Lecture 13. Properties of Graphene Quantum Dots. Applications of Graphene Quantum Dots

The purpose of the lecture: to provide information on the properties and applications of graphene quantum dots.

Expected results: to master the properties and applications of graphene quantum dots.

Opening of a band gap and quantum confinement and edge effects lead to novel optical properties and photoluminescence (PL) in graphene quantum dots. Dispersions of GQDs generally appear light brown in visible light but show fluorescent colors under ultraviolet (UV) irradiation. The GQDs efficiently absorb UV light with strong UV absorption in the 230 nm wavelength corresponding to the π-π* transition of the aromatic sp2 domains but also show new absorption bands that are responsible for the PL behavior that results in emission of bright colors (Figure 1a–c).

Most GQDs show excitation-dependent emission or PL behavior, that is, the PL maximum redshifts and becomes lower in intensity as the excitation wavelength increases, with the strongest peak excited at the absorption band (Figure 1b). The PL excitation (PLE) spectrum recorded with the strongest luminescence exhibits sharp peaks (Figure 1c), which correspond to the new absorption bands that appear in the UV-visible spectra of GQD (Figure 1a), hence new transitions other than the commonly observed π-π* transitions are involved. These new electronic transitions responsible for observed luminescence are σ-π* and π-π* transitions shown in Figure that originate from free zigzag edges with a carbene-like triplet ground state.

The GQDs show pH-dependent PL (Figure 1d). Under alkaline conditions, the GQDs emit strong PL, whereas, under acidic conditions, the PL is nearly completely quenched. If pH is switched repeatedly between 13 and 1, the PL intensity varies reversibly. Under acidic conditions, the free zigzag sites of the GQDs are protonated, forming a reversible complex between the zigzag sites and H+. Thus the emissive triple carbene state is broken and becomes inactive in PL. However, under alkaline conditions, the free zigzag sites are restored, thereby leading to the restoration of PL.

Different colors of graphene quantum dots have been synthesized, ranging from UV to red, and most commonly blue and green with different quantum yields. The PL quantum yield (QY) of GQDs is high due to their crystalline structure. Reaction process parameters influence the photoluminescence properties of GQDs. The OH-GQDs synthesized by mild hydrothermal treatment in aqueous solution emit bright green fluorescence when irradiated by a UV light. By varying the hydrothermal reaction conditions to produce amine-functionalized GQDs, yellow, cyan and blue fluorescent colloidal solutions have been obtained. For GQDs synthesized from different polycyclic hydrocarbons, the maximum emission peak showed a redshift with increased size of PAH precursors due to the different shapes and sizes of the prepared GQDs from different-sized PAHs.

Studies show that though oxygen-containing functional groups on GQDs render them hydrophilic and provide sites for further chemical functionalization, they also serve as emissive traps leading to low quantum yield. Li et al. showed that quantum yield of GQDs almost doubled and the emission color changed to blue by reducing greenish-yellow luminescent oxidized GQDs. The oxidation of GQDs redshifts the emission. Excitationdependent luminescence and up-conversion photoluminescence (i.e., two-photon luminescence leading to emission of shorter wavelength) was observed in N-doped GQDs.

Up-conversion is desirable for *in vivo* imaging because of deep-tissue penetration ability of long excitation wavelength (e.g., near infrared). Compared to conventional organic and inorganic fluorophores, the GQDs show nonblinking photoluminescence and excellent photostability, which are important for single-molecule tracking and long-term real-time imaging, respectively. Photostability of amine-functionalized GQDs was compared with that of semiconductor quantum dots. The conventional semiconductor QDs such as CdSe/ZnS QDs show a typical photobleaching effect that leads to the attenuation of their PL intensity and brightness on UV exposure.

Photoluminescence of GQDs can be tailored to obtain luminescent dots with different emission colors of blue, green, and yellow through varying the size of the GQDs by changing reaction temperature. As processing temperature during synthesis of GQDs by exfoliation of carbon fibers increased from 80°C to 100°C to 120°C, the UV-visible spectrum showed a blue shift indicating reaction temperature could tune the size of asprepared GQDs and affect their absorption properties. Highly oxygenated GQDs synthesized by cage opening of fullerene C60 showcased their broad prospects for chemical modifications through successful functionalization reactions. The luminescence properties varied according to the types of chemical treatments. While as-synthesized oxidized GQDs exhibited strong luminescence properties when excited at 340 nm, hydroxylaminefunctionalized GQDs showed a blueshift of the emission maximum, whereas hydrazinereduced GQDs showed a redshift of the emission maximum.

Besides striking photoluminescence behavior, graphene quantum dots also possess other properties such as electrochemiluminescence behavior, electrochemical properties, low toxicity, water solubility, and biocompatibility.

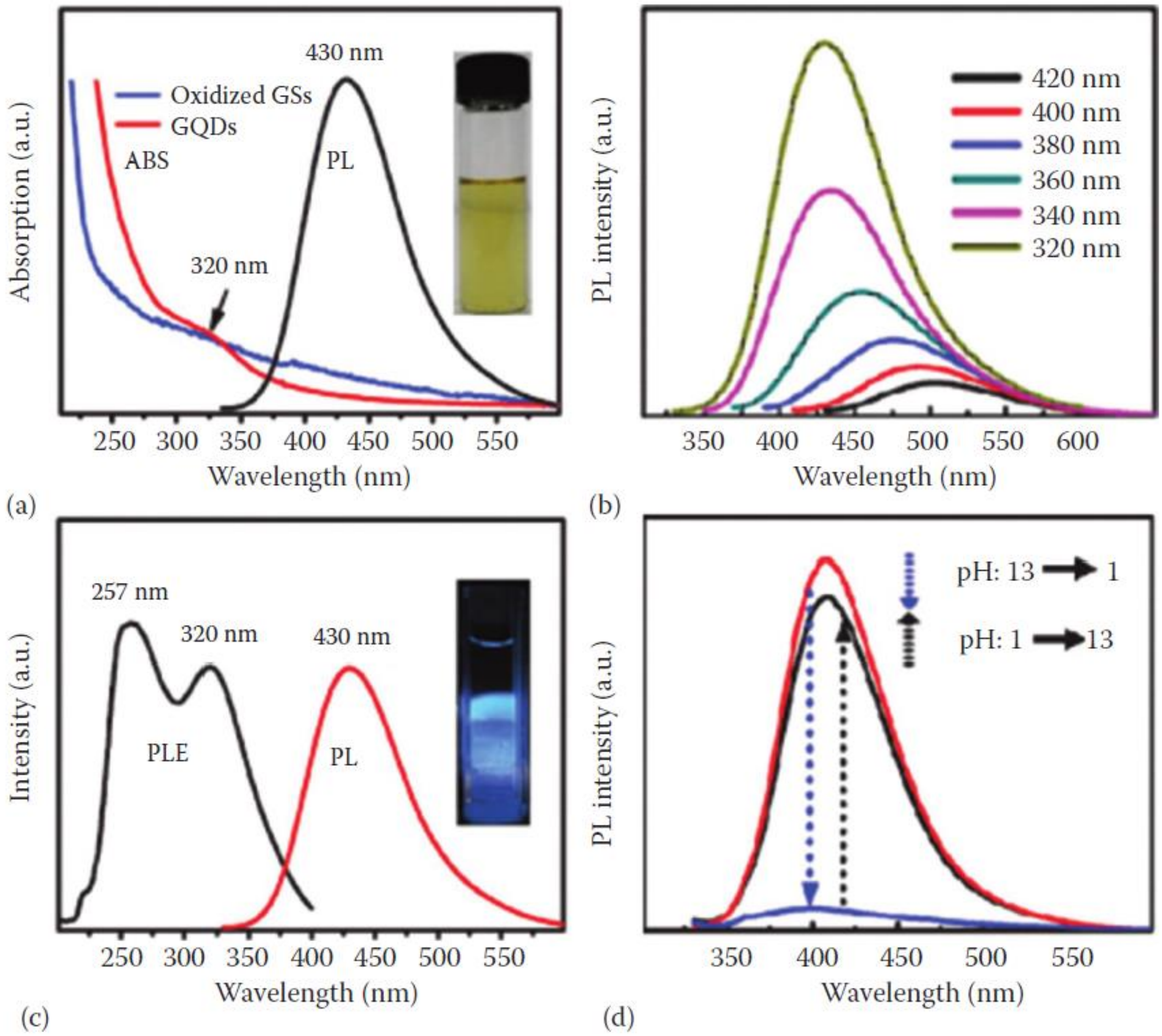

FIGURE 1 (a) UV–vis absorption and PL (at 320 nm excitation) spectra of the GQDs dispersed in water; UV–vis absorption spectrum of oxidized GSs. Inset: Photograph of the GQD aqueous solution taken under visible light. (b) PL spectra of the GQDs at different excitation wavelengths. (c) PLE spectrum with the detection wavelength of 430 nm and PL spectrum excited at 257 nm. Inset: Photograph of the GQD aqueous solution taken under UV light (shows bright blue luminescence) in a fluorescence spectrophotometer. (d) pH-dependent PL spectra when pH is switched between 13 and 1.