Quantum Dots

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Carbon-Based Dots Co-doped with Nitrogen and Sulfur for High Quantum Yield and Excitation-Independent Emission**

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Quantum dots (QDs) are nanoparticles with size-dependent optical and electronic properties that have been proposed for various applications, such as energy-efficient displays and lighting, photovoltaic devices, and biological markers.[1–6] Compared with other fluorescent (FL) materials (conventional dyes, polymers, or propeins), QDs offer many promising advantages, such as bright fluorescence, high photostability, and resistance to metabolic degradation in bioapplications.[7–9] However, most high-performance QDs are limited by toxicity from their metal elements, such as cadmium.[10,11] Extensive efforts have thus been made on the development of non- or low-toxic FL nanomaterials as alternatives to the semiconductor-based QDs. Carbon-based dots (CDs), including carbon nanoparticles of less than 10 nm in size,[12] which are known as carbon quantum dots (CQDs) and graphene nanosheets of less than 100 nm in size,[13] which are known as graphene quantum dots (GQDs), are particularly encouraging owing to their outstanding optical properties, low toxicity, good biocompatibility, and robust chemical inertness.[6,12] Various methods have been demonstrated in preparation of FL CDs, such as electrochemical oxidation processes,[14,15] chemical oxidation methods,[6,12,16–18] hydrothermal cutting strategies,[19,20] and carbonizing organics routes.[21–24] Nevertheless, most of the developed methods are unsatisfactory owing to expensive equipment required, low yields, or complicated procedures. In particular, most obtained CDs have a relatively low FL quantum yield (FLQY, usually less than 50 %) in comparison to the conventional semiconductor QDs. Most recently, doped CDs were proposed for highly FL dots.[25–27] For example, ZnS-doped CDs with the passivation of oligomeric poly(ethylenelycol) diamine (PEG1500N) molecules show a 78 % FLQY after a gel column fractionation.[26] However, the preparation of highly FL ZnS-doped CDs is complicated. Moreover, the poor chemical inertness of the ZnS would be a severe limitation to broad applications of the CDs. Thus, there is a great need to develop a facile, low-cost, and high-yield method for the preparation of CDs with strong FL emission. Herein, citric acid (CA) and L-cysteine were used to produce nitrogen and sulfur co-doped CDs (N,S-CDs) through a one-step hydrothermal treatment. The CA serves as the carbon source, while the L-cysteine provides nitrogen and sulfur. Compared with other reported CDs, the as-prepared N,S-CDs exhibit very high FLQY (73 %) and excitation-independent emission, resulting from the synergy effect of the doped nitrogen and sulfur atoms.

The obtained N,S-CD solution exhibits a long-term homogeneous phase without any noticeable precipitation at room temperature. The transmission electron microscopy (TEM) image (Figure 1 a,g) shows that the size of the as-prepared N,S-CDs is distributed in the range from 5 to 9 nm, with an average size of 7 nm. High-resolution TEM (HRTEM) images (Figure 1 b) reveal the high crystallinity of the N,S-CDs. The lattice spacing of 0.21 nm (Figure 1 c) agrees with that of in-plane lattice spacing of graphene (100 facet), and the lattice spacing of 0.32 nm (Figure 1 d) should be the spacing between graphene layers (002 facet). This result is similar to that of many other reported CDs.[24,28,29] The atomic force microscopy (AFM) image (Figure 1 e) shows the topographic height of the obtained CDs, which is mostly distributed in the range from 0.5 to 3.5 nm, with an average value of 2 nm (Figure 1 h).

Elemental analysis results (Supporting Information, Table S1) and X-ray photoelectron spectroscopy (XPS) results (Figure 2 a) indicate that the N,S-CDs are mainly composed of carbon, nitrogen, sulfur, and oxygen. The high-resolution spectrum of C_{1s} exhibits three main peaks (Fig-

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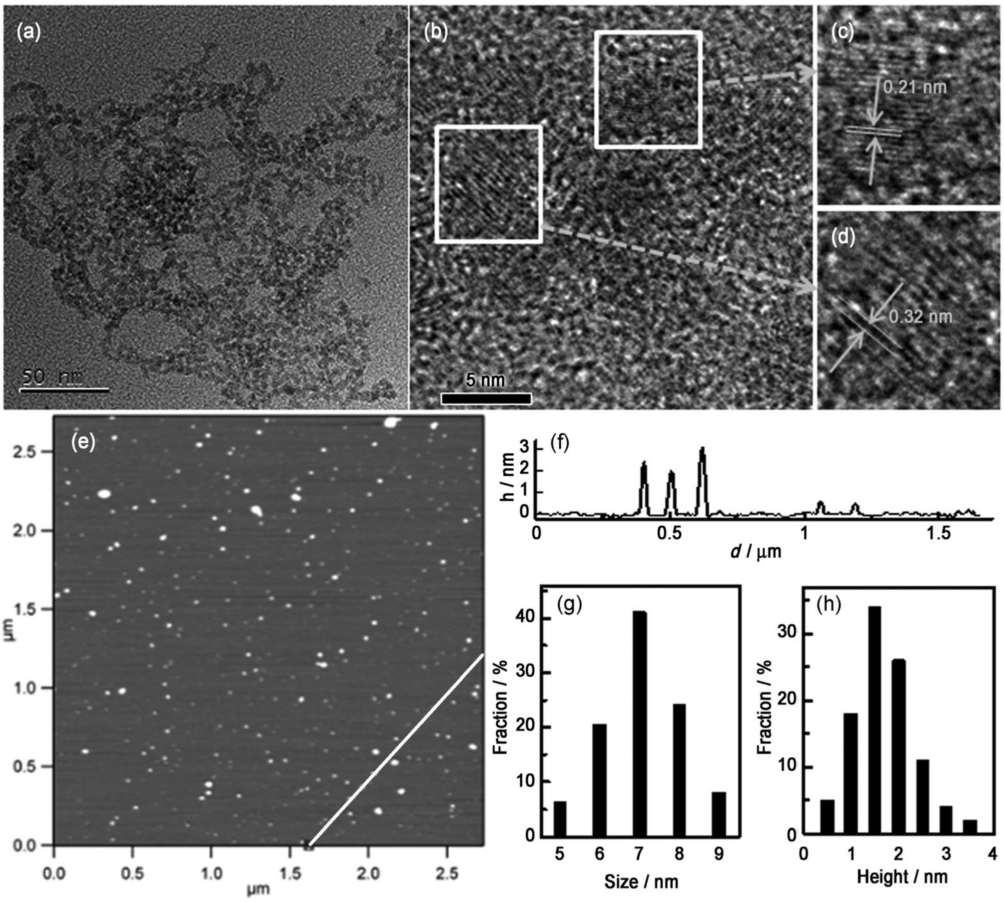

Figure 1. a) TEM and b) HRTEM images of the N,S-CDs. c),d) Typical single CDs with lattice parameters of 0.21 nm and 0.32 nm, respectively. e) AFM image of the N,S-CDs. f) Height profile along the line in (e). g),h) Size and height distributions of the N,S-CDs.

ure 2b). The binding energy peak at 284.5 eV confirms the graphitic structure (sp^2 C−C) of the N,S-CDs. The peak at about 285.5 eV suggests the presence of C−O, C−S, and C−N, and the peak around 288.0 eV could be assigned to C=O. The high-resolution spectra of N_{1s} (Figure 2c) reveal the presence of both pyridinic type (399.7 eV) and pyrrolic type (400.6 eV) N atoms. The high-resolution spectra of S_{2p} (Figure 2d) reveal the presence of C−S−C units.[30–32] Fourier transform infrared (FTIR) spectra (Supporting Information, Figure S1) further confirm the presence of oxygen-containing groups (O−H, $-COO^-$, C=O) and C−S, C=C, and C−N. X-Ray powder diffraction (XRD) was also used to characterize the obtained N,S-CDs (Supporting Information, Figure S2). Like most reported CDs,[15,19,21,24] the N,S-CDs show a broader (002) peak centered at around 25.5°, which further confirms the graphene structure of the N,S-CDs. Raman spectroscopy was used to confirm the quality of the N,S-CDs (Supporting Information, Figure S3). Two major features, a D band and G band, were observed at around 1385 and 1575 cm^{-1} respectively. The relative intensity of the "disorder" D-band and the crystalline G-band (I_D/I_G) for the N,S-CDs is about 0.5, indicating its high quality.[15]

Figure 3 shows that the N,S-CDs in aqueous solution has two typical UV/Vis absorption peaks at 242 and 345 nm, respectively, while the absorption of CA is below 230 nm and the absorption of L-cysteine is very weak above 230 nm. The peak at 242 nm, corresponding to the $\pi\rightarrow\pi^*$ transition of the aromatic sp^2 domains, leads to nearly no observed FL signal.[33] The other transition centered about 345 nm due to the trapping of excited-state energy by the surface states results in strong emission.[25–27] Very bright violet–blue luminescence under the illumination of UV (365 nm) light even at a very low concentration (10 $\mu g\,mL^{-1}$) of the N,S-CD aqueous solution can be clearly seen in the inset of Figure 3. Unlike most CDs, the emission wavelength of the N,S-CDs is independent of the excitation wavelength (when the excitation wavelength is changed from 285 nm to 405 nm, the emission wavelength showed nearly no shift; Supporting Information, Figure S4). The maximum excitation wavelength and emission wavelength of the N,S-CD aqueous solution are 345 and 415 nm, respectively. Usually, excitation-dependent FL behaviors of CDs reflect effect from particles of different sizes in sample and a distribution of different surface states.[12] TEM images indicate that the size of the N,S-CDs is not very uniform, and in fact ranges from 5 to 9 nm. Therefore, the excitation-independent FL behavior suggests that the FL properties of the N,S-CDs are depend on the surface states rather than the morphology, and the surface states of the N,S-CDs should be rather uniform, which will be further discussed below. The FLQY of N,S-CDs excited with 345 nm UV light is calculated to be 73.0% by selecting the quinine sulfate as standard.[23] Selecting 4′,6-diamidino-2-phenylindole (DAPI) dissolved in dimethylsulfoxide as a second standard,[34] the FLQY of N,S-CDs is calculated to be 71.2%. These results confirm that the as-prepared N,S-CDs do show rather high FLQY (70% at least). The FL of the N,S-CDs is strong and stable in a wide range of pH values (5–12; Supporting Information, Figure S5). However, as the pH value is lower than 5, both excitation and emission spectra red shift with the decrease of the pH values. Meanwhile, the FL intensities decrease gradually. The effect of the pH values can be understood in terms of the change in surface charge owing to protonation–deprotonation. The N,S-CDs can also be well dispersed in most common organic solvents, such as acetoni-

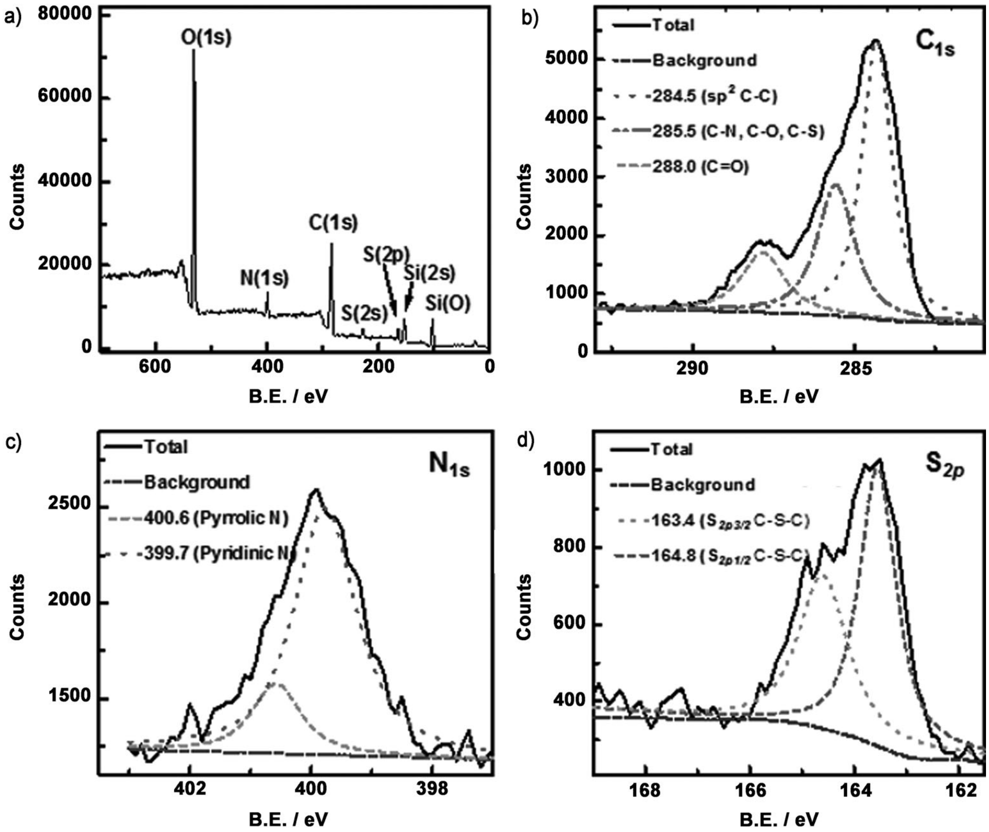

Figure 2. a) XPS spectra of the N,S-CDs. b)–d) High-resolution C_{1s} (b), N_{1s} (c), and S_{2p} (d) peaks of the N,S-CDs.

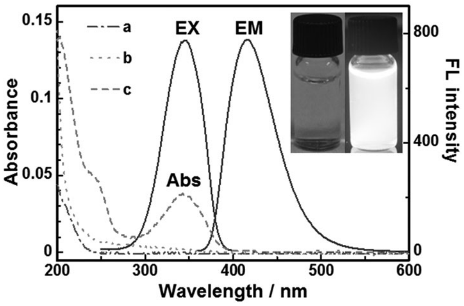

Figure 3. FL spectra (solid lines) of the obtained N,S-CDs and UV/Vis absorption spectra (dotted lines) of CA (a), L-cysteine (b), and the obtained N,S-CDs (c). Inset: Photograph of the obtained N,S-CDs under illumination of white light (left) and UV (365 nm) light (right).

trile, chlorobenzene, and *N*,*N*-dimethylformamide, which is advantageous in non-aqueous and organic phases to fabricate photovoltaic cells.

Although the FL mechanism of CDs is still not clear, two popular hypotheses, namely emissive traps[12,25–27] and electronic conjugate structures,[34,35] have been proposed. As our described experimental results above, the absorption at about 245 nm corresponding to the $\pi\rightarrow\pi^*$ transition of the aromatic sp^2 domains the N,S-CDs produces nearly no observed FL signal, suggesting that the FL of N,S-CDs should not be produced by the electronic conjugate structures. It has been well reported that the surface states should have more prominent impact on the photophysical properties of CDs.[36–38] It is reasonable that the FL of the CDs should be attributed to the radiative recombination of electrons and holes trapped on the CDs surface. Therefore, we argue that the strong FL emission of the N,S-CDs mainly result from the surface-doped nitrogen and/or sulfur atoms. To further confirm this possible explanation, two additional CDs (Supporting Information, Figures S6, S7) were prepared using the same method, of which one was prepared using CA alone as the precursor, labeled as O-CDs owing to their abundant oxygen-containing groups, while another was prepared using CA and a sulfur-free amino acid (glycine) as the precursor, labeled as N-CDs for the existence of nitrogen-containing groups. The optical properties of O-CDs are much different from the N,S-CDs (Supporting Information, Figure S8a): 1) The O-CD solution shows a broad UV/Vis absorption below 500 nm without any obvious peak; 2) the emission spectra of the O-CDs are broad and excitation-dependent, and the maximum emission wavelength (excited with 345 nm UV light) is 435 nm, which is about 20 nm red-shift than that of the N,S-CDs; 3) the FLQY of the O-CDs excited with 345 nm is calculated to be 5.3 %, which is much lower than that of the N,S-CDs; and 4) although both the FL decay of the O-CDs and the N,S-CDs could be fitted by a single-exponential function (Figure 4), the lifetime of the O-CDs (7.45 ns) is much shorter than that of the N,S-CDs (12.11 ns). On the contrary, the N-CDs show a number of optical properties that are similar to the N,S-CDs (Supporting Information, Figure S8b): 1) Although the N-CD solution

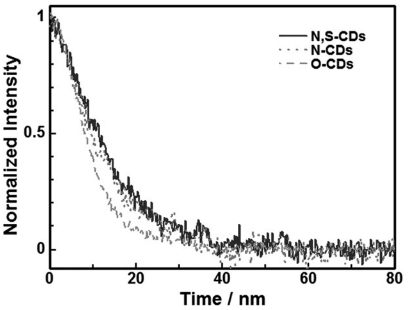

Figure 4. FL decays (345 nm laser excitation, and monitored through 415 nm bandpass filter) of the N,S-CDs, N-CDs, and O-CDs.

shows a broad UV/Vis absorption below 500 nm, two peaks could also be observed around 245 and 345 nm, respectively; 2) although the FL spectra is broad and excitation-dependent, the maximum emission wavelength (excited with 345 nm UV light) is 415 nm, which is identical to the N,S-CDs; 3) the FLQY excited with 345 nm UV light is calculated to be 16.9 %, which is much higher than that of the O-CDs; and 4) the lifetime of the N-CDs is 11.78 ns, which is also quite close to that of the N,S-CDs. These results clearly indicate that the N,S-CDs and the N-CDs should have the same FL origin, which is different from that of the O-CDs.

Therefore, a model for the mechanism is proposed to explain the FL processes of the three CDs (Figure 5). The O-CDs have different kinds of surface states (labeled as O-states) corresponding to a relatively wide distribution of different energy levels to generate a broad UV/Vis absorption band and broad and excitation-dependent emission spectra. The nitrogen-doping introduces a new kind of surface state (labeled as the N-state). Electrons trapped by the new formed surface states are able to facilitate a high yield of radiative recombination. As the density of the N-state is comparable with that of those O-states in the N-CDs, the FL spectra are still broad and excitation-dependent, even though the FLQY of the N-CDs is higher than that of the O-CDs. It has been reported that the sulfur and nitrogen co-doped carbon materials usually exhibit more excellent catalytic activity to the oxygen reduction reaction compared with the nitrogen-doped carbon materials.[30–32] It seems that the introduced sulfur atoms would enhance the effect of nitrogen atoms on the properties of the doped carbon nanomaterials through a cooperative effect. For the N,S-CDs, the introduced sulfur atoms seem to be able to eliminate the O-states and enhance the N-state, leading to that the original surface states nearly neglected in the N,S-CDs. Therefore, the N,S-CDs show a high FLQY and excitation-independent emission. To further test this hypothesis, three other N,S-CDs were prepared by tuning the ratio of CA and L-cysteine in the precursor. When L-cysteine in the precursor is decreased gradually from 1 g to 0.125 g while fixing CA of 2 g, the absorption peak around 345 nm decreases compared with the background absorption (Supporting Information, Figure S9), thus suggesting decreased N-state density and increased O-state density. As a result, the FLQY of the obtained S-CDs decreases from 73 % to 37 % (Supporting Information, Table S2). Furthermore, the N,S-GQDs prepared with low density of N-state also exhibit broad and excitation-dependent emission spectra. Taking the N,S-CDs obtained from the precursor of CA (2 g) and L-cysteine (0.125 g) for example (Supporting Information, Figure S10), the emission wavelength is excitation-independent when the excitation wavelength is lower than 375 nm, but exhibits a red-shift from 415 to 540 nm when the excitation wavelength is increased gradually from 375 to 480 nm.

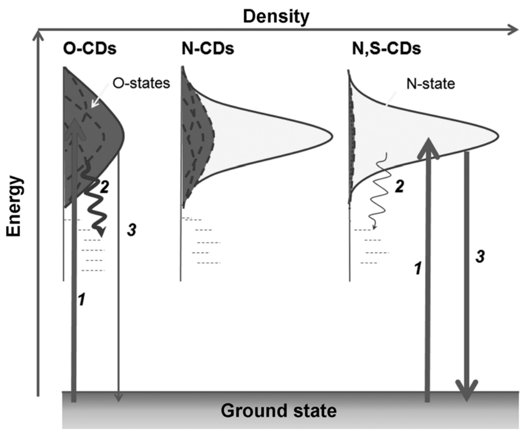

Figure 5. Representation for the FL mechanism of O-CDs, N-CDs, and N,S-CDs. 1) Electrons excited from the ground state and trapped by the surface states; 2) excited electrons return to the ground state via a non-radiative route; 3) excited electrons return to the ground state via a radiative route.

The prospects of the obtained N,S-CDs as a bioimaging material was assessed. HeLa cells were incubated in the presence of 3 mg mL^{-1} N,S-CDs for 30 min, and then well-washed for imaging (Supporting Information, Figure S11). Cells show bright blue luminescence under 365 nm UV excitation, while the control cells incubated in the absence of N,S-CDs are nearly dark. This results suggest that the N,S-CDs have great application potential in bioiaging and biosensing.

In summary, nitrogen and sulfur co-doped CDs have been synthesized from a precursor comprising L-cysteine and citric acid. The obtained N,S-CDs are nanosheets with an average height of 2 nm and an average width of 8 nm. The N,S-CDs show high yield and excitation-independent emission. The N,S-CDs exhibit excellent FL activity; coupled with the low-toxicity of carbon-based materials could provide important broad applications in bioimaging and beyond. Even though the exact mechanism is still unclear, it is reasonable to believe that the doping of nitrogen can introduce the CDs a new kind of surface state, whose density can be increased dramatically by the co-doped sulfur atoms, which offers great scientific insights to FL enhancement mechanism of CDs.

Experimental Section

Citric acid (99.9 %), L-cysteine (97.0 %), glycine (99.0 %), 4′,6-Diamidino-2-phenylindole (> 98 %), and quinine sulfate (≥ 98.0 %) were purchased from Sigma–Aldrich and used as received.

The N,S-CDs were prepared by thermal treatment of molecular organic salts with the mixed carbon source and the surface modifier in the single precursor.[22] In a typical preparation procedure, CA monohydrate (2 g, 9.5 mmol) and L-cysteine (1 g, 8.3 mmol) were dissolved in water (5 mL), followed by evaporation at 70 °C until dry within 12 h. The resulted thick syrup was heated hydrothermally in a Teflon-equipped stainless-steel autoclave at 200 °C for 3 h and a heating rate of 10 °C min^{-1}. The black syrup product was then diluted to 100 mL after neutralized with 1 mol L^{-1} NaOH solution.

The O-CDs were prepared from citric acid monohydrate. In detail, citric acid monohydrate (2 g) was heated hydrothermally in a Teflon-equipped stainless-steel autoclave at 200 °C for 3 h and a heating rate of 10 °C min^{-1}. Finally, the orange syrup product was diluted to 100 mL after neutralized with NaOH solution (1 mol L^{-1}).

The N-CDs were prepared from citric acid monohydrate and glycine. In detail, CA monohydrate (2 g) and glycine (0.62 g, 8.3 mmol) were dissolved in water (5 mL). The solution was then evaporated to dryness at 70 °C for 12 h. The resulting thick syrup was heated hydrothermally in a Teflon-equipped stainless-steel autoclave at 200 °C for 3 h and a heating rate of 10 °C $\mathrm{min^{-1}}$. Finally, the black syrup product was diluted to 100 mL after neutralized with NaOH solution (1 $\mathrm{mol\,L^{-1}}$).

Elemental analysis was carried out using an organic elemental analyzer (Vario MICRO).The height distribution of the obtained CDs was characterized by atomic force microscopy (Nanoman, Veeco, Santa Barbara, CA) by using tapping mode. The crystal structure of the CDs was characterized by X-ray diffraction (Bruker AXS, $\lambda =$ 0.15418 nm). Fourier transform infrared spectra were obtained on a FTIR spectrophotometer (Thermo Nicolet 360). UV/Vis spectra were obtained by a UV/Vis spectrophotometer (UV 2450). Raman spectra were measured using a Renishaw 1000 microspectrometer (excitation wavelength of 514.5 nm). All fluorescence spectra were obtained by a spectrofluorometer (Fluoromax-4). X-Ray photoelectron spectroscopy data for the CD solutions deposited on glass substrates were measured by a Kratos AXIS Ultra spectrometer with a monochromatized Al Kα X-ray source (1486.71 eV) for determining the composition and chemical bonding configurations. High-resolution transmission electron microscopy images were recorded on a HRTEM JEOL 2100 system operating at 200 kV. The specimens were prepared by drop-casting the sample solution onto a carbon-coated copper grid, followed by drying at room temperature.

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