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多彩的纳米材料——2023年度诺贝尔化学奖解读

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2023年诺贝尔化学奖于10月4日授予了来自美国麻省理工学院Moungi G. Bawendi教授、哥伦比亚大学Louis E. Brus教授和俄罗斯科学家Alexei I. Ekimov, 获奖理由是对量子点的发现和合成作出的突出贡献. 正如瑞典皇家科学院称: 今年诺贝尔化学奖的研究成果为纳米科技"播下了重要的种子"("The Nobel Prize in Chemistry 2023: They planted an important seed for nanotechnology").

量子点是一种尺寸极小的纳米材料, 又可以称作半导体纳米晶体. 常见的是由Ⅱ~Ⅵ族或Ⅲ~Ⅴ族元素组成的纳米颗粒. 一个量子点通常由数千原子组成, 尺寸介于1~10 nm[1~4]. 当材料尺寸减小至纳米维度时, 费米能级附近的电子能级由连续态分裂成独立能级结构, 使其磁、光、声、热、电等性能发生显著变化. 量子点独特的尺寸依赖光学特性得到研究者的广泛关注[5,6]. 由于电子和空穴被量子限域, 量子点中的电子在一定光辐射下被激发离开原有位置形成自由电子和空穴, 由于自由电子和空穴距离较近, 可通过辐射复合实现光致发光. 不同尺寸的量子点, 由于电子和空穴量子限域程度差异, 受激发后, 可以发出不同波长的荧光, 其发光颜色可从蓝光到红光的整个可见区连续可调[1~6]. 正如诺贝尔化学委员会主席Johan Åqvist所说: "量子点有许多迷人而不寻常的特性. 重要的是, 不同尺寸的量子点具有不同的发光颜色"("Quantum dots have many fascinating and unusual properties. Importantly, they have different colours depending on their size.").

早期, 研究者从薛定谔方程推导出理论结果, 预测量子点纳米颗粒可表现出尺寸依赖的光学特性, 但如何高效化学制备与表面修饰量子点仍是当时该领域的重大挑战. 起初, 物理学家使用彩色玻璃来过滤特定波长的光信号[6~8], 进一步发现单一物质可以产生完全不同颜色的玻璃. 比如, 通过控制玻璃的熔化温度和冷却方式, 可利用硫化镉(CdS)、硒化镉(CdSe)的混合物制备黄色或红色的玻璃, 而颜色的差异来源于玻璃内部形成的颗粒尺寸. Alexei I. Ekimov在其攻读博士学位期间, 利用光照射材料测试其吸光度, 揭示材料的物质组成与晶体结构的有序程度. 经过初步实验后, Alexei I. Ekimov制备出添加氯化铜的有色玻璃. 通过控制熔融玻璃的温度与加热时间, 对其进行结构表征. 散射的射线显示在玻璃内形成了不同粒径(2~30 nm)的氯化铜纳米晶体. 玻璃的光吸收会受颗粒大小的影响, 较小的氯化铜颗粒, 其吸收光发生显著蓝移. Alexei I. Ekimov教授将其总结为: 量子限域效应[7~9]. 工作于美国贝尔实验室的Louis E. Brus教授使用CdS颗粒作为捕光剂进行太阳能相关化学实验. 利用超小CdS纳米颗粒较大的比表面积, 提升化学反应的效率. 实验过程中Louis E. Brus教授发现, 相较于12.5 nm的大尺寸颗粒, 较小的4.5 nmCdS颗粒的吸收波长发生蓝移[2,10,11]. Moungi G. Bawendi作为胶体量子点研究领域的开创者之一, 发展了有机相制备量子点技术. 在氩气环境下, 用三辛基氧化膦作配位溶剂, 将二甲基镉和硒粉混合溶液作为前驱体, 通过高温注入反应得到硒化镉(CdSe)量子点, 该反应通过快速成核、慢速生长的机制, 高温分解金属有机物与尺寸分离技术制备得到单分散的纳米颗粒, 即"金属有机-配位溶剂-高温"合成方

案，这对胶体化学法合成半导体量子点起到了极大的推进作用[6,10~13]．常见胶体量子点材料主要包括CdSe、CdS、碲化镉(CdTe)、硫化锌(ZnS)等Ⅱ~Ⅵ族半导体量子点以及砷化铟(InAs)、磷化铟(InP)等Ⅲ~Ⅴ族半导体量子点[12,13]．

量子点及其相关应用已经成为纳米科技中重要的研究领域[14~17]，并逐渐出现在商业产品中[18,19]．在生物医学领域，量子点探针的荧光可用来标记生物分子、细胞和组织，在生物光学成像领域展现出独特优势．Moungi G. Bawendi认为，作为一种研究细胞和分子结构的方法，量子点比传统的有机染料更亮、更稳定[20,21]. 在显示领域, 利用量子点发光二极管(QLED)技术的计算机和显示器得到快速发展. 通过改变量子点的大小来控制吸收和释放能量的方式，可用于调控蓝光LED的发射波长, 从而实现显示屏幕所需的三原色光. QLED具有较宽的色域，可以更真实地反映自然颜色．与常规显示器相比，量子点显示器件能量损耗减少30%左右，并可以通过大规模生产, 取代珍贵的稀土材料[22~25]. 此外, 量子点还有望应用于柔性器件、微纳传感器、加密通信和能源催化各个领域. 正如诺贝尔奖官网介绍材料中所说: “我们才刚刚开始探索量子点的潜力”(“So we have just started exploring the potential of these tiny particles.”).

纵观近年来诺贝尔化学奖的获奖经历，其研究成果主要从新的化学结构、新的化学反应规律、新的化学合成手段等领域作出突破，从全方位、多角度有力推动了化学及交叉学科的发展．实验是化学科学领域中重要的组成部分之一，是新科学发现和新科学理论建立的重要途径．年轻科研工作者和大学生，更需注重培养严谨的科学精神，提升实验能力和理论水平，注重学科交叉，为化学及相关交叉学科的发展作出应有贡献.

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Summary for "多彩的纳米材料——2023年度诺贝尔化学奖解读"

The multi-color nanomaterials——A summary of the Nobel Prize in Chemistry 2023

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The Nobel Prize in Chemistry 2023 was awarded to three scientists for their work in the discovery and synthesis of quantum dots: Moungi G. Bawendi from Massachusetts Institute of Technology, Louis E. Brus from Columbia University and Alexei I. Ekimov from Nanocrystals Technology Inc. As the praise from the Royal Swedish Academy of Sciences: they planted an important seed for nanotechnology. In this summary, the backgrounds and scientific significance of these researches and quantum dots are discussed.

Quantum dots (QDs) with sizes ranging from ~1 to 10 nm are constructed by hundreds to a few thousand atoms. As the size of QDs becomes smaller, quantum confinement enhances the effective bandgap, inducing an obvious blue shift of the emission and absorption spectra. An electron excited across the bandgap processes strong interactions with valence band hole. Spin-exchange coupling and Coulomb effects could generate increased confined electron-hole excitons. In QDs, the close proximity in charge carriers leads to enhanced many-body results that will affect their optical properties. "Quantum dots have various fascinating and unique properties. Significantly, they have different colors depending on their size," said Johan Aqvist, chair of the Nobel Committee for Chemistry. Firstly, Alexei I. Ekimov performed pioneering study of quantum confinement effects of QDs in glass. He found that the copper chloride nanocrystals (2−30 nm) could be obtained through controlling the reaction temperature and time in molten glass. The size-dependent absorption spectra further demonstrated the quantum confinement effects in this system. Louis E. Brus was the first researcher in the world to verify size-dependent quantum effects in nanoparticles floating freely in liquid phase. In their solar energy experiments, the QDs with small size and high specific surface area could strengthen the reaction efficiency. Moungi G. Bawendi proposed a relatively simple synthetic approach to produce high-quality QDs. In this synthesis, they controlled the rapid injection of organometallic reagents into coordinating solvent for realizing homogeneous nucleation. During the past decades, a serial of QDs has been designed through various reaction conditions, such as cadmium selenide (CdSe), cadmium sulfide (CdS), cadmium telluride (CdTe), zinc sulfide (ZnS), indium arsenide (InAs), and indium phosphide (InP), etc.

QDs have attracted impressive attentions in the last decades due to their various advantages and characteristics. Many kinds of QDs have been produced and supplied in the form of industrial products. In the past decades, taking advantages of strong emission and robust photostability, scientists have made an extensive effort to establish a QDs system for various biological and biomedicine applications. QDs-based light emitting diodes (QLEDs) have gained great attentions in the virtue of their narrow half-peak width and stable optical performance. Scientists hold the opinion that in the future QDs will apply to flexible display, thinner solar cells and encrypted quantum calculation. As the statement in the Nobel Prize website: "So we have just started exploring the potential of these tiny particles". We anticipate that the fast development of QDs nanotechniques will facilitate significant improvements of nanomaterials, opening new avenues for long-awaited QDs based myriad optical applications.

Quantum dots, Nobel Prize, chemistry, Optical

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