



Multifunctional gold coated rare-earth hydroxide fluoride nanotubes for simultaneous wastewater purification and quantitative pollutant determination



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ABSTRACT

Ce-doped yttrium hydroxide fluoride nanotubes (YHF:Ce NTs) with large surface area are synthesized and conjugated with Au nanoparticles (NPs) to produce Au-YHF:Ce nanocomposites. The Au-YHF:Ce NTs have a hollow structure, rough surface, polymer coating, and good surface-enhanced Raman spectroscopy (SERS) properties. They are applied to wastewater treatment to remove Congo red as a typical pollutant. The materials not only remove pollutants rapidly from the wastewater, but also detect trace amounts of the pollutants quantitatively. The multifunctional Au-YHF:Ce NTs have commercial potential as nano-absorbents and nano-detectors in water treatment and environmental monitoring.

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1. Introduction

The amount of industrial and domestic wastewater containing organic and inorganic pollutants is steadily increasing and pollutants such as heavy metals, fluorides, sulfides, and organic dyes have serious environmental impact [1–5]. In particular, azo-dyes such as Congo red released by the textile industry can transform into toxic and carcinogenic intermediates such as benzene and aniline derivatives during degradation [6]. Therefore, it is crucial to develop an effective detection and treatment process with high efficiency and low energy consumption. Many of the problems confronting water treatment can be resolved or greatly ameliorated by nanostructured materials [7,8] and adsorption is a simple, economical, effective, and environmentally friendly technique [9]. Some nanostructured materials such as metal-based nanoparticles (NPs) [10–17], rare-earth nanowires [18], carbonaceous nanomaterials [19–22], dendrimers [7], natural and

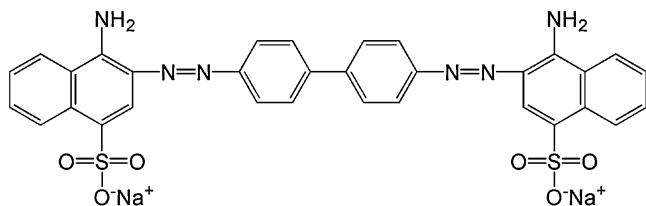
modified clays [23–31] are promising adsorbents due to their abundance, low cost, high efficiency and environmental friendliness. They are attractive to water treatment because they generally have much larger surface areas than their bulk counterparts and can be surface functionalized relatively easily to improve the adsorption capability and efficiency for pollutants [4,32]. Moreover, detection of pollutants such as Ag⁺, Hg²⁺, organic dyes, and so on in sewage has attracted much research interest [33–35]. Metallic nanostructures with “hot spots” where a large electromagnetic field can be generated around the metal NPs can enhance the Raman scattering signals [36,37] and hence, surface-enhanced Raman spectroscopy (SERS) provides an effective means to characterize and detect trace pollutants in wastewater [35,38,39]. Recently, Au and Ag NPs have been synthesized and employed as SERS substrates to detect pollutants in environmental monitoring [40–46].

Simultaneous pollutants adsorption and detection by utilizing the same materials has seldom been reported. In this work, a multifunctional nanocomposite composed of Au coated Ce-doped yttrium hydroxide fluoride nanotubes (Au-YHF:Ce NTs) is fabricated. Owing to the special nano-tubular structure boasting a larger surface area and coated polyethylenimine (PEI) on the surface of the NTs, the Au-YHF:Ce NTs possess excellent capability and efficiency in removing organic pollutants from solutions. The materials can also be utilized to determine the amount of organic

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Scheme 1. Structure of Congo red molecule.

pollutants such as Congo red whose structure is illustrated in the [Scheme 1](#) by taking advantage of the SRES effects rendered by the coated Au NPs. These Au-YHF:Ce NTs thus integrate the capabilities of rapid removal of organic pollutants from water and determination of trace amounts of organic pollutants.

2. Experimental details

2.1. Reagents and materials

YCl_3 , CeCl_3 and PEI ($M_w = 10,000$) were purchased from Sigma-Aldrich and the other reagents were bought from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All the reagents were analytical grade and used as received without further purification. Deionized water was used throughout the experiments.

2.2. Synthesis of the YHF:Ce NTs

In a typical synthesis of the YHF: 31%Ce ($\text{Ce}/(\text{Ce} + \text{Y})$ molar ratio = 31%) NTs [47], the YCl_3 solution (0.25 mL, 0.5 M), CeCl_3 solution (0.1 mL, 0.5 M) and NH_4F solution (0.325 mL, 1.0 M) were dissolved in a mixture of ethanol (7 mL) and deionized water (12 mL), into which PEI (1 mL, 10 wt%) was added to form a milky-white suspension. The mixture was sealed in a 50 mL Teflon-lined autoclave after vigorous stirring under nitrogen for 5 min. The autoclave was heated and maintained at 200 °C for 3 h before cooling to room temperature. The product was collected by centrifugation at 10,000 rpm for 5 min and washed with water and ethanol twice. Finally, the production was re-dispersed in 5.0 mL of water and the YHF:Ce NTs powders were acquired after drying at 40 °C for 12 h.

2.3. Synthesis of Au NPs

The Au NPs were prepared using a seed-mediated process [48]. One mL of 5 mM HAuCl_4 aqueous solution was mixed with 0.5 mL of aqueous 10 mM trisodium citrate solution and 18.5 mL of deionized water. The concentrations of HAuCl_4 and trisodium citrate were both 0.25 mM. Concurrently, 0.6 mL of ice-cold freshly prepared 0.1 M NaBH_4 was added to the mixture under stirring. The resulting mixture turned orange-red immediately, indicating the formation of citrate-stabilized Au NPs with a size of (3.5 ± 0.7) nm [48]. The Au NPs were stored at 25 °C for 3 h to allow excess borohydride to be decomposed by water before use.

2.4. Synthesis of Au-YHF:Ce NTs

In the typical procedures, the Au coated YHF:Ce nanocomposites were obtained by mixing 0.5 mL of YHF:Ce NTs and 7 mL Au NPs under stirring for 5 min. The gray–purple solid was separated by centrifugation at 10,000 rpm, washed with deionized water, and re-dissolved in 7.5 mL of water for further experiments. The Au-YHF:Ce NTs powders were obtained after drying at 40 °C for 12 h.

2.5. Adsorption of Congo red

Different amounts of Au-YHF:Ce NT powders were added to the aqueous Congo red solution (100 mg L^{-1} , 5 mL) under stirring to produce concentrations of Au-YHF:Ce NTs of 0, 0.2 g L^{-1} , 0.3 g L^{-1} , 0.5 g L^{-1} , and 0.7 g L^{-1} . After stirring for 10 min, the NTs were separated by centrifugation at 10,000 rpm for 5 min and the supernatant solutions were analyzed by UV–vis spectrophotometry to determine the concentration of remaining dyes in each solution, respectively.

2.6. Detection of Congo red

In a typical SERS measurement, 100 μL of the Au-YHF:Ce were added to the aqueous Congo red solution resulting in Congo red concentrations of 10^{-5} M, 10^{-6} M, 10^{-7} M, and 10^{-8} M, respectively. In order to ensure complete adsorption, the mixture was stirred for 10 min. The mixture was spun onto a silicon wafer for the SERS measurement. The excitation source was 514 nm with a power of 30 mW and the objective was 100 \times . Spectra were acquired from several different locations including the Au-YHF:Ce NTs and blank.

2.7. Materials characterization

The structure of the product was determined by powder X-ray diffraction (XRD) on a Bruker D8-Advance X-ray diffractometer with $\text{Cu K}\alpha 1$ irradiation ($\lambda = 1.5406 \text{ \AA}$). The morphology of the NTs was examined on a JEM 2010 HT transmission electron microscopy (TEM), JEM 2100F high-resolution TEM (HR-TEM), and field-emission scanning electron microscopy (FE-SEM, Siron, FEI). The NICOLET 5700 Fourier transform infrared (FTIR) spectrometer and Varian Cary 5000 UV–vis-NIR spectrophotometer were used to acquire the FTIR and absorption spectra, respectively. Nitrogen adsorption/desorption isotherms were measured on an ASAP 2020 instrument. The SERS spectra were acquired on a confocal microscopy Raman spectrometer (LabRAM HR800) equipped with a charge coupled device (CCD) detector for Raman mapping.

3. Results and discussions

3.1. Structure and morphology

The powder XRD pattern is depicted in [Fig. 1](#). The peak positions of the as-prepared sample ([Fig. 1a](#)) match well with those of the standard hexagonal-phase $\text{Y}(\text{OH})_{1.69}\text{F}_{1.31}$ structure ([Fig. 1b](#), JCPDS standard card (80-2006)), indicating that it resembles $\text{Y}(\text{OH})_{1.69}\text{F}_{1.31}$ with good crystallinity. However, the peak intensities of the YHF NTs are different from those of the standard $\text{Y}(\text{OH})_{1.69}\text{F}_{1.31}$ pattern possibly because of the doped Ce. The YHF NTs have been suggested to be $(\text{Y}_{0.69}\text{Ce}_{0.31})(\text{OH})_{1.682}\text{F}_{1.318}$ in our previous work [47].

[Fig. 2a](#) and [b](#) shows the typical TEM and SEM pictures of the YHF:Ce NTs and reveal a typical nano-tubular structure with the outer diameter of about 300 nm, length of a few micrometers, and wall thickness of about 50 nm. The insets in the TEM and SEM images reveal a hollow interior and NT ends that tend to be ruptured. The NTs have a hexagonal prism morphology, which is consistent with the reported data of the hexagonal-phase $\text{Y}(\text{OH})_{1.69}\text{F}_{1.31}$ [49].

3.2. Surface properties

The YHF:Ce NTs are characterized by FTIR and HR-TEM. As shown in [Fig. 3a](#), the absorption bands at 3631 cm^{-1} with a broad shoulder on the smaller wavenumber side and the bands around

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