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The Synthesis of Graphene Quantum Dots for Photovoltaic Nanotechnology

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Of the various emerging nanotechnologies, it is quantum dots (QDs) which display a particular promise to revolutionize the energy sector. They possess unique qualities differing from those of their bulk counterparts by means of the quantum confinement effect, whereby energy levels available to electrons are altered by the minute size of the host particle (Jiang 2015). As the diameter of the nanoparticle decreases, these band gaps increase, meaning that particles of a smaller diameter will emit photons of higher energies (Jiang, 2015). This makes QDs ideal for capturing and emitting high energy photons, and thus are useful in photovoltaics. Of the materials used to form QDs, graphene in particular is a subject of interest, as it absorbs a large range of the wavelengths of visible light and can be modified into a semiconductor with varying band gaps (Bacon 2014). In addition, graphene fragments of virtually any size have been shown to exhibit quantum confinement (Bacon *et al*., 2014). However, the effects of quantum confinement are most pronounced when the diameter of graphene QDs (GQDs) is below one hundred nanometers, as discussed in *Graphene Quantum Dots* (Güçlü 2014). This is due to the fact that the GQDs are small enough that their band gaps emit photons in the visible range of the spectrum (Güçlü 2014). One of the problems facing GQDs is manufacturing them in an efficient manner that allows them to be adapted for photovoltaic applications. To this end, multiple methods exist for the purposes of manufacturing GQDs, each with their own merits. These can be divided into the two dominant ideologies of nanomaterials synthesis: top-down and bottom-up.

The top-down approach is grounded in the idea that the most expedient means of nanoscale manufacturing comes from working large nanostructures and macroscale components into progressively smaller pieces (National Nanotechnology Initiative). One such method currently used to synthesize GQDs is the hydrothermal cutting conducted by Pan *et al.* where graphene sheets were derived via thermal reduction of graphite oxide, and then subsequently broken into QDs in the five to thirteen nanometer range (as cited in Bacon 2014). This method requires the use of strong acids and high temperatures in order to obtain GQDs with sufficient quality (Bacon 2014). This demonstrates the energy-intensive nature of the top-down approach for the production of GQDs. It has also been argued by Peng *et al.* that the top-down approach to manufacturing GQDs creates products lacking a uniform diameter, which have emissions typically limited to the green and blue portions of the spectrum (as cited in Bacon 2014). Another top-down method used to manufacture GQDs is electrochemical cutting (Bacon 2014). This method, used by Li *et al.*, involved breaking up a graphene sheet after having treated it with an oxygen plasma to increase the hydrophilicity of the resulting GQD product (as cited in Bacon 2014). These green-luminescing GQDs showed particular promise for photovoltaic operations, being relatively uniform, sustainable in solution, and performing with a power conversion efficiency (PCE) of 1.28% when annealed in a polymer solar cell (Li 2011). This PCE surpasses that of organic photovoltaic cells utilizing functionalized graphene and can compare favourably to other cells of its type, even without optimization (Li 2011). This method is one of the most promising for bringing this nanotechnology to its full potential, yet the product, while more uniform than the other top-down methods, is limited to the blue-green portion of the spectrum still. In summary, the top-down approach usually allows for ease of manufacture of GQDs. However, the greatest failing of this approach is that it has a tendency to produce GQDs of lesser quality than the bottom-up approach, hindering their potential use in photovoltaics and other areas where the precision of nanotechnology is required.

The bottom-up ideology is an approach that involves the self-assembly of nanoparticles and components on the nanoscale itself, eschewing the comparative ease of the top-down approach in favour of precision control of the resulting product (National Nanotechnology Initiative). The method used by Liu *et al.* involved the self-assembly of hexa-*peri*-hexabenzocoronene molecules followed by conversion to artificial graphite and final processing to form GQDs, producing products with precise dimensions (Liu 2011). This synthesis is more difficult than the alternative top-down methods to manufacturing GQDs, as several intermediary steps must be taken. Another method for manufacturing GQDs is the cage opening of fullerenes. In this process, as conducted by Lu *et al.,* fullerene molecules were embedded onto a ruthenium surface at elevated temperatures, opening and fracturing into GQDs (as cited in Bacon 2014). This method not only allows the GQDs to manufacture themselves, but their size can be controlled by the temperature of the process as well (Bacon 2014). The weakness of the bottom-up approach is the great effort which must be expended to produce the end product. GQDs may be made with greater control from a bottom-up perspective, increasing their usefulness in photovoltaic applications, but the complexity of the process may offset any net benefit, at least for the present.

There is substantial potential for GQDs in photovoltaic applications, however, it is limited by current technological barriers to production capacity. The top-down approach contains well-developed methods for isolating GQDs from easily manipulated macroscopic components, but limits control over their size. As a complementary approach, the bottom-up ideology has relatively more elaborate methods to form GQDs, which allow for more precise control of the resulting product. Shared among both sets of manufacturing methods are limiting factors such as the use of very specialized equipment, a generally low yield of GQDs, and the use of a complex series of reactions (Kwon *et al.,* 2014), which are major weaknesses for the future of this nanotechnology. In addition, the current GQDs produced generally have emissions in the blue-green portion of the spectrum, though greater colour variety has been reliably achieved (Bacon 2014). More variable absorption will be required to open up greater potential in photovoltaic applications as well as in other areas. Therefore, the future of GQDs does not belong exclusively to either ideology, but perhaps to a cooperation of both, mixing control and precision with efficient mass-production.

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