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金属纳米团簇的超分子自组装及其应用

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摘要 金属纳米团簇(NCs)是由几个至几千个金属原子通过物理或化学结合力组成的相对稳定的聚集体, 其物理和化学性质具有量子尺寸依赖性. 金属簇的尺寸可与电子的Ferimi波长相当, 一般小于3 nm, 具有异于对应体相块材的物化性质, 如光学、电学、磁学、催化、手性等. 基于自组装策略, 将金属簇与不同类型的分子材料组装, 不但可以实现金属簇的聚集诱导发光, 而且还可以实现多功能的协调. 结合本课题组的研究工作, 本文综述了近期国内外相关研究, 详细介绍了自组装对金属簇发光、组装结构的影响及金属簇组装体的应用等方面的研究进展. 最后对金属簇的未来挑战和发展前景进行了展望.

关键词 金属纳米团簇, 自组装, 聚集诱导发光, 组装结构

金属纳米团簇是由几个至几千个金属原子通过物理或化学结合力组成的相对稳定的聚集体, 其物理和化学性质具有量子尺寸依赖性, 其尺寸可与电子的Fermi波长相当, 一般小于3 nm(图1)[1]. 由于其金属簇自身的特殊结构, 它会表现出类分子的性质, 从而展现出优异的物理化学性质, 如光学、电学、磁学、催化、手性等[1~10]. 金属团簇主要分为两大类: 第一类是还原性金属纳米团簇, 是在多种配体(包括硫醇、炔、胺、磷和氮杂环卡宾)存在的情况下通过溶液中金属阳离子还原产生或者通过其他金属纳米团簇转化而成的. 它们可以被看作是超微小的金属纳米颗粒, 其中一些具有精确的原子结构[11~15]. 第二类是配位团簇, 它通过金属阳离子与配体间的配位获得, 其中分离出的大部分物质通过单晶衍射分析确定其都具有精确的原子结构[16,17]. 对于具有精确结构的金属团簇, 它们的性质与结构之间的关系能得到很好的解析, 有利于我们更加准确地解释其微观结构和现象, 并深入理解结构-性质之间的构效关系, 使得科学深度更上一个台阶[18,19].

超分子自组装作为化学界的热门研究领域之一, 由于操作简单、原料易得等优异特点, 使其在生物医药、环境、传感、光电器件与催化等领域得到广泛的应用[20~23]. 而通过自组装所得到的有序聚集体都是基于多种非共价相互作用完成的, 包括氢键作用、π-π堆积作用、疏水作用、静电作用和主-客体作用[24~31]. 近些年, 金属纳米团簇的自组装逐渐成为一个热门的研究领域[32~35]. 目前研究比较多的是通过自组装策略实现荧光的增强、色彩调变和提高团簇的稳定性. 常见的金属团簇类型主要以金、银、铜、铂和钯为主, 而金属核心和配体的种类可以多样化组合, 使得组装基元的选择性比较丰富, 有利于建立此类簇基材料的数据库. 因此, 本文结合国内外相关研究及本课题组的研究成果, 详细介绍了超分子自组装对金属簇组装结构、发光性质的影响及金属簇组装体的应用等方面的研究进展, 该综述有利于我们对金属簇的超分子自组装研究有更全面更深入的了解, 能够为后续的应用研究提供坚实的基础.

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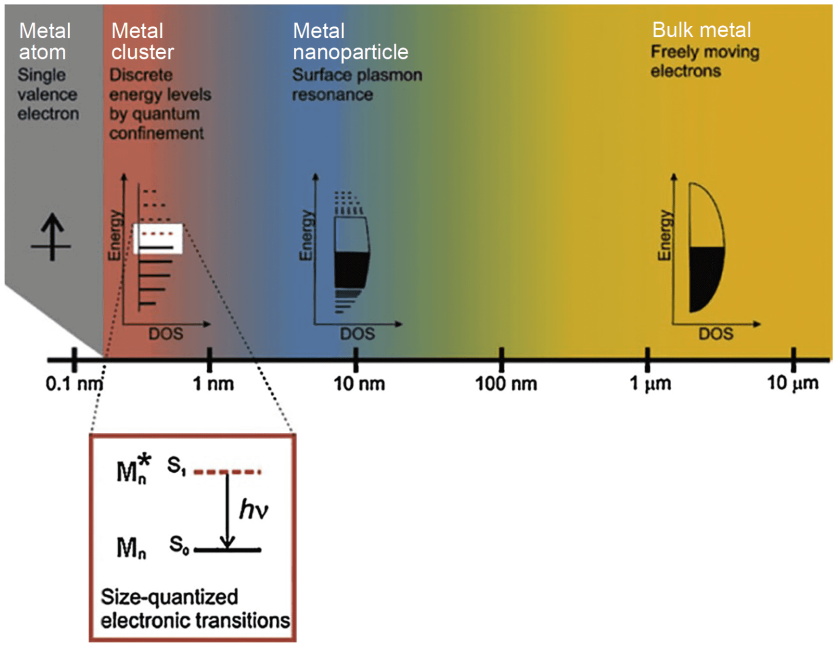


图 1 (网络版彩色)尺寸对金属材料的影响[1]
Figure 1 (Color online) The effect of size on metal materials[1]

1 自组装对金属纳米团簇组装结构的影响

自组装反映了构筑基元的基本信息, 如聚集形态、形貌、尺寸等, 而聚集形态和形貌是自组装领域研究的热点. 目前, 金属簇的主流分为两大类: 一类为多金属氧酸盐; 另一类为金属纳米团簇. 近些年, 涉及多金属氧酸盐(POM)的自组装调控聚集形态和形貌已经研究的相对成熟. 其中, 本课题组[36~40]在POM自组装调控形貌和聚集行为方面也作了一系列的研究, 主要是将Weakly型多金属氧酸盐EuW_{10}和Preyssler型多金属氧酸盐P_5W_{30}通过不同类型的有机小分子进行自组装得到不同聚集形态和形貌的组装体, 并详细研究了它们的组装机理. 而涉及金属纳米团簇聚集形态和形貌的研究目前在国际上刚处于起步阶段, 属于比较热门的研究课题, 因此通过自组装策略实现对金属纳米团簇聚集形态和形貌的调控, 可以丰富自组装的研究领域并实现金属纳米团簇的功能化.

现阶段对金属纳米团簇结构和形貌的调控主要集中在通过对溶剂效应、团簇浓度、温度调控、pH及组装时间等条件的控制来影响其组装的微观作用力, 以使其在临界状态完成组装[14,17,41]. 目前对于金属纳米团簇自组装聚集形态的研究主要停留在溶液中, 且已有一些报道. 例如, 张皓课题组[42]与刘锦斌课题组[43]分别通过调控水溶性金簇和铜簇得到了不同聚集体. 刘洪林课题组[44]与路建美课题组[45]分别通过高聚物与金簇自组装都得到了球形聚集体. Nonappa课题组[46,47]通过溶剂化效应调控水溶性金簇和银簇分别得到了不同的有序聚集体. Sidharth Shibu课题组[48]通过光调控水溶性金簇控制了纳米球的尺寸.

本课题组主要研究水溶性银簇, 研究重点是合成配位性银簇之后, 再对银簇进行进一步的自组装来改变水溶性银簇的聚集行为. 研究发现pH、模板选择及溶剂条件会调控银簇的聚集行为[49~57]. 例如, 本课题组[52]将合成的水溶性Ag_6与高聚物支化聚乙烯亚胺(PEI)共组装, 固定Ag_6的浓度为50 μmol/mL, 选取4种不同分子量的PEI, 改变4种PEI的浓度, 发现高分子量的PEI随着浓度增加, 可以实现从溶液到浊液再到沉淀, 最后恢复澄清的转变. 而低分子量的PEI, 只是经历澄清溶液和沉淀区, 无法得到浑浊区域. 而产生丰富的相行为主要是由于Ag_6和PEI之间的静电作用驱动(图2(a)). 与此同时, 本课题组[50,51,57]合成了九核的水溶性银簇(Ag_9), 分别通过有机酸丁二酸(SA)、酒石酸及无机酸盐酸(HCl)调控Ag_9的酸碱环境, 改变Ag_9外围配体中-COO^-质子化程度, 增强氢键作用, 从而改变Ag_9的聚集状态. 在SA的调控下, 随着SA浓度的增加(也就是体系pH的降低), 可以实现Ag_9从液态到沉淀最后转化为凝

胶的转变过程(图2(b)). 而在HCl的调控下, 随着HCl浓度的增加, 体系实现了由溶液到沉淀的转变(图2(c)). 此外, 本课题组[49]也探索了不良溶剂的种类与比例对于Ag_9聚集行为的影响. 有趣地发现, 随着不良溶剂乙醇比例的增加, 银簇的聚集行为可以实现从溶液态到凝胶态再到沉淀态的转化(图2(d)), 同时在其他醇类和常见的有机溶剂也可以实现类似相行为的转化, 而引起转化的原因与溶剂的介电常数、亲疏水性及氢键作用密切相关. 可以发现, 通过不同手段实现对金属簇聚集行为的调控, 可以有效地拓宽金属簇的应用范围及性能开发.

与此同时, 金属簇组装体的尺寸及形貌也可以决定其电子结构, 进而决定其功能, 具有重要的意义[58~64]. 目前调控无机纳米材料形貌的手段主要是两种: 可控的结晶、自组装及常见的物理手段(温度、压强)[65~73]. 自组装手段主要是通过非共价键作用力, 使得构筑基元得到稳定有序的纳米结构, 其金属簇组装的非共价弱相互作用主要以范德华力、静电、氢键、疏水、π-π堆积等作用为主. 通过自组装策略来调节金属簇得到不同的形貌已有一定量的报道. Nonappa课题组[74]通过氢键作用将原子精确的金簇构筑具有六方相的纳米结构, 同时通过折叠可以变形形成球形空壳结构; 谢建平课题组[75]报道了Au纳米团簇(NCs)在弱的碱性环境中通过π-π堆积作用可以产生具有清晰结构的纳米带结构; 张皓课题组[72]通过反应温度、反应时间、升温速度以及金簇浓度等的调节使金簇在范德华力和偶极力作用下组装成了不同的聚集形貌(纳米片、纳米花等), 他们还通过控制不同退火温度制备了从黄色到蓝绿色的二维CuNC组件. 较高温度的退火处理有助于配体在NC上的动态迁移, 从而允许形成具有很高致密性的CuNC纳米带. 相反, 低温抑制了配体的迁移, 从而形成了具有松散组装结构的CuNC组装纳米

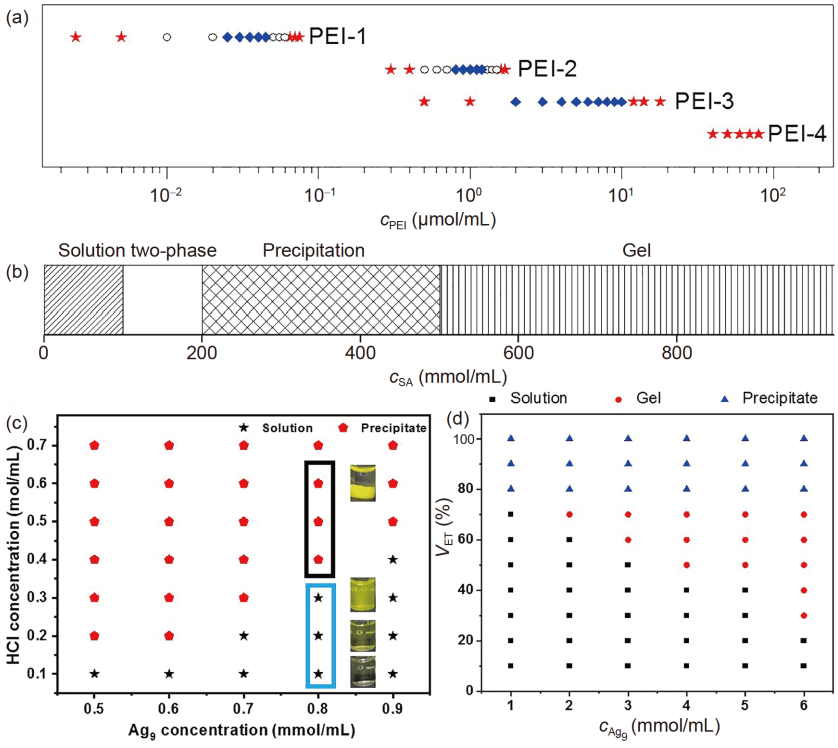


图 2 (网络版彩色)银簇与各类分子自组装的聚集行为. (a) 50 μmol/mL Ag_6与不同浓度PEI(c_{PEI-1} = 0.001, 0.005, 0.02, 0.025, 0.03, 0.04, 0.045, 0.05, 0.055, 0.06 μmol/mL)的聚集行为; (b) 5 mmol/mL Ag_9与不同浓度丁二酸的聚集行为; (c) Ag_9与盐酸随浓度变化的聚集行为; (d) Ag_9与乙醇随浓度及体积分数变化的聚集行为

Figure 2 (Color online) Aggregation behavior of various silver clusters. (a) Aggregation behavior of 50 μmol/mL Ag_6 and different concentrations of PEI (c_{PEI-1} = 0.001, 0.005, 0.02, 0.025, 0.03, 0.04, 0.045, 0.05, 0.055, and 0.06 μmol/mL); (b) aggregation behavior of 5 mmol/mL Ag_9 and different concentrations of succinic acid; (c) aggregation behavior of Ag_9 and hydrochloric acid with changes in concentration; (d) aggregation behavior of Ag_9 and ethanol with changes in concentration and volume fraction

片(图3(a))[73].

本课题组对于金属簇形貌的调控主要集中在通过对溶剂效应、pH、模板选择等条件的控制来影响其组装的微观作用力. 通过丁二酸和盐酸来调控Ag_9水溶液的pH, 改变Ag_9外围配体的-COO^-质子程度, 从而增加银簇之间的氢键作用及π-π堆积作用, 促使以Ag_9NCs作为构筑基元形成有序的纳米结构. 通过透射电子显微镜(TEM)、扫描电子显微镜(SEM)、原子力显微镜(AFM)、激光扫描共聚焦显微镜(CLSM)等表征可以观察到纳米带(图3(b))[50]和纳米棒结构(图3(c))[51]. 选取乙醇和二甲基亚砜(DMSO)作为溶剂分别调控水溶性Ag_9NCs和Ag_6@C_{16}mim-NCs, 通过不同的电子显微镜表征也分别得到了纳米纤维(图3(d))[49]和六角形纳米片结构(图S1(a))[54]. 结果表明当c_{Ag9}=5.0 mmol/mL和V_{EtOH}=70%时, 构筑了稳定的有机凝胶, 其凝胶内部的微观结构为高度有序的纳米纤维结构; 当固定Ag_6@C_{16}mim-NCs浓度为0.3 mg/mL, 调控DMSO和水的比例, 发现当DMSO体积占比为70%时, 形成均匀的六角形纳米片结构. 另外, 本课题组[52]也探索了以高聚物PEI为模板与Ag_9NCs的共组装, 在c_{Ag_6NCs}/c_{PEI} = 50/0.055 μmol/mL的溶液中, 在静电作用的驱动下形成了纳米囊泡(图S1(b)).

2 自组装对金属簇发光的影响

目前, 荧光(PL)是金属簇最重要的性质之一, 通过自组装可以有效地限制金属核外围配体的振动和旋转, 减小非辐射跃迁, 从而实现荧光的增强. 而通过对于金属簇组装条件的控制可以实现金属簇荧光强度和荧光发射波长的调控. 常见的调控手段主要有: 组装的溶剂条件、pH环境、模板选择、温度调节、组装时间、配体选择、缺陷态处理以及表面修饰. 目前金、银、铜簇甚至是合金簇的组装诱导荧光增强都有相应的报道[32~35].

2.1 溶剂影响

溶剂可以影响金属簇的荧光性能, 通过调控溶剂的比例和类型皆可实现荧光增强及荧光发射峰的位置改变. 溶剂调控的手段, 其优点是操作简单、溶剂种类丰富, 但是溶剂调控会导致聚集体的尺寸不均匀、形貌不单一及聚集体易团聚现象. 谢建平课题组[14]通过调控不良溶剂乙醇的比例, 实现了硫醇化的金纳米团簇的聚集诱导发光(aggregation-induced emission, AIE). 他们发现不发光的低聚Au(I)-硫醇配合物会因添加不良溶剂乙醇而产生相对较强的聚集发射. 同时发现, 发光的强度和波长取决于聚集的程度, 随着不良溶剂比

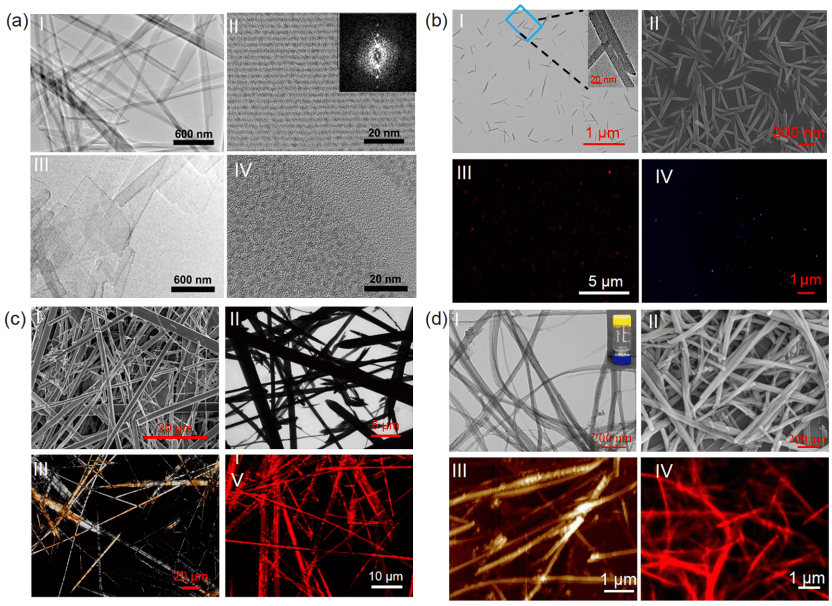


图 3 (网络版彩色)各种金属簇组装体的形貌. (a) Cu NCs自组装形成的纳米带和纳米片[73]; (b) Ag_9/HCl自组装形成的纳米棒图像; (c) Ag_9/SA自组装形成的纳米带; (d) Ag_9/乙醇自组装形成的纳米纤维

Figure 3 (Color online) The morphology of the assembly of various metal clusters. (a) The image of Cu NCs self-assembled nanoribbon and nanosheet[73]; (b) the image of Ag_9/HCl self-assembled nanorod; (c) the image of Ag_9/SA self-assembled nanoribbon; (d) the image of Ag_9/ethanol self-assembled nanofibers

例的增加, 体系除了荧光强度增加之外, 荧光发射峰位还会发生明显的蓝移(图4(a), (b)). 这主要是由于随着聚集度的增加, 相比于聚集体内亲金相互作用, 聚集体间亲金相互作用占主导地位. 因此, 聚集体的亲金相互作用中Au(I)···Au(I)距离越长会导致更高的发射能量. 本课题组[52]合成的Ag_6@C_{16}mim-NCs在良溶剂DMSO中是处于单分散状态, 没有荧光; 选取水作为不良溶剂, 调控水的比例(f_{H_2O}), 随着f_{H_2O}的增加, Ag_6@C_{16}mim-NCs发生不同程度的聚集, 从而实现了银簇的AIE(图4(c)~(d)).

此外, 金属簇自身的网络通道与不同溶剂分子之间的特定相互作用, 使得金属簇在不同溶剂中具有不同的荧光发射峰[17,76]. 王泉明课题组[77]评估了多核Au(I)复合物纳米簇在CH_2Cl_2中的PL强度比在CH_3CN或CH_3OH中的PL强度强得多. 通过改变溶剂的极性和氢键合能力, 可以控制三重态金属-配体电荷迁移(metal-to-ligand charge transfer, MLCT)状态的相对数量和纳米团簇的发射特性. 比如, 在CH_3OH中, 与纳米簇配体的芳环形成了另外一个特定位置的O-H···π, 这增强了氢键稳定的$^3MLCT_{Au}$状态的超快非辐射衰减, 并减少了$^3MLCT_{Ag}$发射态的数量. 因此, 相对于其他溶剂, Au_6Ag_2-C在CH_3OH中的PL强度较弱(图5(a), (b)). 与此同时, 他们还发现体系的发射强度大幅度提高, 半峰宽变窄. 伍志鲲课题组[78]发现$M_1Ag_{24}(SR)_{18}$纳米团簇的PL强度受溶剂的影响很大. 例如, 乙腈中Ag_{25}、Pd_1Ag_{24}和Pt_1Ag_{24}的PL强度要比甲苯、二氯甲烷、丙酮和二甲基亚砜中的PL强度高得多. 然而, Au_1Ag_{24}在二氯甲烷中的PL强度高于其他溶剂. 另外, 这4个同源纳米簇在晶体或溶液状态下的PL强度顺序是不同的, 可能是由于这些纳米簇在不同状态下的发射机理和纳米团簇-大气相互作用不同所致.

本课题组[49,53]系统研究了不同溶剂对银簇(Ag_6和Ag_9)自组装后荧光性质的影响. 结果很有趣: 通过紫外灯照射下的直观照片可以观察到, Ag_6在不同溶剂中的荧光颜色是不同的, Ag_6在DMSO中是黄色, 在甲醇和乙腈中为蓝色, 在乙二醇中为绿色(图5(c), (d)). 通过理论模拟计算可以证明Ag_6分子中存在着分子内电荷转移现象(intramolecular charge transfer, ICT), 即这种类型的分子, 其发光行为和溶剂的极性有关. 随着溶剂极性的减小, Ag_6最大发射波长发生了蓝移. 在高极性溶剂中, Ag_6分子和溶剂之间的偶极-偶极作用增强, 这促进了激发态的非辐射跃迁, 导致能量的损失. 此外, Ag_6和溶剂之间的相互作用也可能改变发光分子基态和激发态之间的能级差, 从而导致在不同溶剂中发光颜色的变化. 由于Ag_6的配体巯基烟酸在相同浓度下几乎不发光, 因此可以推断, Ag_6的发光主要来自配体向金属的电荷转移(ligand-metal charge transfer, LMCT)以及金属

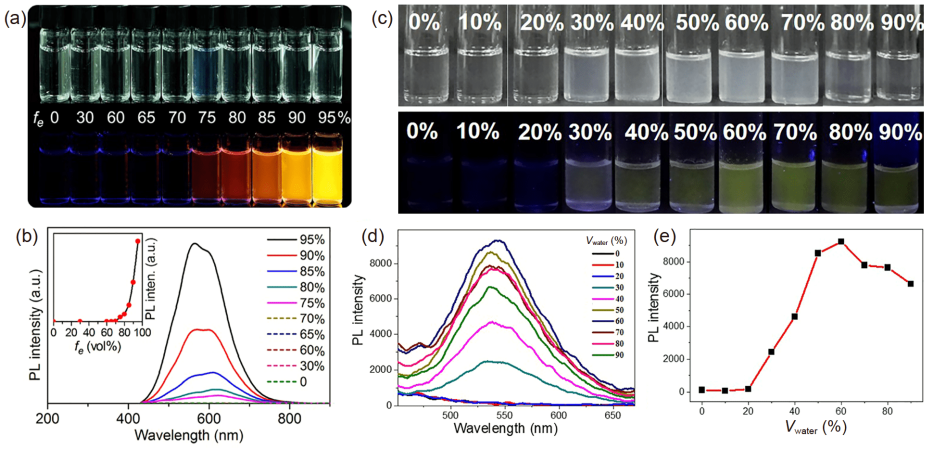


图 4 (网络版彩色)不同溶剂环境对金属纳米团簇PL性质的影响. (a) 在可见光和紫外光下在具有不同体积分数的乙醇/水混合物中的Au(I)-SR络合物的照片[14]; (b) 不同体积分数的乙醇/水混合物中的Au(I)-SR的PL光谱[14]; (c) 在可见光和紫外光下在具有不同体积分数的水/DMSO混合物中的Ag_6@C_{16}mim-NCs络合物的照片; (d) 不同体积分数的水/DMSO混合物中的Ag_6@C_{16}mim-NCs络合物的PL光谱; (e) DMSO/水溶剂中540 nm下Ag_6@C_{16}mim-NCs(c = 0.3 mg/mL)的荧光强度

Figure 4 (Color online) Effects of different solvent environments on the PL properties of metal nanoclusters. (a) Photographs of Au(I)-SR complexes in ethanol/water mixtures with different volume fractions under visible light and ultraviolet light[14]; (b) PL spectra of Au(I)-SR complexes in ethanol/water mixtures with different volume fractions[14]; (c) photographs of Ag_6@C_{16}mim-NCs complex in fractional water/DMSO mixture with different volumes under visible light and ultraviolet light; (d) PL spectra of Ag_6@C_{16}mim-NCs complex in fractional water/DMSO mixture with different volumes; (e) PL intensity of Ag_6@C_{16}mim-NCs (c = 0.3 mg/mL) at 540 nm in DMSO/water solvent

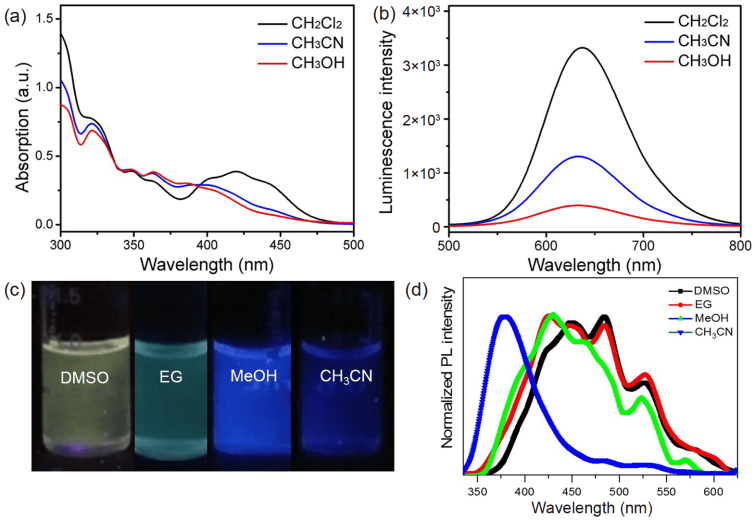


图 5 (网络版彩色)溶解在3种溶剂中的$[Au_6Ag_2(C)\text{-}(dppy)_6](BF_4)_4$的归一化稳态吸收光谱(a)和PL光谱($\lambda_{ex}$ = 350 nm)(b)[78], 以及紫外灯照射下, Ag_6在不同溶剂中的直观样品图(365 nm照射)(c)和在不同溶剂中的PL光谱(λ_{ex} = 320 nm)(d)

Figure 5 (Color online) Normalized steady-state absorption spectrum (a) and PL spectrum (λ_{ex} = 350 nm) (b) of $[Au_6Ag_2(C)\text{-}(dppy)_6](BF_4)_4$ dissolved in three solvents[78], and UV lamp irradiation below, the visual sample diagram of Ag_6 in different solvents (365 nm irradiation) (c) and the PL spectrum (d) of Ag_6 in different solvents (λ_{ex} = 320 nm)

核之间的电子转移(cluster-centered, CC). 此外, 我们研究了Ag_9在乙醇的调控下, 可以得到发强荧光的金属有机凝胶(metal-organic gels, MOGs). 为了检验当前工作中所制定策略的普遍性, 探讨了不同醇类诱导MOG形成的能力, 在检测的6种醇类溶剂中, 其中正丙醇和异丙醇能成功诱导MOG形成. 进一步分析表明, 当给定醇的介电常数约为20, 其烷基链中的碳原子数为2~3时, 凝胶化较好. 同时还检测了其他7种常见的有机溶剂, 发现*N*,*N*-二甲基甲酰胺、丙酮和四氢呋喃能够诱导Ag_9形成MOG. 研究表明, 可用于诱导Ag_9凝胶化的有机溶剂的多样性进一步拓宽了MOGs的应用范围(图S2 (a), (b)).

2.2 pH影响

金属簇的酸碱环境可以影响金属簇的组装与解组装, 从而调控金属簇荧光的产生和猝灭. 在探索金属NCs自组装动力学的基础上, 金属NCs在pH控制下可实现荧光的切换. 因此, 在pH的控制下, 可以进一步研究NCs发光增强的机理, 并制备出强荧光的NCs材料. 通过精确调控溶液pH, 可以在不同的pH范围内调控聚集体的聚集形貌及荧光强度, 并且可以实现荧光开关的切换. 但pH的调控对于金属簇的配体修饰具有一定的限制, 金属簇的外围配体需含有羧基、氨基等能够去质子化和质子化的基团.

刘锦斌课题组[43]报道了一种简便的pH调控策略, 用于制备由聚集诱导发射产生的稳定而明亮的发光水溶性蛋白质/铜纳米簇(CuNCs)杂化纳米结构. 他们使用L-半胱氨酸作为还原剂和封端剂, 合成的CuNCs在溶液中显示出可逆的pH响应聚集和分散. CuNCs在不同pH时能够形成沉淀物, 其中在pH 3.0时具有稳定的红色发射(620 nm), 但在pH<1.5或pH>4.0时却具有弱发光性. CuNCs高度可逆的pH响应特性使其在没有任何外力(例如超声处理)的情况下, 同时合成的CuNCs与蛋白质相互作用可获得水溶性蛋白质/CuNCs杂化纳米结构(图6(a)). 苏磊课题组[79]通过增加pH可以导致金(I)-硫醇盐聚合物聚集体/超分子分解. 以GSH保护的AIE型AuNCs为模型, 在pH驱动下的分解过程中, 发现了具有单分散的AuNC, 其发光强度增强, 量子产率大约为14%. pH的增加会导致粒径分布的缩小和颗粒尺寸的减小, 这表明pH的作用导致了金簇的聚集和解体. 另一方面, 随着溶液pH的增加, AuNC溶液的PL强度增强(图S3(a), (b)), 主要是因为Au(I)-硫醇化的AuNCs具有类似“订书钉”的模式, 形成稳定的结构, 限制配体的振动和旋转, 实现荧光的增强.

本课题组[50,51]发现pH可以调控Ag_9的聚集行为、形貌和荧光性质. 分别通过有机小分子酸丁二酸和无机小分子酸盐酸来调控Ag_9水溶液的pH, 可以得到在室温下发强磷光的水溶液(图6(b), (c)), 并且得到高度

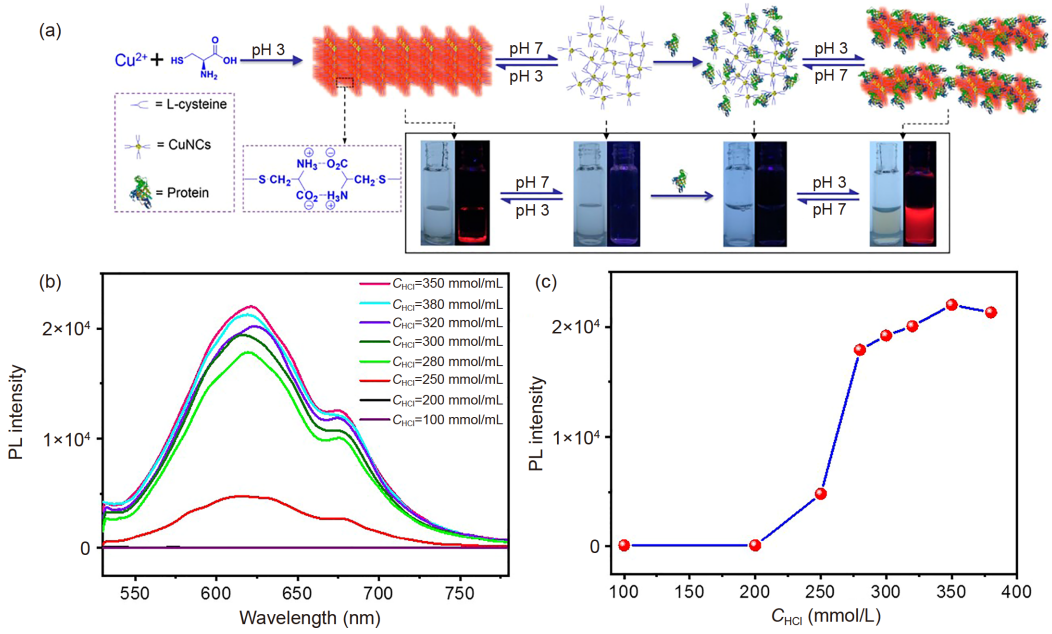


图 6 (网络版彩色)pH引导策略在水溶性蛋白/CuNCs杂化纳米结构制造中的示意图(a)[43], 500 nm处激发的不同浓度HCl水溶液的PL光谱(b)和λ= 615 nm(λ_{ex}= 500 nm)下的荧光强度(c)

Figure 6 (Color online) Schematic diagram of the pH-guided strategy in the fabrication of water-soluble protein/CuNCs hybrid nanostructures (a)[43], the PL spectra of aqueous solution with different concentrations HCl for excitation at 500 nm (b) and their fluorescence intensity at λ = 615 nm (λ_{ex} = 500 nm) (c)

有序的纳米带和纳米棒结构. Ag_9的pH聚集诱导发光主要是由于Ag核的配体(H_2mba)为−COO^-, 当减低Ag_9水溶液的pH, 使得−COO^-质子化, 而质子化的配体旋转振动受到氢键的限制, 有利于实现配体到金属的电荷转移(LMCT)或配体与金属到金属的电荷转移(LMMCT). 同时具有d^1电子结构的Ag(Ⅰ)中心之间的强同核相互作用在氢键的驱动下趋于上升, 而具有富Ag(Ⅰ)表面的相邻组分通过纳米团簇之间的强亲银相互作用可以导致Ag_9荧光的增强. 因此, Ag_9在非共价力(氢键、π-π堆积、疏水作用)作用下锁定了Ag_9的非辐射失活通道, 增加了Ag_9的自旋轨道耦合效应, 同时实现了系间穿越, 实现三重态跃迁, 得到发强磷光的银簇聚集体.

2.3 高聚物影响

聚合物诱导的聚集是提高不发光或弱发光纳米团簇PL强度的另一种有效方法[80~84]. 具体来说, 引入聚丙烯酸[80]、聚烯丙基胺盐酸盐[81]、壳聚糖[82]、聚乙烯吡咯烷酮和聚乙烯基[83]、聚(乙二醇)或聚(*N*-异丙基丙烯酰胺)[84]可使不发光或弱发光的离散金属纳米簇聚集, 然后诱导高荧光强度. 由于高聚物的稳定性及多功能性, 高聚物的诱导调控可以得到稳定的纳米团簇聚集体及多功能性团簇聚集体, 但高聚物分子量不明确, 对于体系的定性分析研究具有一定难度.

Yahia-Ammar等人[81]通过阳离子聚合物介导的AuNCs自组装成纳米颗粒(NPs), 发现聚烯丙胺盐酸盐(PAH)的浓度对荧光性质有很强的影响. 研究表明随着PAH的引入, Au-GSH-PAH荧光强度增强, 同时发射峰蓝移(~10 nm)(图7(a), (b)). 在不同的PAH浓度下进行了荧光测量, 结果表明, 用2.90 μmol/L PAH制备的自组装Au-GSH-PAH的荧光强度几乎是Au-GSH荧光强度的4倍, 同时量子产率从Au-GSH的7%提高到25%. 但对于高浓度的PAH, 荧光强度降低, 这可能是由于聚集物种的沉降所致(图7(c)).

本课题组[52]研究了Ag_6水溶液中加入支化聚乙烯亚胺(PEI-1)后的荧光光谱, 可以发现, 随着PEI-1的加入, 荧光增强了10倍(图7(d), (e)), 并且在c_{PEI1}=0.02和0.055 μmol/mL时达到了两个最大值(图7(f)). 随后又研究了固定Ag_6/PEI-1比例分别为50/0.02、50/0.055时荧光强度随体系浓度的变化规律. 对于纳米球和纳米囊泡, 临界聚集浓度(critical aggregation concentration, CAC)均为c_{Ag_6}=5 μmol/L. 有趣的是, 在两者浓度达到

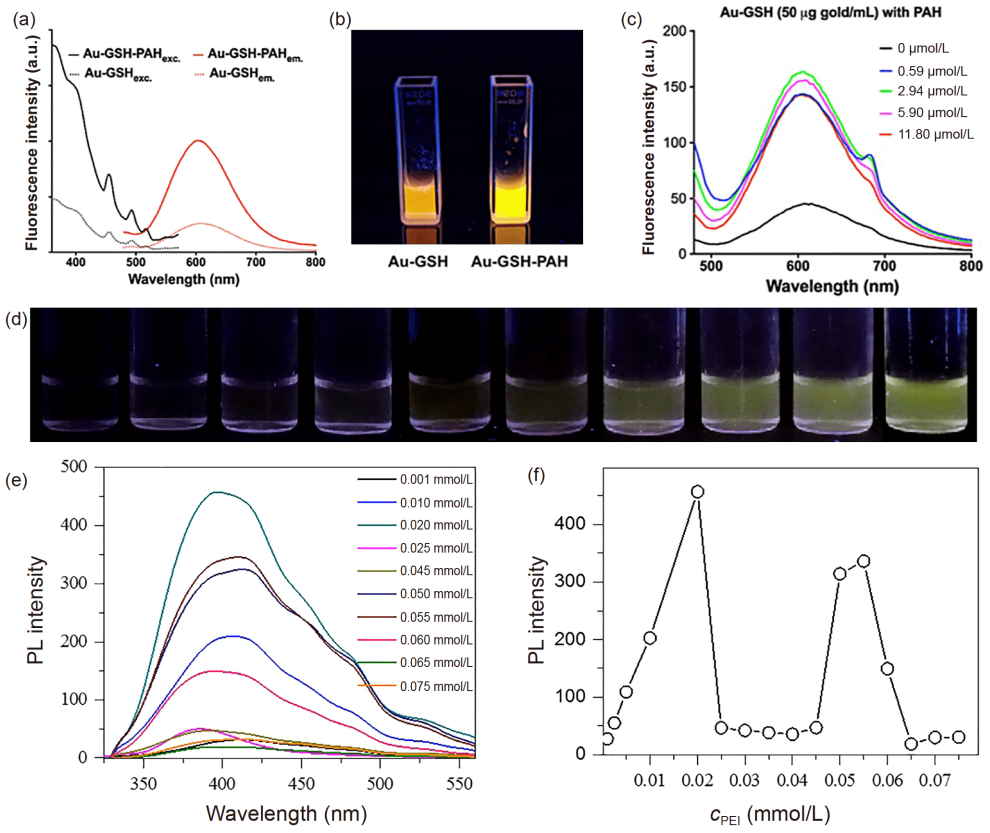


图 7 (网络版彩色)高聚物的类型和浓度对金属纳米团簇PL性质的影响. (a) Au-GSH(虚线)和Au-GSH-PAH(实线)溶胶的激发和发射光谱; Au-GSH和Au-GSH-PAH溶液在紫外线照射(b)和荧光发射谱(λ_{ex} = 450 nm)(c)[81]; (d) 手提式紫外灯下观察到的, 固定Ag_6/PEI-1比例为50/0.02, 改变c_{Ag_6}=4、6、8、10、20、40、60、80、100、200 μmol/mL的样品直观图; 固定c_{Ag_6}=50 μmol/mL, 不同PEI-1浓度下的荧光光谱图(e)和在λ = 420 nm处的荧光强度图(λ_{ex} = 300 nm)(f)

Figure 7 (Color online) Effects of polymer type and concentration on the PL properties of metal nanoclusters. (a) Excitation and emission spectra of Au-GSH (dashed lines) and Au-GSH-PAH (solid lines) sols; Au-GSH and Au-GSH-PAH solutions under UV illumination (b) and fluorescence emission (λ_{ex}=450 nm) (c)[81]; (d) observed under a portable UV lamp, the ratio of Ag_6/PEI-1 is fixed to 50/0.02, and the c_{Ag_6} = 4, 6, 8, 10, 20, 40, 60, 80, 100, 200 μmol/mL sample visual diagram; fixed c_{Ag_6}=50 μmol/mL; fluorescence spectra at different concentrations of PEI-1 (e) and fluorescence intensity at λ = 420 nm (λ_{ex} = 300 nm) (f)

其CAC后, 纳米球荧光强度的斜率比纳米囊泡的大, 这说明, 纳米球的AIE能力要强于纳米囊泡. 可以推测, 荧光增强的原因是Ag_6/PEI-1之间的静电作用, 形成了紧密有序的组装体, 这限制了Ag_6配体的分子内振动, 阻断了非辐射方式的能量损耗, 增大了辐射跃迁几率. 此外, 纳米球中的长寿命组分高于纳米囊泡中的组分, 这也说明Ag_6在纳米球聚集体中排布更紧密.

3 金属簇组装体的应用

与传统的荧光材料(如有机荧光材料、量子点或荧光蛋白)相比, 荧光金属纳米团簇及其组装体具有前所未有的吸引力和优势. 例如, 尽管有机荧光团存在于各种各样的化合物中, 但是它们易于光致漂白[85]. 量子点虽然具有荧光可调性, 并具有良好的光稳定性, 但是它们相对较大的尺寸阻碍了它们的应用[86~89]. 而荧光贵金属纳米团簇虽然已经在化学传感[90~96]、生物领域[97~102]、催化[103]及光转换材料[34]得到了一定的应用, 但是其金属纳米团簇自身的稳定性比较差、且荧光比较弱. 而纳米团簇的组装体可以很好地解决上述缺点, 团簇聚集体具有很强的PL强度、良好的光稳定性、宽的发射波长, 这使其成为用于化学传感、生物领域、催化及光转换材料的新型荧光团.

3.1 化学传感

由于荧光金属纳米簇具有简单性、敏感性和特异性, 因此可作为荧光探针应用于离子检测、生物分子

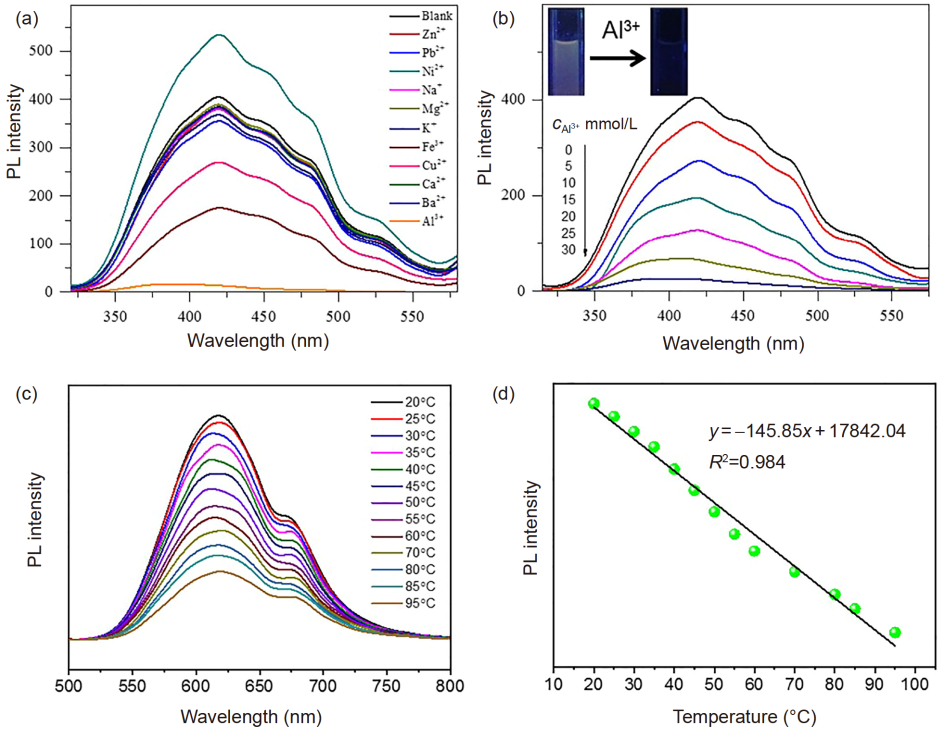


图 8 (网络版彩色)向纳米囊泡中加入金属离子后的荧光光谱(c_{metal}=50 μmol/mL) (a)、向荧光囊泡中加入不同浓度的Al^{3+}后的荧光光谱(b)、不同温度下样品的PL光谱(c)和相应的发光强度(λ_{ex}=470 nm, λ_{em}=625 nm)(d)

Figure 8 (Color online) Fluorescence spectra of nanovesicles after adding metal ions (c_{metal} = 50 μmol/mL) (a), fluorescence spectra of fluorescent vesicles after adding different concentrations of Al^{3+} (b); PL spectra of samples at different temperatures (c), and corresponding luminous intensity at different temperatures (λ_{ex}=470 nm, λ_{em}=625 nm) (d)

检测及温度检测等方面. 本课题组通过自组装策略得到Ag_6的组装体用于快速有效地检测Al^{3+}(图8(a), (b))和生物小分子精氨酸(图4S(a), (b)), 且存在很好的选择性和灵敏度. 由于金属簇在低温环境下, 可以实现强磷光的发射, 因此可以实现低温范围内的温度检测. 孙頔课题组[104~106]报道了大量不同类型银簇作为温度检测来实现低温的检测. 然而, 金属簇实现常温(20~100°C)检测的报道相对较少, 主要是由于合成的金属簇在室温条件下没有荧光或者荧光较弱. 而本课题组[49~51]通过自组装策略实现金属簇在室温条件下的荧光增强, 可以作为温度检测器, 实现常温范围内(20~100°C)的温度检测(图8(c), (d)).

3.2 光转换材料

金属纳米团簇由于其特殊的性质, 包括HOMO-LUMO电子跃迁、依赖尺寸的荧光发射和强光吸收, 被认为是发光二极管(LED)中最具竞争力的颜色转换材料之一[34]. 但未组装的金属纳米碳化物的发射颜色单一、发射稳定性和强度低, 严重限制了其广泛应用. 受“AIE”概念的启发, 高度有序的金属簇组装体打开了解决这些问题的大门. 金属簇自组装后, 提高了金属簇组件的发射稳定性和强度, 可以作为优异的颜色转换材料. 但目前金属簇组装体作为光转换材料的报道很少. 张皓课题组[34]报道了利用二维CuNC自组装作为LED的颜色转换材料, 制备了发不同颜色的LED器件. 本课题组[50]也通过自组装策略得到Ag_9组装体, 组装体冻干成粉末后具有强烈的橙红色荧光, 可以作为优异的光转换材料来制取发白光的LED. 为了评价Ag_9组装体粉末作为橙红色荧光粉的潜在应用价值, 将组装体粉末与商用蓝色荧光粉和商用绿色荧光粉机械混合, 分别制备了制造蓝色、绿色和黄色的LED器件(图9(a)~(c)、(f)~(h)), 及以组装体粉末、蓝色荧光粉和绿色荧光粉按照10:5:1的进料比制备了色坐标为(0.33, 0.33)的白光发光二极管(WLED)原型白粉(图9(d), (e), (i)). 由此可见, Ag_9组装体可以用于光转换材料以拓宽LED的应用领域.

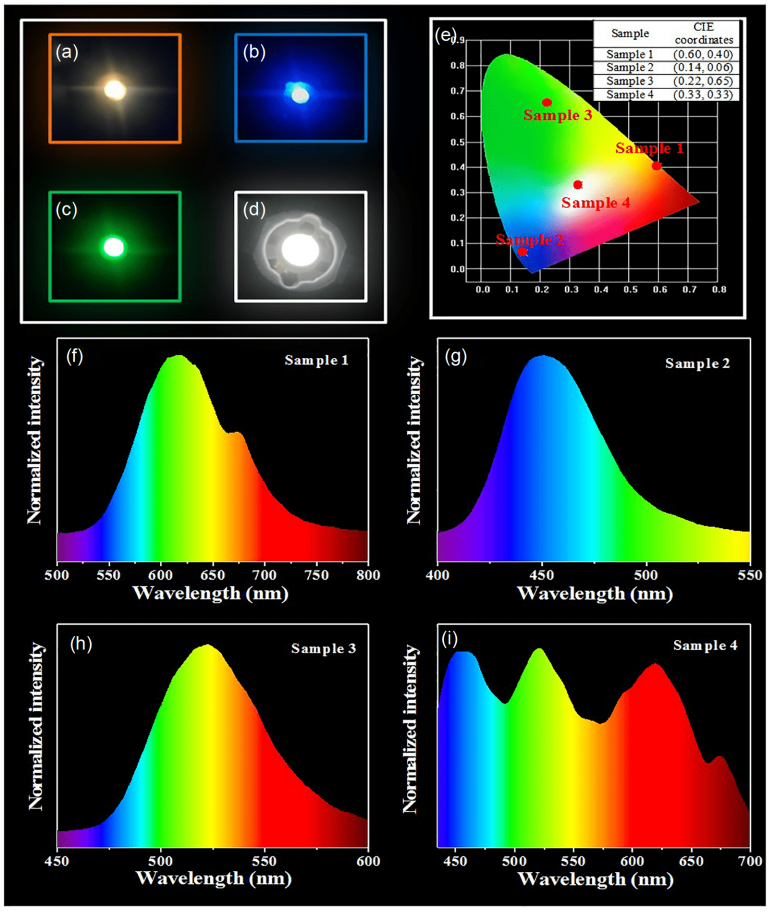


图 9 (网络版彩色)组装体、蓝色荧光粉、绿色荧光粉及三者混合LED的荧光图像(a)~(d)、发射光谱(f)~(i)和相对应的CIE色度坐标(e)

Figure 9 (Color online) The fluorescent images (a)–(d), corresponding emission spectra (f)–(i) and CIE chromaticity coordinates (e) of the LED in the assembly, blue phosphor, green phosphor, and the mixture of the blue phosphor, green phosphor and assembly

3.3 生物诊疗和催化材料

目前对于金属团簇在生物催化方面已经有较多的报道, 而对于金属团簇的组装体在生物诊疗和催化等方面, 正处于研究的热门领域. 任劲松课题组[107]通过自组装AuNCs并使用FITC修饰的透明质酸(HA)来对高活性氧(hROS)进行比例传感来制备纳米探针. 该纳米探针在活细胞hROS成像中表现了出色的性能(图10(a)). 谢建平课题组[45]制备了光稳定的发光金纳米簇(L-AuNC)作为生物相容性诊断探针, 该探针与叶酸(FA)修饰的pH响应两亲聚合物系统共轭, 可控制药物释放. 与此同时, 金属团簇组装体在催化领域也具备潜在的应用. Sourov Chandra课题组[15]研究表明了金纳米团簇框架(gold nanocluster framework, GNCF)可以承担高的光催化活性, 可以对UV和可见光下的亚甲基蓝(MB)降解进行初步测试. 结果表明, 在GNCF-300的存在下, 在UV辐射(350 nm波长)下, MB的完全降解在5.5 min内发生. 相比之下, 在类似条件下, 金纳米团簇(GNC)需要112 min. 相反, 在对照实验中, 在没有任何催化剂的情况下, 降解时间超过140 min. 降解速率按照GNCF-300>GNCF-200>GNCF-100>GNC的顺序排列(图10(b)). GNCF的光催化活性增加归因于其三维(3D)结构, 染料分子在其表面和内部的吸附增强, 这将促进GNCF对水中单个GNC的排他性催化活性. 而且, 与GNC本身相比, GNCF对可见光驱动的光活性具有很高的功效. 图10(c)表示在蓝光(455 nm)照射下, 光活性来自蓝光的吸收以及高催化网络和表面, 通过使用GNCF-300作为催化剂, 仅需30 min即可完全降解染料. 相比之下, GNC花费了几天时间才能完成降解过程, 而在没有催化剂的情况下, MB的完全降解不会在观察到的几天内发生.

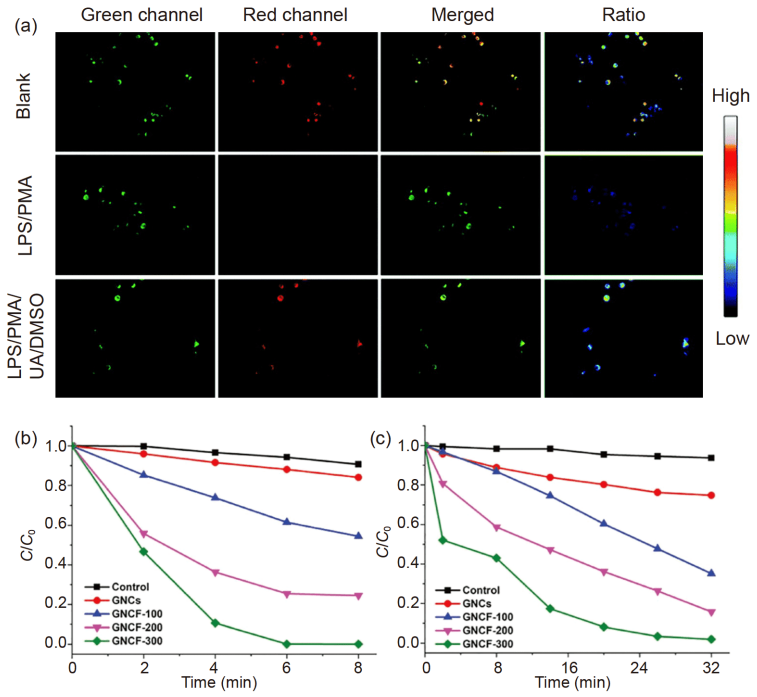


图 10 (网络版彩色)FHAuNCs处理的RAW264.7细胞的荧光图像[107](a)以及350 nm(b)和455 nm(c)波长激发的GNC、GNCF和不存在催化剂的情况下MB的降解速率[15]

Figure 10 (Color online) Fluorescence images of RAW264.7 cells treated with FHAuNCs[106] (a), and the rate of degradations of MB in presence of GNCs, GNCFs, and absence of a catalyst, excited at 350 nm (b) and 455 nm (c) wavelengths[15]

4 结语与展望

受“聚集诱导发射”和“超分子化学”概念的启发, 本课题组总结了原子精确纳米团簇通过自组装策略可以实现金属团簇聚集体结构的调控及荧光性质的调控. 通过自组装策略, 在不同非共价键作用的驱动下, 可以有效地限制纳米团簇配体的振动和旋转, 从而实现金属纳米团簇组装体聚集诱导发光. 常见的调控手段为溶剂调控、pH调控或将纳米团簇作为构筑基元与其他物质(小分子、高分子材料)进行的自组装, 并通过自组装策略有效地提高了金属簇组装体的发射稳定性和强度的工作. 通过这些进展以及对PL机理更深入的了解, 预计荧光纳米团簇将成为荧光团类别中一个有希望的新成员, 并影响化学传感、光转换材料、生物成像、催化等领域. 尽管在调控纳米簇荧光特性方面取得了显著进展, 金属纳米团簇的自组装仍有很大的发展空间. 最后, 我们相信, 通过对金属簇超分子自组装的研究必将产生新的智能纳米材料, 为环境、生物和人类健康相关问题提供可能的解决方案.

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补充材料

图S1 Ag_6@C_{16}mim-NCs自组装形成的六边形纳米片和Ag_6/PEI自组装形成的纳米囊泡
图S2 不同类型溶剂和混合溶剂中的Ag_9照片
图S3 AuNC溶液的DLS数据和pH对AIE型AuNCs PL强度的影响
图S4 Ag_6@C_{16}mim-NCs对Arg的选择性和Ag_6@C_{16}mim-NCs溶液的发光光谱

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Summary for “金属纳米团簇的超分子自组装及其应用”

Supramolecular self-assembly and application of metal clusters

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Metal nanoclusters (NCs) are relatively stable aggregates composed of several to several thousand metal atoms through physical or chemical bonding, and their size is generally less than 3 nm. It has excellent quantum size effect and has outstanding applications in many fields such as optics, electricity, magnetism, catalysis, chirality, etc. However, NCs have poor optical properties at room temperature, which limits their further applications in the optical field. Therefore, the assembly of metal clusters with different types of molecular materials is driven by non-covalent bonds inspired by the concepts of “aggregation-induced emission” (AIE) and “supramolecular chemistry”, which can not only regulate the optical properties of metal clusters, but also can realize multi-functional coordination. As an important category of supramolecular chemistry, self-assembly provides a way to construct ordered structures from the bottom up. Self-assembly mainly uses non-covalent interactions to precisely control the specific structure of the building element to obtain functionalized micro-nano materials. Supramolecular self-assembly is one of the hot research fields in the chemical industry. It has been widely used in biomedicine, environment, sensing, optoelectronic devices and catalysis due to its simple operation and easy availability of raw materials. Herein, firstly, this paper introduces the effect of self-assembly on the assembly structure in detail combining the research work of this research group and related research on the self-assembly of design metal clusters at home and abroad. The research involving the aggregation morphology and morphology of metal nanoclusters is currently in its infancy in the world, and is a relatively popular research topic. Therefore, the self-assembly strategy to achieve the control of the aggregation morphology and morphology of metal nanoclusters can enrich the research field of self-assembly and realize the functionalization of metal nanoclusters. Secondly, fluorescence is one of the most important properties of metal clusters. Compared with traditional PL materials, the quantum yield (QY) of metal nanoclusters is relatively low. In addition, the proportion of fluorescent metal nanoclusters is also very low. Therefore, precise control of the metal composition and clearly defined surface chemistry factors not only provide a basis for a firm understanding of the structure and fluorescence, but also provide a method for the design and preparation of new nanoclusters with PL enhancement and adjustable emission wavelength. Hence, the vibration and rotation of the ligands around the metal core can be effectively restricted, and non-radiative transitions can be reduced, thereby achieving enhanced fluorescence through self-assembly. The fluorescence intensity and emission wavelength of the metal clusters can be controlled by controlling the assembly conditions of the metal clusters. The effect of self-assembly on the luminescence of metal clusters is commonly regulated by solvent regulation, pH, and co-assembly of other molecules to obtain highly stable luminescent clusters. In addition, the research progress in the application of metal cluster assembly and other aspects are summarized. Although precious metal nanoclusters have been used in chemical sensing, biological fields, catalysis and light conversion materials, the stability of the metal nanoclusters itself is relatively poor and the fluorescence is relatively weak. The assembly of nanoclusters can well solve the above shortcomings. The cluster aggregates have strong PL intensity, good light stability, and wide emission wavelength, which makes it a new type of fluorophore used in chemical sensing, biological fields, catalysis and light conversion materials. Finally, the improved scope and future prospects of the new nanoclusters are summarized and emphasized. Our review is expected to open up new horizons for these scientists to effectively control the functional properties of nanoclusters.

metal nanoclusters, self-assembly, aggregation-induced emission, assembly structure

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