Oxidation-Induced Paramagnetic Spins in Graphene Quantum Dots for Metal-Free MRI Contrast Agents

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The development of biocompatible, metal-free magnetic resonance imaging (MRI) contrast agents is of paramount importance to address the long-term toxicity and nephrogenic systemic fibrosis concerns associated with conventional gadolinium-based agents (Gd^{3+}) [1]. While graphene quantum dots (GQDs) have been widely highlighted as a promising Gd^{3+} alternative, previous research has predominantly focused on enhancing their magnetic properties through heteroatom doping with elements such as nitrogen (N) or boron (B) [2][3]. However, the intrinsic contribution of oxygen functional groups to the paramagnetic centers-independent of external dopants-has remained largely unexplored. This study demonstrates that pristine GQDs can serve as robust T1 contrast agents by leveraging oxygen-stabilized spins. Electron Spin Resonance (ESR) spectroscopy revealed that GQDs exhibit significantly higher spin intensity than graphene oxide (GO), suggesting that quantum-confined edges are uniquely suited for stabilizing localized radicals. Systematic thermal annealing showed a progressive reduction in ESR intensity as oxygen groups were removed, with a critical chemical transition at 600°C marking the quenching of paramagnetic centers. Furthermore, the increase in ESR linewidth (ΔH_{pp}) with temperature indicates a transformation in the spin-relaxation environment due to deoxygenation. MR phantom analysis confirmed concentration-dependent T1 contrast enhancement, producing brighter images as GQD concentration increased. These findings underscore that oxygen functional groups are fundamental stabilizers of paramagnetic states, rather than mere structural defects. By precisely tuning the oxygen-mediated chemical environment, GQDs can be optimized as high-performance, metal-free MRI contrast agents for safer diagnostic imaging.

References

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Figures

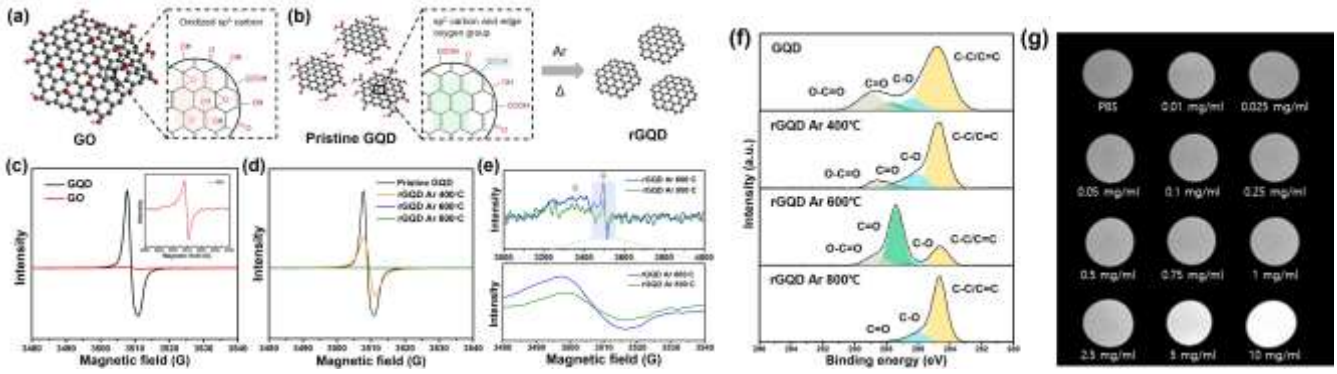

Figure 1: Schematic illustration of (a) GO and (b) GQD structures. ESR spectrum of (c) GO and (d-e) thermal reduced GQDs. (f) XPS C1s spectra of thermal reduced GQDs. (g) Concentration dependent MRI signal of GQDs