

埃洛石表面锚定四苯乙烯构建铜离子响应型纳米复合材料

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摘 要: 埃洛石纳米管(HNTs)是一种具有管状结构的天然纳米材料, 具有水分散性良好、成本低廉、低毒性、易于实现表面改性等优点。本工作以 HNTs 为基材, 通过表面改性将四苯乙烯和香豆素基团引入其表面结构中, 制备具有 Cu(II)离子响应性能的纳米复合材料(HNTs-TPE-Cou)。红外光谱、X 射线光电子能谱、固体核磁、热重分析和透射电镜等测试表明产物结构与预期相符。HNTs-TPE-Cou 水分散液在 365 nm 紫外光激发下, 于 560 nm 处出现荧光发射峰。Cu(II)离子与 HNTs-TPE-Cou 的螯合作用导致水分散液荧光迅速淬灭, 以此实现了水中 Cu(II)离子的快速检测, 且显示出良好的特异性、精确性和重复性。通过进一步将 HNTs-TPE-Cou 与多孔材料复合, 制备凝胶状分离柱, 并将其成功应用于水中 Cu(II)离子的同步检测分离。上述埃洛石纳米管改性产物为水中重金属离子的同步检测分离提供了一种有益尝试。

关键词: 埃洛石纳米管; 表面改性; 铜离子; 四苯乙烯

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近年来, 重金属的残留问题引起了社会的广泛关注^[1]。重金属的过度蓄积将直接对动物和人类造成严重的健康危害^[2]。Cu(II)离子是常见的重金属污染物之一^[3], 与阿尔茨海默氏症、帕金森氏症、门克斯病和威尔逊氏病等多种疾病的发病直接相关^[4]。目前, 已经建立的有关 Cu(II)离子的检测分析方法, 主要包括原子吸收光谱法(AAS)、电感耦合等离子体发射光谱仪(ICP-OES)、等离子体质谱仪(ICP-MS)、全反射 X 射线荧光光谱仪(TXRF)、电化学工作站等^[5-6]。上述方法应用于检测 Cu(II)离子时, 虽具有较高的准确性, 但难以摆脱对耗能型设备的依赖, 也难以满足野外水质监测等场景下非耗能、实时、快速、裸眼可视和同步分离的相关需求。有鉴于此, 开发一种能够同时检测和去除水中 Cu(II)离子的智能材料将为解决上述问题提供一种有效途径。

埃洛石纳米管(HNTs)是一种天然的中空铝硅酸盐矿物, 其化学成分类似于高岭石 $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}]^{[7-8]}$ 。较大的空腔体积和表面电荷作用,

使 HNTs 呈现优异的水分散性^[9]。HNTs 还具有低成本^[10]、环境友好^[11]、生物相容性良好^[12]、稳定性高^[13]和易于表面改性等优点^[14], 使其在环境保护^[15]、催化^[16]、生物医学材料^[17]和传感器^[18]等领域呈现良好的应用前景。研究表明, 将含有平面共轭基团的生色团固定在 HNTs 表面, 可以有效地抑制聚集引起的荧光淬灭(ACQ)效应^[19], 这使得 HNTs 基纳米复合材料有望在水中具有良好的分散性和荧光性能。有鉴于此, 将 Cu(II)离子敏感型生色团锚定在 HNTs 表面, 对开发水相适用的 Cu(II)离子同步分离检测型材料具有积极意义。

本工作通过对 HNTs 的表面改性, 将四苯乙烯(TPE)基团引入胺基化埃洛石纳米管(HNTs-NH₂)表面结构中, 得四苯乙烯改性产物(HNTs-TPE-NH₂)。然后利用胺醛缩合反应, 将香豆素基团引入 HNTs-TPE-NH₂ 结构中, 得产物纳米复合材料(HNTs-TPE-Cou)。Cu(II)离子的特殊电子构型使其能够与 HNTs-TPE-Cou 结构中的 N、O 等原子进行配位或螯合^[20], 从而诱导 HNTs-TPE-Cou 荧光性

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能发生变化, 并通过配位或螯合作用对 Cu(II) 离子进行吸附分离, 以此实现对 Cu(II) 离子的同步检测分离。

1 实验

1.1 样品制备

所用主要材料包括: 埃洛石纳米管参考本团队报道方法纯化后使用^[21]; HNTs-NH_2 , 酰氯化改性埃洛石纳米管(HNTs-COCl)和 8-甲酰基-7-羟基-4-甲基香豆素(M1)参考本团队已报道方法合成^[22–23]; 1,2-二苯基-1,2-双(4'-氨基苯)乙烯(TPE-2 NH_2)参考文献^[24]合成。

HNTs-TPE- NH_2 的合成: 将 100 mg HNTs-COCl 和 TPE-2 NH_2 (184 mg, 0.5 mmol)溶于 10 mL 二甲基甲酰胺中, 在 60 °C 加热 8 h。冷却至室温后, 将上述体系离心(7000 r/min)收集固体, 使用二甲基甲酰胺, 四氢呋喃和乙醇对收集固体进行洗涤。真空干燥后, 得浅黄色粉末 HNTs-TPE-NH_2 , 如图 1 所示。

HNTs-TPE-Cou 的合成: 将 1 g HNTs-TPE-NH_2 和 8-甲酰基-7-羟基-4-甲基香豆素(50 mg, 0.25 mmol)溶于 15 mL 无水乙醇中, 氩气保护, 70 °C 加热回流反应 12 h。冷却至室温后, 将上述体系离心(7000 r/min)收集固体, 使用四氢呋喃和乙醇进行洗涤。真空干燥后, 得浅黄色粉末 HNTs-TPE-Cou 。

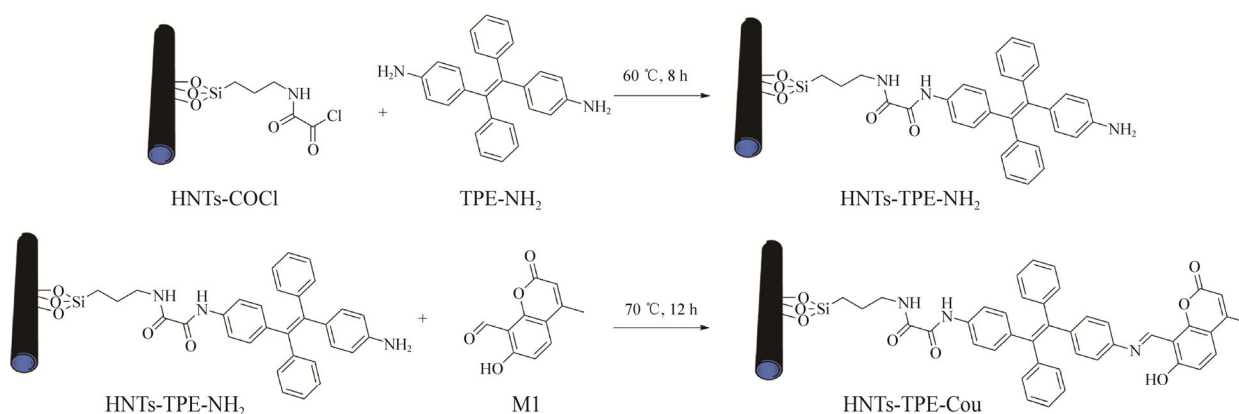


图 1 HNTs-TPE- NH_2 和 HNTs-TPE-Cou 的合成路线图

Fig. 1 Synthesis of HNTs-TPE- NH_2 and HNTs-TPE-Cou

HNTs-TPE-Cou 复合多孔材料: 将聚氨酯多孔泡沫浸入 HNTs-TPE-Cou 水分散液(2 mg/mL), 充分挤压浸泡 3 min。将多孔泡沫取出后, 压力排空液体后, 真空干燥, 得 HNTs-TPE-Cou 复合多孔材料。

1.2 样品表征

采用 Nicolet iS10 型红外光谱仪和溴化钾压片法, 采集样品的红外光谱, 扫描次数 32 次, 扫描范围为 400~4000 cm^{-1} 。采用 Bruker Avance III 型核磁共振波谱仪采集固体核磁谱。采用 BUXI-I 400 MHz 型核磁共振波谱仪测试有机分子的核磁氢谱和碳谱, 所用溶剂为氘代二甲基亚砜。采用 Thermo Scientific ESCALab 250Xi 200 W 型能谱仪(200 W, 单色 Al K_α 源)记录样品的 X 射线光电子能谱。采用 Specord 200 plus 型分光光度计测试样品的紫外-可见吸收光谱。采用 F-7000 型荧光分光光度计测试样品的荧光发射光谱, 激发波长为 365 nm。采用 Tecnai G2 F20 S-TWIN 型透射电子显微镜和 PHENOM PROX 型扫描电子显微镜, 对样品的微观形貌进行考察。

2 结果与讨论

2.1 HNTs-TPE-Cou 的结构和微观形貌

图 2 为 HNTs-TPE-Cou 和 HNTs 的红外光谱。 HNTs 在 3695 cm^{-1} 和 3621 cm^{-1} 处存在 2 个尖峰, 归属为铝氧八面体结构中羟基的伸缩振动峰。

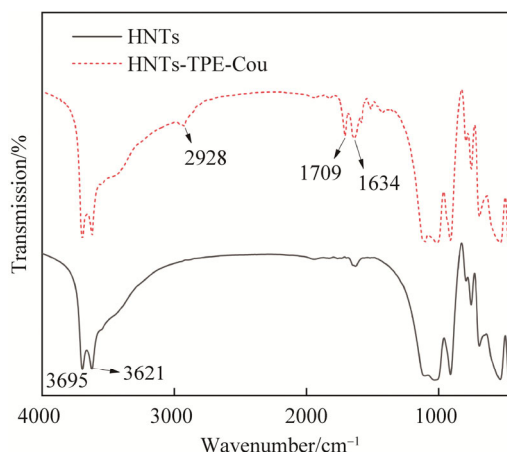


图 2 HNTs-TPE-Cou 和 HNTs 的红外光谱

Fig. 2 FTIR spectra of HNTs and HNTs-TPE-Cou

1640 cm^{-1} 附近为羟基弯曲振动峰。 1033 cm^{-1} 处的峰应归属为 Si-O-Si 伸缩振动峰^[25]。HNTs-TPE-Cou 的红外光谱包含上述全部特征峰, 并在 2928 、 1709 cm^{-1} 和 1634 cm^{-1} 处出现了新的振动峰, 应分别归属为 C-H、C=O 和 C=C 键的振动峰, 这与 HNTs-TPE-Cou 的结构信息相符。图 3 为 HNTs-TPE-Cou 的固体核磁 ^{13}C NMR 谱, 以及原料 M1 和 TPE-2NH₂ 的 ^{13}C NMR 谱。HNTs-TPE-Cou 的固体核磁 ^{13}C NMR 谱中 165 处的宽峰应归属为香豆素单元中临近氧原子的芳香碳原子的振动峰。

135 、 125 和 111 处的信号峰应归属为苯基和乙烯基中碳原子的振动峰。 46 、 24 和 14 处的信号峰可归属为连接硅、氮分子链中碳原子的振动峰。上述结果与 HNTs-TPE-Cou 的预期结构和反应机制相符。透射电子显微镜观察揭示了 HNTs-TPE-Cou 的微观形貌特征。

图 4 为 HNTs-TPE-Cou 的透射电子显微镜照片。由图 4 可见, HNTs-TPE-Cou 具有开放内腔的纳米管形貌, 纳米管分散良好, 且在改性过程中维持了原始管状形貌特征。

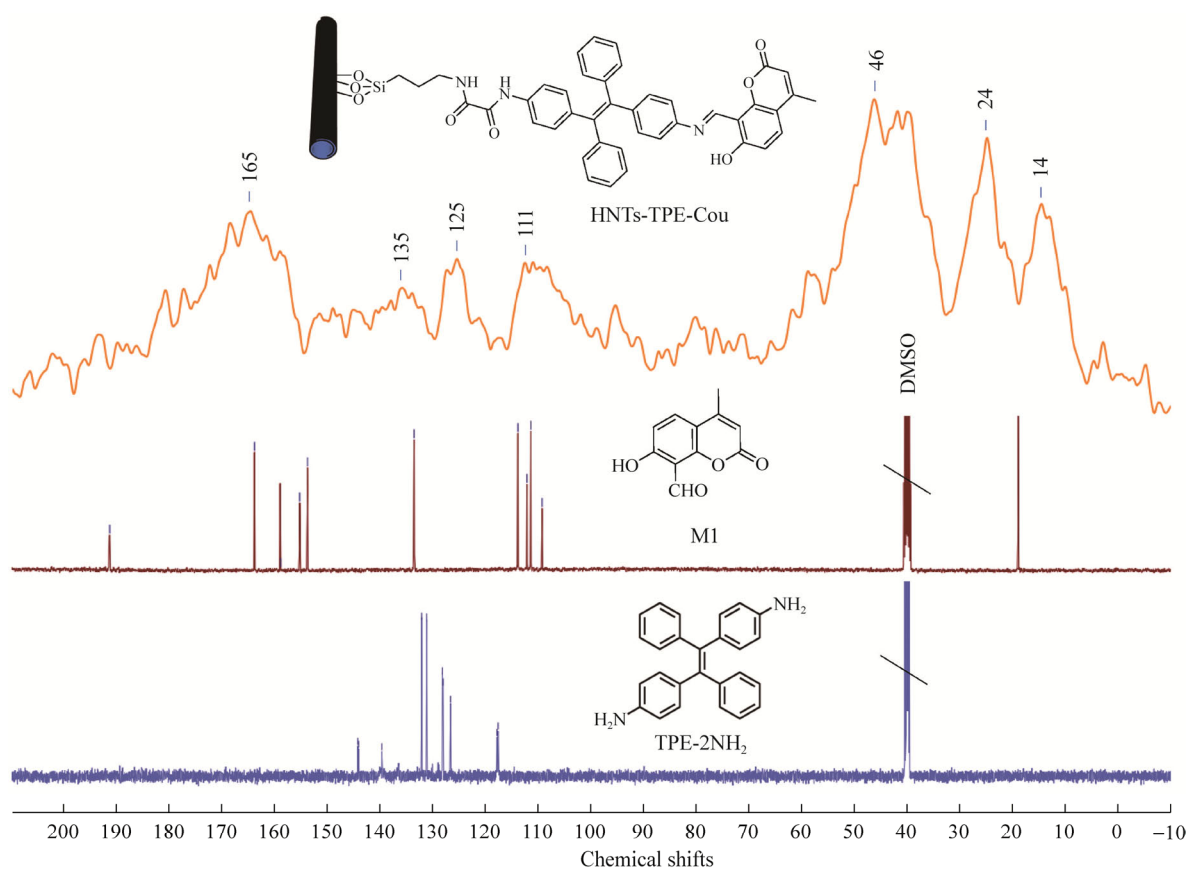


图 3 HNTs-TPE-Cou 的固体核磁 ^{13}C NMR 谱和 M1、TPE-2NH₂ 的 ^{13}C NMR 谱
Fig. 3 ^{13}C solid-state NMR spectra of HNTs-TPE-Cou and ^{13}C NMR spectra of M1 and TPE-2NH₂

图 5 为 HNTs-TPE-Cou 和 Cu(II) 离子处理后 HNTs-TPE-Cou 的 X 射线光电子能谱。由图 5 可见, HNTs-TPE-Cou 的 X 射线光电子能谱中, 531.4 、 102.4 、 74.0 、 284.6 eV 和 400.1 eV 处的 O 1s、Si 2p、Al 2p、C 1s 和 N 1s 信号峰, 表明其结构中存在氧、硅、铝、碳和氮元素。HNTs-TPE-Cou 中未检测出 Cu 相关信号峰, 而 Cu(II) 离子处理后样品的 X 射线光电子能谱在 932.8 eV 处出现 Cu 2p 信号峰, 验证了 HNTs-TPE-Cou 与 Cu(II) 离子的结合行为。热重分析曲线进一步验证了上述结合行为。HNTs 和

HNTs-TPE-Cou 在 800°C 下的残余质量分数分别为 82.7% 和 80.2% 。Cu(II) 离子处理后的 HNTs-TPE-Cou 在 800°C 的残留质量分数增加到 83.6% , 较原始 HNTs-TPE-Cou 含有更多的无机成分, 这与 HNTs-TPE-Cou 结合 Cu(II) 离子的行为相符。

2.2 HNTs-TPE-Cou 对 Cu(II) 离子检测性能

HNTs-TPE-Cou 水分散液的荧光发射光谱如图 6 所示。由图 6 可见, 在 365 nm 激发下, 可以清楚地观察到 560 nm 处的发射峰。这是由于四苯乙烯单元的分子内运动受到限制, 非辐射弛豫受限, 进

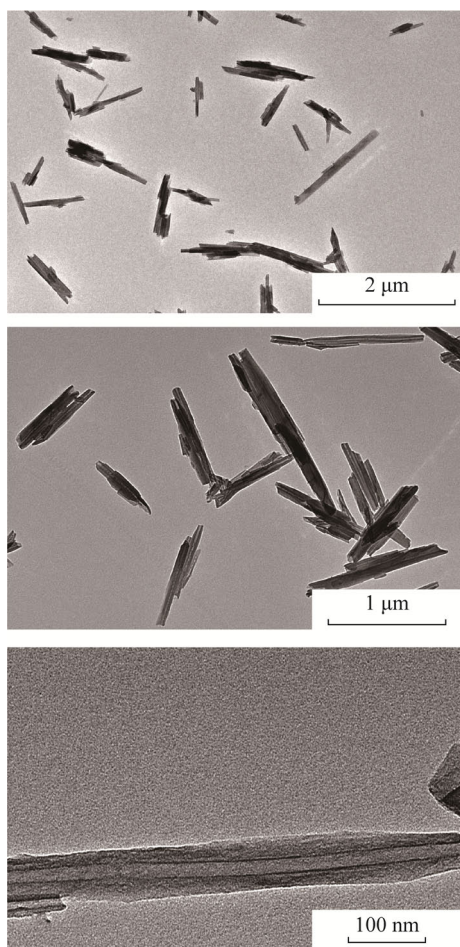


图4 HNTs-TPE-Cou 的透射电子显微镜照片
Fig. 4 TEM images of HNTs-TPE-Cou

而导致荧光发射^[26]。Cu(II)离子加入后，Cu(II)离子对 HNTs-TPE-Cou 的螯合作用破坏了四苯乙烯单元的聚集状态，因此，对 HNTs-TPE-Cu 水分散液的荧光强度产生淬灭效应。因此，当 Cu(II)离子浓度为 0 时，水分散液荧光强度最高，随着 Cu(II)离子浓度的增加，HNTs-TPE-Cou 的荧光强度逐渐降低，并表现出典型的浓度依赖性。本工作考察了酸性(利用盐酸进行配制)和中性环境下 HNTs-TPE-Cou (1 mg/mL)水分散液的荧光强度。HNTs-TPE-Cou (1 mg/mL)水分散液在 pH 值为 3、4、5、6、7 环境下，荧光强度相对标准偏差(RSD)仅为 2.4%，上述结果表明弱酸性和中性环境下，pH 值对荧光强度无显著影响。

使用 F_0 和 F 分别表示 HNTs-TPE-Cou 水分散液原始发射谱中 560 nm 处的荧光强度和添加不同浓度 Cu(II)离子时 560 nm 处的荧光强度，进一步对浓度和荧光强度的关系进行研究。以浓度为横坐标(x)， F_0 和 F 的比值为纵坐标(y)，结果表明，当 Cu(II)离子浓度在 0.2~0.6 $\mu\text{mol/L}$ 时， x 和

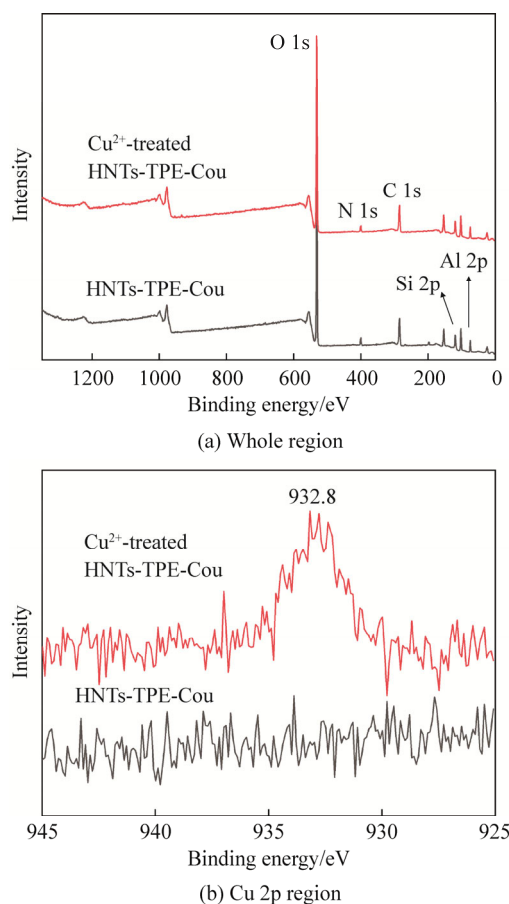
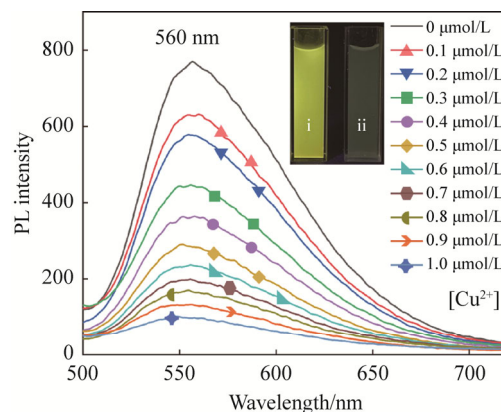


图5 HNTs TPE-Cou 和 Cu(II)离子处理后 HNTs TPE-Cou 的 X 射线光电子能谱
Fig. 5 XPS spectra of HNTs-TPE-Cou and Cu(II)-treated HNTs-TPE-Cou



i and ii are the photograph of HNTs-TPE-Cou aqueous solution and the solution after treating with Cu^{2+} ion under 365 nm, respectively.

图6 HNTs-TPE-Cou 水分散液和加入不同浓度 Cu(II)离子的荧光发射光谱

Fig. 6 Photoluminescence (PL) spectra of HNTs-TPE-Cou aqueous solution treating with Cu^{2+} ion in different concentrations

y 值间存在良好的线性关系。专属性研究中，考察了 Ni(II)、Mg(II)、Ca(II)、Co(II)、Mn(II)、Al(III)、

Na(I)、K(I)、Zn(II)和 Cd(II)等金属离子对 Cu(II)检测的影响, 上述离子加入量为 Cu(II)离子的 5 倍当量。结果表明, 仅有 Cu(II)离子可对 HNTs-TPE-Cou 的荧光实现瞬时淬灭, 时间小于 5 s, 荧光强度降低超过 95%, 其他金属离子加入对 HNTs-TPE-Cou 水溶性的荧光无显著影响(图 7&S1)。Fe(III)和 Fe(II) 2 种离子虽然也可造成荧光强度的下降(图 S2), 但是并不能造成荧光的淬灭, 与 Cu(II)的淬灭效应具有明显差别。平行配置 HNTs-TPE-Cou 浓度为 1 mg/mL 的水分散液 6 份开展重复性验证实验, 随后上述溶液中加入 Cu(II)离子, 使溶液中 Cu(II)离子浓度为 0.5 $\mu\text{mol/L}$, 测试 6 组平行样品的 560 nm 处的荧光强度, 数据表明荧光强度相对标准偏差 (RSD)为 3.6% (表 S1), 重复性良好。上述结果表明,

HNTs-TPE-Cou 对 Cu(II)离子检测具有灵敏性、准确性、高选择性、操作便捷性, 且适用于水相检测等优点。

2.3 HNTs-TPE-Cou 复合多孔材料及分离柱的制备

埃洛石纳米管表面存在电荷分布, 其利于电荷吸附的机制可实现多种复合材料的构建^[27]。将上述 HNTs-TPE-Cou 原位吸附于聚氨酯多孔材料表面, 得复合多孔材料, 并使用扫描电子显微镜对聚氨酯多孔材料改性前后的微观形貌进行了考察。

图 8 为 HNTs-TPE-Cou/聚氨酯多孔复合材料的表征和应用。由图 8a 可见, 原始聚氨酯多孔材料呈现典型的多孔形貌, 且孔壁光滑, 无明显附着。由图 8b 可见, 样品呈现与改性前类似的微观形貌, 说明 HNTs-TPE-Cou 在多孔材料中附着均匀。通过

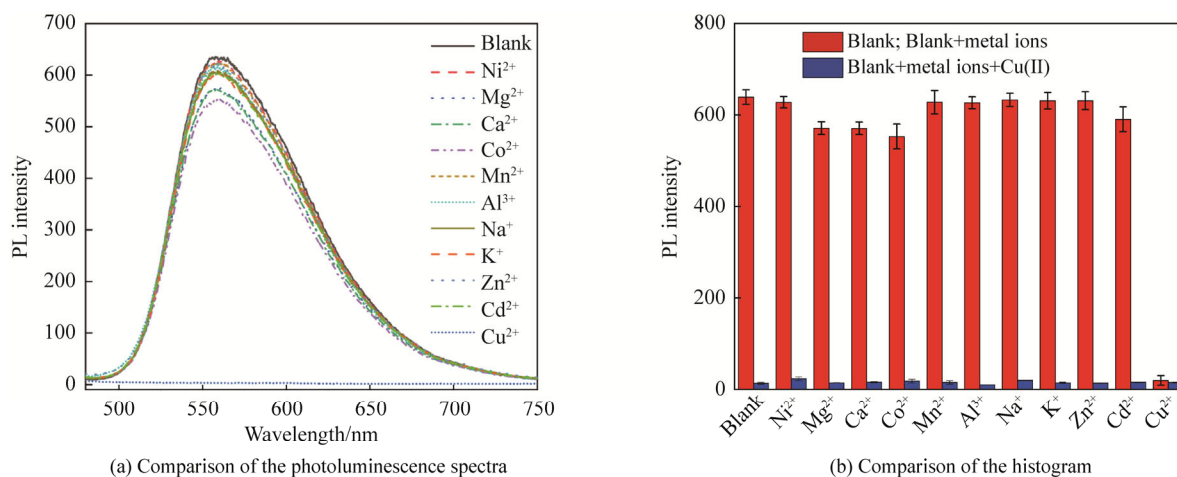


图 7 特异性考察
Fig. 7 Specificity studies

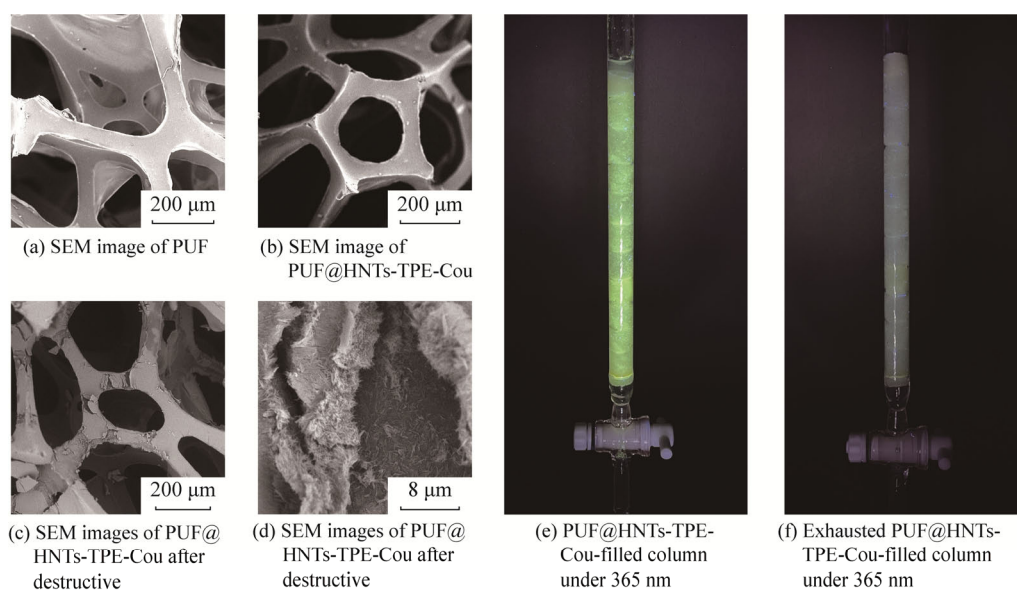


图 8 HNTs-TPE-Cou/聚氨酯多孔复合材料的表征和应用
Fig. 8 Characterizations of PUF@HNTs-TPE-Cou

机械破坏性实验, 复合多孔材料的孔壁出现明显开裂(图 8c)。在图 8d 中可观察到明显的纳米管状结构, 进一步验证了 HNTs-TPE-Cou 已成功附着于聚氨酯多孔材料表面。

将上述复合多孔材料切割为特定形状, 填充入玻璃色谱柱中, 制得用于检测分离 Cu(II)离子的分离柱。由图 8e 可见, 在 365 nm 紫外光照下, 分离柱呈现肉眼可视的绿色荧光。当使用 Cu(II)离子水分散液($c[\text{Cu(II)}] = 1 \times 10^{-4} \text{ mol/L}$)对分离柱进行淋洗后, 分离柱的荧光强度逐渐减弱, 直至消失(图 8f); 另一方面, 使用 HNTs-TPE-Cou 对流经分离柱的洗脱液进行了原位测试, 荧光消失前的淋洗液中 Cu(II)离子均为未检出状态。

3 结论

开发了一种对水中 Cu(II)离子具有刺激响应荧光淬灭性质的埃洛石纳米管基复合材料——HNTs-TPE-Cou, 并进行了结构和微观形态考察, 证明产物结构与预期相符。利用 HNTs-TPE-Cou 构建的水中 Cu(II)荧光检测方法, 该法呈现出良好的线性关系, 适用于铜离子浓度高于 $0.1 \mu\text{mol/L}$ 的定性检测, 及 $0.2 \sim 0.6 \mu\text{mol/L}$ 浓度范围内的定量检测, 并且具有良好的专属性和重复性。通过将 HNTs-TPE-Cou 与聚氨酯多孔材料复合, 制得了对 Cu(II)具有同步吸附检测分离的复合材料, 并将其进一步加工为用于检测分离 Cu(II)离子的分离柱, 并可利用荧光强度作为分离柱使用寿命的指标。综上, 本工作制备的 HNTs-TPE-Cou 具有良好的 Cu(II)离子响应性和水分散性, 易于制备和加工, 呈现良好的应用前景, 也为其他金属离子的检测和分离提供了一种新的思路。

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Tetraphenylethylene-Modified Halloysite Nanotubes Enabling Cu(II)-Sensitive Nanocomposite

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Extended Abstract

Introduction The increasing risk of heavy metals causes many concerns as one of the nonnegligible problems in modern environmental conservation. As one of the most common heavy metals, copper (II) has a dominant effect in such a pollution. The accumulation of copper (II) in water can eventually give rise to the overexpression of copper in humans, showing to be directly associated with Alzheimer's, Parkinson's, Menkes, and Wilson's disease. As a result, the residue of copper (II) in wastewater becomes a ubiquitous environmental challenge. The development of smart materials that are capable of detecting and removing copper (II) simultaneously can pave an effective approach to solving this puzzling issue. Halloysite nanotubes (HNTs) are natural hollow aluminosilicate clays with a chemical composition similar to kaolin (*i.e.*, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$). HNTs display a superior water dispersibility due to the large cavity volume and surface charge repulsion. The attractive properties including low-cost, environmental friendliness, biocompatibility, good stability, and ease of surface modification also make HNTs promising composite materials in the fields of environmental protection, catalysts, bio-medical materials, and sensors. In this study, tetraphenylethene (TPE) moiety was immobilized on aminated HNTs with oxalyl chloride for the preparation of TPE-functionalized HNTs (HNTs-TPE-NH₂).

Methods TPE-2NH₂ (184 mg, 0.5 mmol), HNTs-COCl, mL and 10 *N,N*-Dimethylformamide (DMF) were mixed in a flask. The system was stirred at room temperature to make nanoparticles well-dispersed and then reacted at 60 °C for 8 h. After cooling to ambient temperature, the suspension was centrifugated and the obtained residue was washed by DMF, tetrahydrofuran (THF), and ethanol.

The coumarin unit was bonded to the HNTs-TPE-NH₂ via a condensation reaction by treating 7-hydroxy-2-oxo-2H-chromene-5-carbaldehyde with HNTs-TPE-NH₂ to afford the Schiff base-containing product (HNTs-TPE-Cou). HNTs-TPE-NH₂ (1.0 g) and compound M1 (50 mg, 0.25 mmol) were added to a flask containing absolute ethanol (15 mL), and vacuum-filled with argon gas was repeated for three times. The mixture was refluxed and stirred at 70 °C for 12 h. After cooling to ambient temperature, the suspension was centrifugated and the obtained residue was washed sequentially by THF and ethanol. After vacuum-drying, the product HNTs-TPE-Cou was obtained as a faint yellow solid. The obtained HNTs-TPE-Cou was then deposited on the surface of polyurethane foam (PUF) to afford the composite PUF@HNTs-TPE-Cou based on the surface charge of the nanotubes. The obtained product HNTs-TPE-Cou was characterized by Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, solid-state nuclear magnetic resonance spectroscopy, thermogravimetric analysis, transmission electron microscopy, respectively.

Results and discussion HNTs-TPE-Cou aqueous solution has a fluorescence emission peak at a wavelength of 560 nm. The chelation between Cu²⁺ and HNTs-TPE-Cou can destroy the aggregation state of TPE units and give rise to a “turn off” effect on the fluorescence intensity of HNTs-TPE-Cou aqueous solution. The maximum fluorescence intensity of HNTs-TPE-Cou appears as the Cu²⁺ ion concentration is 0 μmol/L. The fluorescence intensity of HNTs-TPE-Cou decreases gradually with the increase of Cu²⁺ ion concentration, showing a typical concentration-dependent manner. F_0 and F represent the fluorescent intensities at 560 nm without and with different concentrations of Cu²⁺ ion, respectively. The F_0/F of HNTs-TPE-Cou at 560 nm has a good linear correlation to the concentration of Cu²⁺ ion when the Cu²⁺ ion concentration in the solution to be measured is between 0.2 μmol/L and 0.6 μmol/L. Other metal ions, including Ni²⁺, Mg²⁺, Ca²⁺, Co²⁺, Mn²⁺, Al³⁺, Ba²⁺, Na⁺, K⁺, Zn²⁺, and Cd²⁺, do not exhibit the quenching phenomenon with the addition to HNTs-TPE-Cou aqueous solution.

The yielded PUF@HNTs-TPE-Cou composites are cut into special shapes to fill the glass columns. A Gel-like separation column is prepared, which can be used to retain Cu^{2+} ions selectively. Moreover, the fluorescence intensity can serve as a naked-eye identified indicator, which is useful to display the degree of usage. When the fluorescence intensity changes to non-emission, it means the end of useful life, and new columns are needed. The column ($20\text{ cm} \times 2\text{ cm}$) is used to purify the Cu^{2+} -containing water ($[\text{Cu}^{2+}] = 1 \times 10^{-4}\text{ mol/L}$). The concentration of Cu^{2+} effluent water is detected. The results indicate the concentration of Cu^{2+} is lower than LOD calculated in the first 100 mL eluting water, having a high purification efficiency.

Conclusions In this study, HNTs were used as scaffolds and surface modified with tetraphenylethylene and coumarin moieties. The obtained product HNTs-TPE-Cou could be used to detect and separate of Cu^{2+} ions in water solution. HNTs-TPE-Cou displayed an intense fluorescence emission peak at a wavelength of 560 nm in water under the excitation of 365 nm light, while a repaired “turn off” effect on fluorescence appeared, showing a chelation behavior after the addition of Cu^{2+} ions. The as-prepared HNTs-TPE-Cou had high specificity and precision in detecting and removing Cu^{2+} without the recourse to energy consumption. Furthermore, HNTs-TPE-Cou was developed as composite materials by a facile deposition method, which could be further used as gel-like separation columns. The established method could pave a path on the simultaneously detecting and removing metal ions in aqueous solution.

Keywords halloysite nanotube; surface modification; copper (II); tetraphenylethylene