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Fe₃O₄/Carbon quantum dots hybrid nanoflowers for highly active and recyclable visible-light driven photocatalyst

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Water dispersible Fe₃O₄@carbon quantum dots (CQDs) hybrid nanoflowers show highly efficient photocatalytic activities because of their strong absorption in visible light range and upconversion photoluminescence. The magnetic Fe₃O₄ nanocrystals not only allow an efficient magnetic separation and recycling of the photocatalyst, but also promote the photocatalytic activities of the CQDs.

Organic pollutants such as dyes and additives from industrial wastewater have generated great concern with their potential carcinogenic, mutagenic and bactericide properties in the past decades. Among various sequestration strategies, photocatalytic degradation of organic compounds is a compelling approach due to their relatively low operation costs without second time pollution. A major challenge is to find potent photocatalysts for such a task. A good photocatalyst should be able to utilize natural visible light and be photostable, inexpensive, and nontoxic. Nanoscale wide-band-gap semiconductors and oxalic salt have been recently developed for photodegradation of dyes. However, they usually require UV light excitation. In order to achieve visible light driven photodegradation of organics, various hetero or composite-structured semiconductors and silica quantum dots have been developed for photocatalysts. In particular, the carbon coated or graphene composites could significantly enhance the photocatalytic activity of these semiconductor nanoparticles.

Recent study shows that photoactive carbon quantum dots (CQDs) are both excellent electron donors and excellent electron acceptors. Compared to conventional semiconductor quantum dots, CQDs not only display low-toxicity and eco-friendliness, but also exhibit broad absorption spectrum, large absorption coefficient, upconversion luminescence properties, and good solubility in polar solvents.

These properties endow CQDs great opportunities to be used as a new class of photocatalysts. The upconversion luminescence properties are especially attractive because the CQDs can emit low-wavelength light under the excitation of long wavelength light, which enable the CQD-based photocatalysts workable under visible light induction. On the other hand, from a practical point of view, the application and recycling of photocatalysts require an additional separation step from the reaction solution, which can be a largish expense. It is highly desirable to develop photocatalysts that can be easily collected for re-use. Magnetic iron oxide nanoparticles can be collected easily by an external magnetic field, and hence have advantages as a carrier to facilitate separation and recycling of nanomaterials in aqueous solutions.

Herein, we report a facile route for one-pot solvothermal preparation of highly dispersible and highly active photocatalysts for degradation of organic dyes under visible light, based on the hybrid nanoflowers (NFs) composed of superparamagnetic iron oxide (Fe₃O₄) nanocrystals clustered in the core and fluorescent CQDs assembled on the surface of the Fe₃O₄ nanocrystals. The water-dispersible Fe₃O₄@CQDs hybrid NFs were synthesized through an improved one-pot solvothermal method with ferrocene as precursor in the presence of hydrogen peroxide (H₂O₂). H₂O₂ is important and necessary for the fabrication of Fe₃O₄@CQDs hybrid NFs. Without addition of H₂O₂, no product could be obtained under the same reaction conditions. The formation of Fe₃O₄@CQDs hybrid NFs in the reaction medium should involve very complicated chemical process. The role of H₂O₂ could be briefly explained as follows. In the sealed reactor containing ferrocene and H₂O₂ dissolved in acetone (with some water from H₂O₂ aqueous solution) at 200°C, the ferrocene quickly decomposes to form iron and cyclopentadiene. The chemical bonds of C-H in the cyclopenta-1,3-diene are ruptured, leading to the formation of carbon-based free radicals. These small carbon free radicals can form relatively large carbon-based fragments or CQDs under the high reaction temperature and high pressure from the gasification of acetone and water in reactor. Meanwhile, the O₂ decomposed from the H₂O₂ can oxidize the Fe atoms to form Fe³⁺ and iron oxide. The presence of Fe³⁺ in turn catalyze the decomposition of H₂O₂ to form highly reactive free radicals such as hydroxyl HO· and hydroperoxyl HOO· and form more gaseous O₂ and H₂O. These highly reactive free radicals can speed up the oxidation of Fe to form iron oxide nanocrystals and rapidly react with the carbon fragment free radicals to form the hydrophilic hydroxyl and carboxyl groups. On the other hand, the produced gaseous O₂ and H₂O can further increase the pressure of the reaction medium, which in turn help the reaction of...
carbon-based free radicals to form highly crystallized CQDs. The as-prepared FeO@CQDs hybrid NFs demonstrate excellent photoluminescent (PL) properties including excitation ($\lambda_{ex}$) tunable emission, upconversion PL, and excellent photostability. The absorption in visible light range with a broad band at 556 nm and upconversion PL remarkably improves the catalytic activity of the FeO@CQDs hybrid NFs for the degradation of methylene blue (MB) dye molecules under visible light. The magnetic FeO@nanocrystals in the core not only allow an efficient separation, purification, and recycling of the photocatalyst by simply applying an external magnetic field, but also promote the photocatalytic function of the CQDs. The excellent dispersibility of the FeO@CQDs hybrid NFs in water enables the photo-reduction of dye molecules under essentially a homogeneous reaction condition.

A series of FeO@CQDs hybrid NFs were synthesized by adding different amount of 30% H$_2$O$_2$ aqueous solution into the autoclaves holding the same amount of precursor ferrocene and solvent acetone. Specifically, 3.0, 4.5, and 6.0 ml of H$_2$O$_2$ solution were respectively used. The resultant samples were coded as FeO@CQDs-$3.0$, FeO@CQDs-$4.5$, and FeO@CQDs-$6.0$, correspondingly. The crystallographic structure and phase purity of the as-prepared samples were examined by X-ray powder diffraction (XRD) and Raman scattering techniques. The observed reflections of 220, 311, 400, 422, 511, 440 in the typical XRD patterns [Fig. S1a in the Electronic Supplementary Information (ESI)] can be indexed to the cubic FeO$_2$ nanocrystals. In typical Raman scattering patterns (Fig. S1b in the ESI), the peak at around 1583 cm$^{-1}$ involves the in-plane bond stretching motion of sp$^2$-hybridized carbon atoms in a two-dimensional hexagonal lattice, which also exists as the G mode with the E$_2g$ symmetry. The D mode of graphite around 1371 cm$^{-1}$ is related to the vibrations of carbon atoms with dangling bonds in the termination plane of disordered graphite or glassy carbon. It is interesting to note that the intensity ratio ($I_D/I_G$) in the Raman scattering curves of the FeO@CQDs hybrid NFs increases with the increase in the amount of H$_2$O$_2$ presented in the synthetic reaction medium, suggesting that the high feeding of H$_2$O$_2$ is necessary to produce crystalllographic CQDs. The $I_D/I_G$ ratios for the FeO@CQDs-$3.0$, FeO@CQDs-$4.5$, and FeO@CQDs-$6.0$ hybrid NFs are 1.24, 1.25, and 1.32, respectively. The high $I_D/I_G$ ratios suggest that these hybrid NFs contain much more crystalline graphitic CQDs than the amorphous carbon. Fig. S1c shows the FTIR spectrum of the FeO@CQDs-$6.0$ hybrid NFs. The sharp absorption peak at 1710 cm$^{-1}$ can be attributed to the C=O stretching of the carboxylic acid groups conjugated with condensed aromatic carbons, while the broad absorption around 3408 cm$^{-1}$ should be from the –OH groups. These hydrophilic functional groups enable the resultant FeO@CQDs hybrid NFs to be dispersed in aqueous media very well. Fig. S1d shows typical UV-Vis absorption spectra of the FeO@CQDs hybrid NFs in the visible light region. A broad band at about 556 nm could be clearly observed for samples synthesized with high content of H$_2$O$_2$, although the overall absorption intensity in visible light region is weaker than the sharp absorption peak at 244 nm originated from the multiple polyaromaticchromophores (Fig. S2 in the ESI). The strong absorption in the visible light region is important for the resultant hybrid NFs to be used for photodegradation of organics under visible light irradiation.

The morphology and structures of the resultant FeO@CQDs hybrid NFs are further elucidated by transmission electron microscopy (TEM). Fig. 1a manifests that the FeO@CQDs-$6.0$ hybrid NFs are nearly uniform in size and shape with an average diameter of 100 nm. The TEM image of an individual FeO@CQDs hybrid NF (Fig. 1b) further reveals that the flower-like particle is composed of FeO$_2$nanocrystals clustered in the core region and CQDs assembled on their surface. Fig. 1c displays a high-resolution TEM (HRTEM) image of the sectional hybrid NF showing a single CQD and FeO$_2$nanocrystal. It can be seen that both the FeO$_2$nanocrystal particle (~20 nm) and the crystallographic CQD (~17 nm) have a clear lattice fringe. From the 2D lattice fringes of the CQDs, an interplanar distance about 0.335 nm is determined, which corresponds to the (006) lattice planes of the graphitic (sp$^2$) carbon. To further confirm the compositions of the nanocrystals in the inner core and outer shell of the hybrid NFs, energy dispersive analysis of X-ray were conducted. The energy dispersive spectrum (EDS) of the single crystal on the outer shell (Fig. 1d) only reveals the presence of C and Cu elements. Because the Cu is from the copper grid for TEM sample preparation, this result indicates that the nanocrystals in the shell only contain carbon. In contrast, the EDS of the nanocrystal in the inner core (Fig. 1e) shows the existence of Fe, O, C, and Cu elements. While the Cu is from the copper grid, the Fe, O, and C should be attributed to the magnetic FeO$_2$nanocrystals clustered in the carbon matrix. The HRTEM and EDS results of the FeO@CQDs-$3.0$ and FeO@CQDs-$4.5$ (Fig. S3 and S4) show similar results, except that the crystallinity of the FeO$_2$nanocrystals and CQDs in FeO@CQDs-$3.0$ is relatively lower than that in FeO@CQDs-$4.5$ and FeO@CQDs-$6.0$ samples. Combining all these analytical results on the hybrid NFs, it is reasonable to conclude that the FeO@CQDs NFs are composed of iron oxide nanocrystals clustered in the core and crystallographic CQDs assembled on the surface as shell.

![Fig. 1](image1)

**Fig. 1.** (a and b) TEM images of the FeO@CQDs-$6.0$ hybrid NFs; (c) High resolution TEM image of the sectional hybrid NF in Fig. 1b, showing single CQD and FeO$_2$nanocrystals; (d) and (e) Energy dispersive spectrum of the single CQD and FeO$_2$ nanocrystal, respectively.

To further explore the optical properties of the FeO@CQDs NFs, a detailed PL study was carried out under different excitation wavelengths. Fig. 2a shows the evolution of PL spectra of the FeO@CQDs-$6.0$ NFs obtained with excitation light wavelength increasing from 240 nm to 460 nm. The emission peak gradually shifts to longer wavelength and increases its strength until reaching the maximum intensity at 547 nm obtained with an excitation wavelength of 460 nm, which indicate a distribution of the different surface energy traps of the CQDs. The PL quantum yield of the FeO@CQDs-$6.0$ sample was determined to be 9.8 %. Fig. 2b shows the PL spectra of the FeO@CQDs-$6.0$ NFs excited by long-wavelength light from 960 to 500 nm, which clearly demonstrate the upconverted emissions from 560 to 390 nm. The upconversion PL property of the FeO@CQDs NFs can be attributed to the multiphoton active process similar to the previously reported carbon dots. The samples of FeO@CQDs-$3.0$ and FeO@CQDs-$4.5$ hybrid NFs synthesized with less amount of H$_2$O$_2$ demonstrate similar PL properties (Fig. S5 and S6), including excitation wavelength ($\lambda_{ex}$) tunable emissions and upconversion PL. One
difference is that the Fe$_3$O$_4$@CQDs-6.0 NFs shows the maximum PL intensity at a much longer wavelength than Fe$_3$O$_4$@CQDs-3.0 and Fe$_3$O$_4$@CQDs-4.5 NFs, which might be attributed to the higher crystallinity of the CQDs formed in the Fe$_3$O$_4$@CQDs-6.0 sample.

Fig. 2. (a) PL spectra and (b) upconverted PL spectra of the Fe$_3$O$_4$@CQDs-6.0 hybrid NFs obtained with different excitation wavelengths.

Given the excellent optical properties, the photocatalytic activity of the Fe$_3$O$_4$@CQDs hybrid NFs was evaluated for the degradation of methylene blue (MB) dye molecules under visible-light irradiation. As shown in the photos of Fig. 3a, the color of the bright blue MB solution (0.001 M, 3.0 mL) can completely disappear after adding 1 mg of Fe$_3$O$_4$@CQDs-6.0 NFs for 15 min under visible light irradiation, revealing that the Fe$_3$O$_4$@CQDs-6.0 hybrid NFs are highly efficient catalysts for photodegradation of MB. Fig. 3 also compares the time-dependent photodegradation profiles of MB in the presence of different catalysts under 75 W Xenon lamp with a cut off at 420 nm for visible light (a) and without cut off for whole spectrum (b), respectively. Without the addition of Fe$_3$O$_4$@CQDs hybrid NFs, only slight reduction (< 5.4 %) of MB was observed for 30 min from the Fe$_3$O$_4$@CQDs-6.0 sample. Furthermore, the upconversion PL light emitted from the Fe$_3$O$_4$@CQDs hybrid NFs for 15 min.

Fig. 3. The photodegradation profiles of MB under 75 W Xenon lamp (a) with a cut off 420 nm for visible light and (b) without cut off for the whole spectrum in the presence of different catalysts (●: control with no catalyst; ○: CQDs-6.0; ▲: Fe$_3$O$_4$@CQDs-3.0; ◆: Fe$_3$O$_4$@CQDs-4.5; ▼: Fe$_3$O$_4$@CQDs-6.0), respectively. The inset in (a) shows the photos of MB aqueous solutions before and after the addition of Fe$_3$O$_4$@CQDs-6.0 NFs for 15 min.

Fig. 4 illustrated the possible mechanism for the photocatalytic degradation of MB upon the Fe$_3$O$_4$@CQDs hybrid NFs. When the Fe$_3$O$_4$@CQDs hybrid NFs were illuminated using visible light, the light with shorter wavelength (390 to 560 nm) will be emitted as a result of the upconversion PL property of the CQDs. These photons could excite the MB dye molecules by 80% in 10 min for both Figures. This results indicate that catalysts of Fe$_3$O$_4$@CQDs hybrid NFs are necessary for efficient photodegradation of MB dye under visible light. The degradation fractions of MB in the presence of different photocatalysts are 79.7%, 88.4%, and 94.4% for Fe$_3$O$_4$@CQDs-3.0, Fe$_3$O$_4$@CQDs-4.5, and Fe$_3$O$_4$@CQDs-6.0, respectively, after the MB solution was exposed to visible light for 30 min (Fig. 3a). After removing the cutting off filter at 420 nm, the degradation fractions of MB in the presence of different photocatalysts under the whole spectrum from the Xenon lamp for 30 min are 84.6%, 91.2%, and 95.8% for Fe$_3$O$_4$@CQDs-3.0, Fe$_3$O$_4$@CQDs-4.5, and Fe$_3$O$_4$@CQDs-6.0, respectively (Fig. 3b).

The slightly higher photodegradation activity for MB of the Fe$_3$O$_4$@CQDs catalysts under the whole spectrum (without cut off) than under the visible light (cut off at 420 nm) should be attributed to the contribution of the small fraction of UV light from the whole spectrum of Xenon lamp. The gradually increased photocatalytic activity of the three catalysts may partially result from the enhanced $\pi-$ attachment ability of the MB molecules on the highly crystallographic and conjugated CQDs assembled on the surface of the Fe$_3$O$_4$@CQDs-4.5 and Fe$_3$O$_4$@CQDs-6.0 samples. In terms of the amount of MB dye molecules degraded by per gram of photocatalyst in the same exposure time period under visible light, our Fe$_3$O$_4$@CQDs hybrid NFs exhibited much higher photocatalytic activity than the previously reported catalysts including P25-graphene, Fe$_3$O$_4$@TiO$_2$ nanosheets, CNT-confined TiO$_2$, and the Fe$_3$O$_4$@CQDs hybrid NFs were removed via acid-dissolution with the resultant hollow CQDs shell being coded as CQDs-6.0. As shown in Fig. 3a, only about 42.5 % of the MB was degraded by the CQDs-6.0 catalyst after 30 min under the same experimental conditions as the Fe$_3$O$_4$@CQDs hybrid NFs catalysts. This much lower photocatalytic ability for MB degradation of the CQDs-6 than the Fe$_3$O$_4$@CQDs hybrid NFs indicates that the excellent photocatalytic activities of the Fe$_3$O$_4$@CQDs hybrid NFs should be attributed to the synergistic interaction of the shell CQDs with the Fe$_3$O$_4$ nanocrystals in the core.

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The photocatalytic stability of the catalysts should be attributed to the NFs for five runs under the visible light with a cut off at 420 nm. The magnetic properties of the Fe₃O₄@CQDs hybrid NFs have been investigated using a superconducting quantum interference device (SQUID) magnetometer prior to the recycling experiments of photocatalysts. Fig. 5a shows a hysteresis loop of Fe₃O₄@CQDs-6.0 measured at 300 K in an applied magnetic field of up to 10000 Oe, which indicates that the saturation magnetization (Ms) of the hybrid NFs is 33.8 emu/g. No obviously remanence or coercivity was observed at room temperature, indicating a superparamagnetic behavior of the hybrid NFs, which is essential for the magnetic separation and recycling of these NFs as photocatalysts. As demonstrated in the inset of Fig. 5a, the magnetic moment of the Fe₃O₄ nanocrystals in the core is sufficiently high so that a complete separation of the catalyst colloids from solution can be achieved within 1 min under the induction of an external magnet (0.3 T). The separated catalyst from a reaction solution was repeatedly washed with deionized water and dried. The recovered catalyst can be then used for second run for the photodegradation of MB. Fig. 5b compares the catalytic performance of the Fe₃O₄@CQDs-6.0 hybrid NFs for five runs under the visible light with a cut off at 420 nm. The hybrid NFs demonstrate a remarkable photostability as the degradation percentage of MB only drops slightly after each reused cycle, which may result from the loss of small amount of catalysts during the recycling process of magnetic separation, washing, drying, and redispersion. Even so, the degradation fraction of MB based on the Fe₃O₄@CQDs-6.0 photocatalysts still reaches 91.6% after five runs. Fig. 5c compares the catalytic performance of the Fe₃O₄@CQDs-6.0 hybrid NFs under the whole spectrum light from xenon lamp for ten runs of catalytic reaction and recycling. Similarly, the catalyst demonstrated high stable photocatalytic activity with only a slight decrease in the degradation fraction of MB from 95.8% to 91.1% after ten repeated runs. This excellent photocatalytic stability of the catalysts should be attributed to the very stable nanostructures of the Fe₃O₄@CQDs hybrid NFs. As shown in Fig. 5d, the recycled Fe₃O₄@CQDs-6.0 hybrid NFs after ten runs of catalytic reaction and recycling shows a similar structure to that of the as-synthesized hybrid NFs (Fig. 1a) with CQDs still combined on the surface of Fe₃O₄ nanocrystals. These results show that the catalysts of Fe₃O₄@CQDs hybrid NFs can be recovered efficiently from the reaction solution by using external magnetic fields for repeated use.

In summary, we have demonstrated a facile one-pot solvothermal method to synthesize a series of highly stable and highly active photocatalysts of Fe₃O₄@CQDs hybrid NFs for degradation of organic dye under visible light. The flower-like nanostructure with the highly fluorescent CQDs (quantum yield about 9.8%) assembled on the surface of Fe₃O₄ nanocrystals is essential for the excellent optical properties and high photocatalytic performance of the resultant Fe₃O₄@CQDs hybrid NFs. The hybrid NFs can be easily recovered by external magnetic field for repeated use. The combined stable dispersibility in water, magnetic recycling and targeting ability, upconverted PL properties, and excellent photostability of the Fe₃O₄@CQDs hybrid NFs provide a promising candidate for highly efficient, reusable, and visible-light driven photocatalysts in environmental remediation technology.

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Notes and references


