Editorial

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Photoluminescent gold nanomaterials as sensitive probes

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Jinshun Cang,[1] Huan-Tsung Chang[2,3]
[1]Department of Chemical Engineering, Yancheng Institute of Industry Technology, China
[2]Department of Chemistry, National Taiwan University, Taiwan
[3]Department of Chemistry, Chung Yuan Christian University, Taiwan

Correspondence: Huan Tsung Chang, Department of Chemistry, National Taiwan University, Taipei, 10617, Taiwan, Email changht@ntu.edu.tw

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Editorial

Photoluminescent gold nanomaterials have become interesting sensing materials because of their ease in preparation and conjugation, large Stokes shift, long lifetime, and biocompatibility.[1–3] They are often called gold nanodots (Au NDs) or gold nanoclusters (Ag NCs), with sizes usually smaller than 2nm; Au NCs are commonly reffered to the one having less than 30Au atoms per cluster. The molecular-like optical properties (photoluminescence) of Au NDs and NCs are highly dependent on the size of Au core and the number of Au atoms per templates, respectively.[4,5] The Au complexe on the surface of Au core and its surface density affect the stability and optical properties of Au NDs, while the nature and size of the template affect that of Au NCs. Thus, the optical properties of AuNDs/NCs can be easily tuned by selecting suitable templates or ligands and controlling their molar concentration ratio to Au^{3+}. Their emission wavelengths are usually longer than 600nm when excited with a UV light (commonly at 365nm). With a support of having a large Stoke shift and long lifetime, it is believed that their photoluminescen is mainly through the ligand-metal charge transfer transition (LMCT) or ligand-to-metal-metal charge transfer transition (LMMCT).

Au NDs can be prepared from etching of small Au nanoparticles (<3 nm in diameter) by thiol compounds such as 11-mercaptoundecanoic acid (11-MUA) under alkaline conditions.[6] On the other hand, proteins such as bovine serum albumin (BSA), lysozyme, and horseradish peroxidase as a template and reducing agent are commonly used to prepare stable Au NCs.[7] The reducing ability of these proteins mainly comes from their tyrosine residues that can reduce Au^{3+} at pH values>10.0. Although Au NCs can also be prepared using thiol compounds such as glutathione as a reducing agent, they are usually less stable and have weaker photoluminescence intensity than that of BSA-Au NCs. Protein-Au NCs are more stable than 11-MUA -Au NDs against photo irradiation and salt induced quenching, mainly because large protein molecule protect Au core more efficiently, which minimizes the access of quenchers such as oxygen to the core. While, large amounts (usually>several mM) of expensive proteins are required to prepare stable and bright Au NCs.

Au NDs and NCs have been employed for sensing of various analytes such as metal ions, anions and proteins, as well as for cell imaging. 11-MUA-Au NDs were used for quantitation of Hg^{2+} using 2,6-pyridinedicarboxylic acid (PDCA) as a masking agent to prevent the interference from Pb^{2+} and Cd^{2+}, with limit of detection (LOD) 5 nM.[6] In the presence of Hg^{2+}, photoluminescence quenching of 11-MUA-Au NDs occurs, due to the Au-Hg aurophilic interaction and aggregation of the Au NDs through the interaction of Hg^{2+} ions with the carboxylate groups present on the surfaces of the 11-MUA-Au NDs. To minimize salt quenching, poly(N-isopropylacrylamide) microgels (PNIPAM MGs) containing 11-MUA-Au NDs were prepared and used for quantitation of Hg^{2+} in the presence of 500mM NaCl, with LOD of 1.7 nM.[8] Because H_2O_2 can oxidize the Au core of 11-MUA-Au NDs, leading to photoluminescence quenching, the Au NDs is selective for quantitation of glucose when using glucose oxidase to catalyze the reaction of glucose and oxygen.[9] 11-MUA-Au NDs conjugated with platelet-derived growth factors (PDGF) were used for quantitation of PDGF receptor, with great selectivity and sensitivity (LOD of 0.25nM).[10] Au NDs prepared from Au nanoparticles using different etching agents have been used for quantiation of various analytes, including S^{2-}, NO_2^-, concanavalin A (*Con A*), Phospholipase C, and so on.[11–14] Based on analyte-induced PL quenching, lysozyme-Au NCs were used for quantitation of Hg^{2+}, with LODs of 10nM.[15]

Through core-etching induced PL quenching, BSA-Au NCs were used for the detection of cyanide with a LOD of 200nM.[16] BSA-Au NCs were used for determination of the activity of trypsin, with LOD of 86pM.[17] Through digestion of BSA by trypsin, the BSA shell was destroyed, leading to PL quenching as a result of oxidation of Au NCs by oxygen. To specifically target cancer cells, BSA-Au NCs can be conjugated with recognition elements such as small ligands and antibodies. For example, folic acid-BSA-Au NCs are specific toward cancer cells over-expressed folate receptors.[18] A ratiometric probe using BSA-Au/Ce NCs was developed for monitoring the pH values of HeLa cells.[19] The BSA-Au/Ce NCs possess dual emission bands at 410 and 650nm when excited at 325 nm, which separately correspond to the BSA-Ce complexes and Au NCs. The PL at 410 nm is pH-dependent while that at 650 nm is pH-insensitive. Because the red fluorescence of BSA-Au/Ce NCs is quenched by H_2O_2, the NCs with glucose oxidase were used for quantitation of glucose.[20]

Although biocompatible Au NCs and NDs have shown their potential for sensing of various analytes and for cell imaging, their quantum yields are generally lower than that of quantum dots[21] and carbon dots.[22] To provide specifiity toward tumors, strategies for improved stability and affinity through functionaliztion of Au NDs and NCs with biopolymers, synthetic poymers, small ligands are still highly demanded. It is also interesting to prepare theranostic nanomaterials (therapeutic drugs and diagnostic agents into one single platform) using other reporters and drugs to conjugate AuNCs/NDs.[23] With advances in nanotechnology, it is our belief that more stable and brighter Au NCs/NDs will soon be realized. They may have great potential for cell tracking and for single molecule detection.

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Conflict of interest

The author declares no conflict of interest.

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