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厦门大学

博　士　学　位　论　文

Mn 掺杂 ZnS 量子点室温磷光传感体系的构建及应用

Development of Room Temperature Phosphorescence Sensing System Based on Mn-doped ZnS Quantum Dots and Their Analytical Applications

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缩略语表

缩写	全称	中文
GSH	L-glutathione	谷胱甘肽
GSH-Mn-ZnS	GSH capped Mn-doped ZnS	谷胱甘肽修饰 Mn 掺杂 ZnS
Mn-ZnS	Mn-doped ZnS	Mn 掺杂 ZnS
QDs	Quantum dots	量子点
RTP	Room-temperature phosphorescence	室温磷光
ms	millisecond	毫秒
FRET	Fluorescence resonance energy transfer	荧光共振能量转移
PET	Photoinduced energy transfer	光诱导能量转移
ICP-MS	Inductively coupled plasma mass spectrometry	电感耦合等离子体质谱
HPLC	High performance liquid chromatography	高效液相色谱
MPA	Mercaptopropionic acid	巯基丙酸
HRTEM	High resolution transmission electron microscopy	高分辨率透射电子显微镜
XRD	X-ray diffraction	X 射线衍射
FTIR	Fourier transform infrared spectroscopy	傅里叶变换红外光谱

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中文摘要

量子点具有尺寸可控、发射光谱可调、光稳定性高等优点，已引起化学、物理、材料科学、环境科学等领域研究者的广泛关注。量子点的光学性质极易受到量子点表面物理和化学性质的微小变化影响，基于此，量子点被广泛应用于各种化学物质的检测。其中，室温磷光量子点因其无需除氧、磷光寿命长、可有效避免自发荧光和散射光干扰等特性，已成为当前研究的一大热点。将室温磷光量子点应用于分析检测领域，具有十分重要的意义。因此，本论文拟合成室温磷光量子点，探索其在环境污染物和生物医药检测中的应用，并讨论相关的检测机理，主要研究内容和结果包括：

(1) 建立基于谷胱甘肽(L-glutathione, GSH)修饰 Mn 掺杂 ZnS(GSH capped Mn-doped ZnS, GSH-Mn-ZnS)量子点检测 Pb^{2+}的室温磷光法。在最佳实验条件下，所建方法检测 Pb^{2+}的线性范围为 1.0-100 $\mu g\cdot L^{-1}$，检出限(3σ)为 0.45 $\mu g\cdot L^{-1}$。将该方法应用于河水和湖水中 Pb^{2+}的检测，加标回收率为 97.4%-104.0%，所得检测结果和 ICP-MS 法检测结果无显著差异(P>0.05)。

(2) 将磷酸盐和 Ce^{3+}的高度亲和性应用于 Mn-ZnS 量子点体系，建立了磷酸盐高选择性室温磷光检测方法。Ce^{3+}通过静电相互作用将 Mn-ZnS 量子点聚集，聚集的量子点导致局部电场增强，进而诱导 Mn-ZnS 量子点产生更有效的激发，从而导致磷光强度增强。加入磷酸盐后，磷酸盐和量子点竞争结合 Ce^{3+}，使得 Ce^{3+}从量子点表面脱离，Mn-ZnS 量子点解聚，磷光强度下降。在最佳实验条件下，所建方法检测磷酸盐的线性范围为 0.1-10.0 $\mu mol\cdot L^{-1}$，检出限(3σ)为 0.072 $\mu mol\cdot L^{-1}$。将该方法应用于湖水中磷酸盐的检测，加标回收率为 103.7%-104.4%，所得检测结果和营养盐分析仪检测结果无显著差异(P>0.05)。

(3) 利用 SeO_3^{2-}和 GSH 的反应产物 HSe^-高效猝灭 Mn-ZnS 量子点磷光，建立了一种快速、简便、高选择性的定量检测 SeO_3^{2-}的方法。在最佳实验条件下，所建方法检测 SeO_3^{2-}的线性范围为 0.1-5.0 $\mu mol\cdot L^{-1}$，检出限(3σ)为 0.085 $\mu mol\cdot L^{-1}$，加标回收率为 94.7%-105.5%。将本方法应用于亚硒酸钠药品中亚硒酸钠的检测，

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检测结果与药品标签的含量相吻合。

(4) 将组氨酸和 Ni^{2+}的高度亲和性应用于 Mn-ZnS 量子点体系，建立了组氨酸“Turn off-on”室温磷光检测方法。Ni^{2+}通过静电相互作用吸附在 Mn-ZnS 量子点表面，量子点发生光诱导电子转移，磷光猝灭。加入组氨酸后，组氨酸和量子点竞争络合 Ni^{2+}，使得 Ni^{2+}从量子点表面脱离，光诱导电子转移失效，磷光恢复。在最佳实验条件下，所建方法检测组氨酸的线性范围为 0.1-10.0 $\mu mol\cdot L^{-1}$，检出限(3σ)为 0.078 $\mu mol\cdot L^{-1}$。将该方法应用于尿样中组氨酸的检测，加标回收率为 97.0%-104.5%。

关键词：Mn 掺杂 ZnS(Mn-ZnS)量子点；室温磷光；传感器；离子；小分子

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Abstract

Quantum dots (QDs) received great interest for their distinct advantages, such as narrow and symmetric emission with tunable colors, broad and strong absorption, reasonable stability, and solution processibility. The optical properties of the QDs are highly susceptible to the small physical or chemical changes of the QDs surface. Based on these, QDs are widely applied in the detection of various kinds of chemicals. The room-temperature phosphorescence (RTP) QDs do not need the use of dexoidants and other inducers, and allow detecting analytes without interference from autofluorescence and scattering light. These features of RTP QDs offer many opportunities for research workers to develop RTP detection. The purpose of this dissertation is to explore the application of RTP QDs in the detection environmental pollutants and biological medicine. The main contents are summarized as follows:

(1) The room-temperature phosphorescence (RTP) of glutathione-capped Mn-doped ZnS quantum dots (GSH-Mn-ZnS QDs) was effectively quenched by the addition of Pb^{2+}. A simple and sensitive RTP method for Pb^{2+} detection based on the quenching effect was developed. Under the optimal experimental conditions, a good linear correlation was obtained for Pb^{2+} over a concentration range from 1.0 to 100 $\mu g \cdot L^{-1}$, and the detection limit (3σ) was 0.45 $\mu g \cdot L^{-1}$. The established method has been successfully applied for the determination of Pb^{2+} in water samples without complicated sample pretreatment with the recoveries in the range of 97.4%-104.0%. The analytical results for Pb^{2+} in water samples obtained by the proposed method were in good agreement with those obtained by the standard ICP-MS method (P>0.05).

(2) RTP detection for phosphate based on Ce^{3+}-modulated Mn-ZnS QDs by taking the advantages of this well-known phosphate-Ce^{3+} affinity pair and RTP QDs. The RTP of Mn-ZnS QDs can be enhanced by Ce^{3+} due to the binding of Ce^{3+} to the

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MPA on the surface of the QDs. The high affinity of phosphate to Ce^{3+} enables Ce^{3+} to be dissociated from the surface of Mn-ZnS QDs, thereby recovering the RTP of Mn-ZnS QDs. Under the optimal experimental conditions, the developed method gives excellent selectivity for phosphate with the detection limit (3σ) of 0.072 $\mu mol\cdot L^{-1}$. The developed method was applied to the detection of phosphate in water samples with recoveries from 103.7%-104.4%. No significant correlation between the results of the proposed method and nutrient analyzer ($P>0.05$).

(3) The RTP of Mn-doped ZnS quantum dots (Mn-ZnS QDs) was quenched by the addition of selenite in the presence of glutathione. The quenching of the RTP emission of Mn-ZnS QDs was due to HSe^{-} ions which was the reaction product of selenite and glutathione. Based on the above finding, a simple, rapid, sensitive probe for selective detection of selenite was successfully fabricated. Under the optimal experimental conditions, a linear relationship was obtained covering the linear range of 0.1-5.0 $\mu mol\cdot L^{-1}$ and the detection limit (3σ) was 0.085 $\mu mol\cdot L^{-1}$. The proposed method was successfully applied for the determination of selenite in sodium selenite samples with satisfactory results.

(4) Turn off-on RTP detection for histidine based on Ni^{2+}-modulated GSH-Mn-ZnS QDs by taking the advantages of this well-known Ni^{2+}-histidine affinity pair. The RTP of GSH-Mn-ZnS QDs was effectively quenched by Ni^{2+} due to the binding of Ni^{2+} to the GSH and the electron transfer from the photoexcited QDs to Ni^{2+}. Addition of histidine restored the RTP of GSH-Mn-ZnS QDs due to the competitive binding of histidine with Ni^{2+} from the surface of GSH-Mn-ZnS QDs. Selective detection of histidine with the detection limit (3σ) of 0.078 $\mu mol\cdot L^{-1}$ and a linear rang of 0.1-10.0 $\mu mol\cdot L^{-1}$. The developed method was applied to the detection of histidine in human urine samples with recoveries from 97.0%-104.5%.

Keyword: Mn-doped ZnS quantum dots (Mn-ZnS QDs); Room-temperature phosphorescence (RTP); Sensor; Ion; Small molecule

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