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Cage Breaking of C_{60} Into Photoluminescent Graphene Oxide Quantum Dots: An Efficient Peroxidase Mimic

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The C_{60} cage is broken by chemical oxidation to produce graphene oxide quantum dots (GOQDs), which show an average diameter of 2.02 ± 1.53 nm and consist of a high content of oxygen-containing functional groups. The resulting GOQDs exhibit apparent photoluminescence and might serve as an effective peroxidase mimic with a kinetic rate constant more than three times higher than that of conventional graphene oxide nanosheets.

1. Introduction

H_2O_2 can be activated by peroxidases to participate in numerous oxidation processes in biological systems.[1,2] Colorimetric detection represents a simple and effective route to chemical sensing of H_2O_2, where 3,3′,5,5′-tetramethylbenzidine (TMB) is usually used as an indicator as it can be oxidized by H_2O_2 in the presence of a peroxidase to produce a blue-colored product.[1,3,4] Low-cost carboxyl-modified graphene oxide sheets (GOSHs-COOH) have been found to show intrinsic peroxidase-like activity,[4,5] with apparent advantages over the biological counterparts, such as the ability to work in harsh conditions/environments, ease of synthesis, purification and storage.[6,7] However, the large lateral size of GOSHs-COOH (up to several microns) not only limits the number of −COOH groups at sheet edge and hence compromises the catalytic activity, but also restricts their in vivo applications in organisms. Within this context, rupturing large GOSHs into nanoscale fragments represents a viable "top-down" strategy in the preparation of graphene oxide quantum dots (GOQDs).[8–10] However, GOQDs prepared with this strategy usually show a broad size distribution.[11–13]

Herein, C_{60}, with a well-defined diameter as low as 0.78 nm, is used as precursor to synthesize photoluminescent GOQDs by a facile chemical oxidation method. The resulting GOQDs show a diameter of *ca.* 2.5 nm, consist of rich oxygen-containing groups, and exhibit characteristics of an efficient peroxidase mimic.

2. Experimental Section

2.1. Synthesis of GOQDs

GOQDs were synthesized by a modified Hummer's method. As illustrated in **Figure 1**, C_{60} (0.2 g) was dispersed in 8.0 mL of H_2SO_4 (anhydrous, 98%) in a beaker and stirred overnight at room temperature, then 1.0 g of $KMnO_4$ was slowly added to the solution cooled with an ice bath, then the solution was heated to 70 °C in a water bath for 40 min and subsequently quenched by massive ice, followed by the addition of 5 mL of a 30 wt.% H_2O_2 solution. The resulting solution was dialyzed ($100\,g\,mol^{-1}$ cutoff) until a neutral solution was achieved, leading to GOQDs with a yield of about 50%. GOSHs were synthesized with a similar fashion using graphite powder as precursor.

2.2. TMB-H_2O_2 Reaction

Experimentally, 3.0 mL of a freshly prepared TMB solution (800 μM in water), 5 μL of GOSHs or GOQDs ($2.0\,mg\,mL^{-1}$) and 100 mM H_2O_2 were mixed in a glass vial, with the solution pH controlled by an acetate buffer at about 4.0. The solution was transferred to a quartz cuvette for UV–vis absorption measurements.

3. Results and Discussion

Figure 2a,b and Figure S1 (see Supporting Information) depict the TEM images of GOQDs prepared by oxidative breaking of the C_{60} cage, where a large number of carbon fragments with a diameter ranging from 0.5 to 3.5 nm are observed. From the core-size histogram in Figure 2c, the average diameter of GOQDs is estimated to be *ca.* 2.02 ± 1.53 nm. For comparison, GOSHs (Figure 2d) entailed crumpled sheets with a much larger size on the micron scale. After drying, GOSHs showed marked

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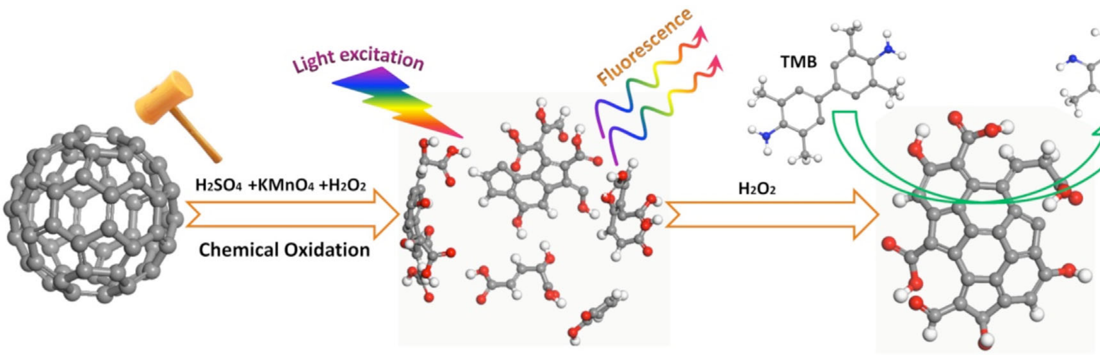

Figure 1. Breaking of C_{60} cage into GOQDs as a peroxidase mimic.

aggregation due to strong π-π interactions between the GO sheets (Figure 2e). In addition, obvious Tyndall effect can be observed in the GOSHs dispersion, using a laser pointer ($\lambda = 650\,nm$), indicative of the sol nature (Figure 2f). In sharp contrast, no apparent Tyndall effect can be seen for the GOQDs dispersion at the same concentration of $2.0\,mg\,mL^{-1}$. This signifies that the GOQDs dispersion can be considered as a real solution.

After chemical oxidation, the characteristic Raman peak at $1458\,cm^{-1}$ for C_{60} disappears and two new peaks emerge at around 1350 and $1570\,cm^{-1}$ that are the D and G band, respectively,[14] indicating the breakage of C_{60} cage (**Figure 3**b). FTIR measurements (Figure 3b) suggest the formation of oxygenated species in both GOQDs and GOSHs as supported by the presence of hydroxyl (O—H) stretch bands at 3334 and $1430\,cm^{-1}$, carbonyl (C═O) stretch band at $1726\,cm^{-1}$, and C═C and epoxy (C—O) stretch bands at 1640 and $1232\,cm^{-1}$.[15,16] More quantitative results were obtained in XPS measurements (Figure S2a, in Supporting Information), where the C/O atomic ratio was estimated to be 1.21:1 for GOQDs, and 2.6:1 for GOSHs (Figure S2b, in Supporting Information), indicating a higher concentration of oxygen-containing functional groups on GOQDs than on GOSHs. Deconvolution of the high-resolution C 1s spectra in Figure 3c and Figure S2c (Supporting Information) yields four peaks for GOQDs and GOSHs at 284.7, 285.6, 286.8, and 288.5 eV, which are assigned to the C–C bond, C—OH bond, C—O—C bond and C═O double bond, respectively. Note that the molar ratio of C═O/C—OH for GOQDs (0.74) is much higher than that of GOSHs (0.56), indicating a larger fraction of —COOH groups on GOQDs than on GOSHs, in good agreement

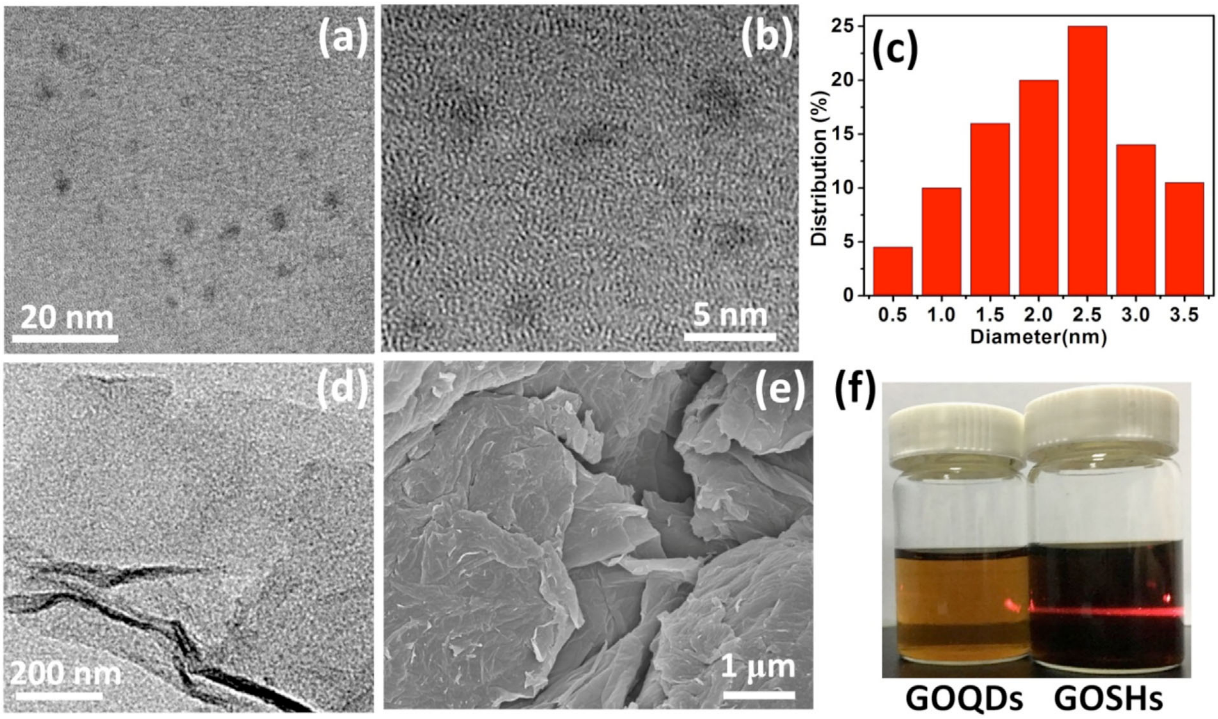

Figure 2. a, b) TEM images of GOQDs. c) The core-size histograms of GOQDs determined by dynamic light scattering measurement. d) TEM and e) SEM images of GOSHs. f) Photograph showing a laser transmitting through the aqueous dispersions of GOSHs and GOQDS.

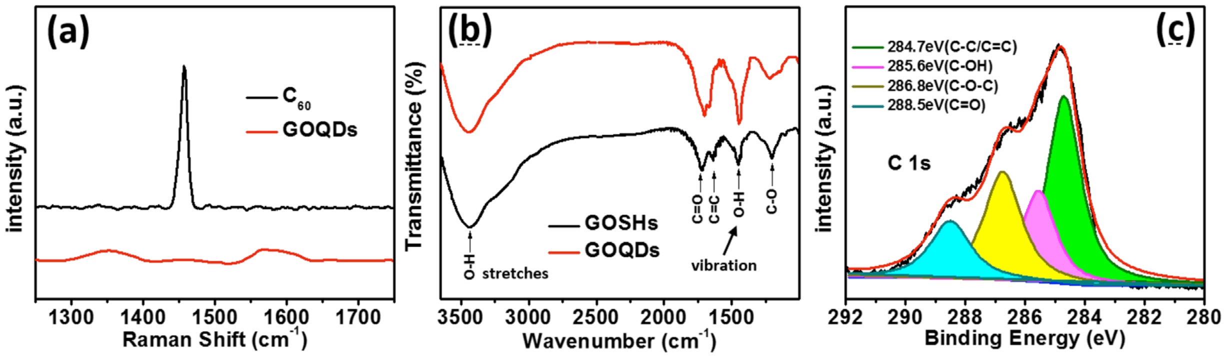

Figure 3. a) Raman spectra of C_{60} and GOQDs; b) FT-IR spectra of GOSHs and GOQDs; c) XPS C1s scan of GOQDs. Black curve is experimental data and colored peaks are deconvolution fits.

with the FTIR results in Figure 3b. The rich oxygen-containing groups endow GOQDs not only with good dispersibility in water, but also with apparent catalytic activity as a peroxidase mimic.

Interestingly, the C_{60}-derived GOQDs exhibited apparent photoluminescence (inset to **Figure** 4a), and the emission maximum varied with the excitation wavelength (Figure 4a**)**. Furthermore, the resulting GOQDs show peroxidase-like catalytic activity, as exemplified by the oxidation of TMB by H_2O_2. As shown in Figure 4b, upon the addition of GOQDs into the diluted solution of TMB and H_2O_2, the transparent solution undergoes a remarkable color evolution from colorless to blue

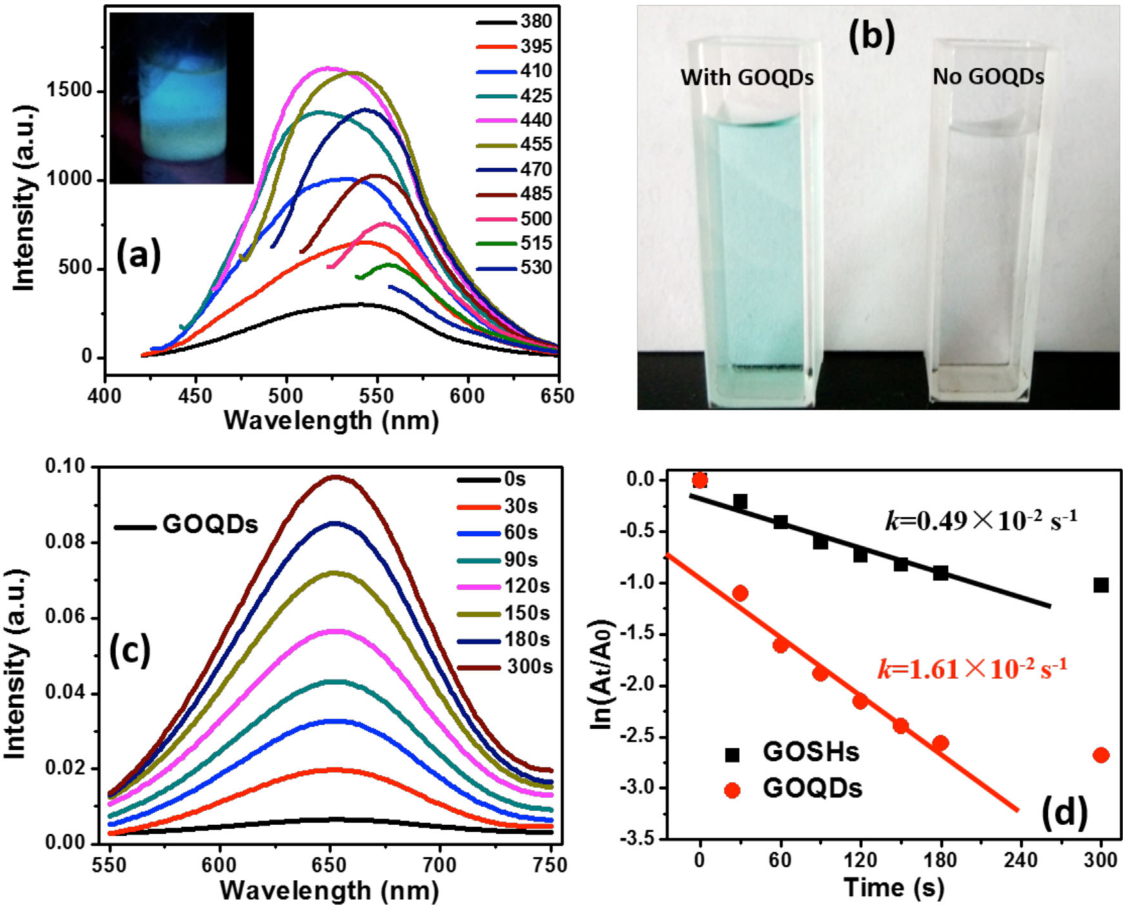

Figure 4. a) Photoluminescence spectra of GOQDs in water at different excitation wavelengths (specified in the figure legends). Inset is a photograph of GOQD solution when excited at 365 nm. b) Photographs of the TMB + H_2O_2 solution with and without the addition of GOQDs. c) UV–vis absorption spectra of TMB + H_2O_2 solution with the addition of GOQDs. d) Plot of $\ln(A_t/A_0)$ as a function of time for the reaction catalysed by GOQDs and GOSHs.

due to the production of blue-colored 3,3,5,5-tetramethylbenzidine diimine. This oxidation process is accomponied by gradual increase of the absorption peak at about 650 nm (Figure 4c), suggesting that GOQDs might indeed serve as an efficient peroxidase mimic.

Because of a large excess of H_2O_2, the oxidation of TMB exhibited a quasi-first-order reaction kinetic with respect to the TMB concentration in solution. Figure 4d shows the plot of $\ln(A_t/A_0)$ against reaction time (t), where A_t and A_0 are the absorbance at 650 nm at time t and 0, respectively. A kinetic rate constant (k) of $1.61 \times 10^{-2}\,s^{-1}$ can be derived from the linear regression of experimental data (red circles) determined wihin a reaction time of 200 s, which is more than three times higher than that of GOSHs ($0.49 \times 10^{-2}\,s^{-1}$). This might be accounted for by the larger fractions of oxygenated speices in GOQDs and their markedly better dispersibility in water. When the reaction proceeds for more than 200 s, the slope of linear regression is markedly reduced, indicative of an equilibrium state for the reaction.

In summary, photoluminecent GOQDs with a diameter of *ca.* 2.5 nm were prepared by oxidative breaking of the C_{60} cage. These C_{60}-derivated GOQDs might serve as an effective peroxidase mimic in the oxidation of TMB by H_2O_2, with a kinetic rate constant over three times higher than that of conentional GOSHs, likely due to the high concentration of oxygenated speices and good dispersibility in water.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

chemical oxidation, fullerene, graphene oxide quantum dot, peroxidase, photoluminescence

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