQDs-0.02 system under visible light irradiation.

The photoinduced charge transfer and separation behaviors were confirmed via electrochemical experiments. EIS revealed that the aerogel hybrids had a small diameter of semicircular Nyquist curve, indicating that electronic impedance was reduced and mobility was improved (Fig. 7a). As a zero-band-gap semiconductor, rGO is electrically conductive with a low photocurrent density. The aerogel hybrids had a strengthened photocurrent transient photocurrent response, and photocurrent density improved by about 2 times higher than that of g-CN₃ (Fig. 7b).

On the basis of these results, the mechanism of photodegradation of rGO/CNQDs-0.02 under visible light irradiation was proposed (Fig. 8). When the aerogel hybrids are irradiated under visible light, the CNQDs generated electrons, which are transferred into the valence band of the CNQDs and then rapidly transferred by rGO to avoid the recombination of photogenerated electron–hole pairs. Finally, the electrons on the surface of GO capture the adsorbed O₂ on the composite catalyst surface and reduce it to ’O₂⁻ radicals to further degrade CIP. Given that the VB holes of g-CN₃ are more positive than the energy level of OH⁻ or H₂O, g-CN₃ cannot directly oxidized OH⁻/H₂O into ’OH radicals. Therefore, ’OH may be generated by ’O₂⁻ radicals that are partially oxidizing H₂O.

4. Conclusions

In conclusion, we successfully fabricated a convenient and recyclable 3D rGO/CNQD aerogel via a facile hydrothermal process. We investigated its photocatalytic properties for degradation of CIP and TC under visible light. The CNQDs produced photoelectrons and holes under visible light, and they could be effectively separated by rGO because of its exceptionally high conductivity. The photodegradation for CIP and TC under visible light demonstrated the excellent performance of the as-prepared aerogel hybrids. The photocatalytic performance of the aerogel hybrids in CIP and TC degradation was slightly reduced after four runs. Results of scavenger tests, PL tests, and ESR revealed that the active species ’O₂⁻ and ’OH were produced in the photocatalyst system. This work provides new insight into the designing of CNQD-based heterostructural
photocatalysts with an effective charge separation and CNQDs as an excellent semiconductor.

**Conflicts of interest**

There are no conflicts to declare.

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