Supporting Information

Plasmon Enhanced Photoluminescence of Carbon Dots-Silica Hybrid Mesoporous Sphere

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1. Experimental

1.1 Materials

Analytic grade reagents of citric acid monohydrate (C$_6$H$_8$O$_7$·H$_2$O), cetyltrimethyl ammonium bromide (CTAB), tetraethyl orthosilicate (TEOS), sodium hydroxide (NaOH), anhydrous ethanol, concentrated hydrochloric acid (HCl) (36–38 wt%) and acetic acid were from Beijing Chemical Reagent Co. N-(β-2-aminoethyl)-γ-aminopropyltrimethoxysilane (AEAPTMS) was purchased from Xiangqian Chemical Factory (Nanjing, China). All the reagents were used as received without further purification. Deionized water was used in experiments.

1.2 Synthesis of Ag-CDSiMs

The silane-functionalized CDs (Si-CDs) were prepared by the pyrolysis of citric acid in the presence of AEAPTMS at the temperature of 234 °C. For the surface-passivation of silane, Si-CDs demonstrated bright blue photoluminescence (PL) with a quantum yield (QY) of ~30% (excited at 360 nm, quinine sulfate in 0.5 M sulfuric acid as a reference). DLS measurement showed the particle size of CDs (Si-CDs) centered at 1.8 nm.

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Then, Si-CDs, TEOS and silver ammonia solution (Ag(NH$_3$)$_2^{2+}$) were used as a precursor to prepare Ag NPs-decorated carbon dots-silica hybrid mesoporous sphere (Ag-CDSiMs). The typical procedure was as the following. Under vigorous magnetic stirring and at 80 °C, 0.2 g of CTAB was dissolved in 99 mL of sodium hydroxide (NaOH) aqueous solution (~1.5x10$^{-2}$ mol/L). Then, the 1.3 ml of the mixture of TEOS and Si-CDs (the volume ratio: 12:1) was quickly injected into the above solution followed by the addition of 1.8 ml of 10$^{-2}$ mol/L Ag(NH$_3$)$_2^{2+}$ aqueous solution. After 3 hours stirring at 80 °C, a pale yellow precipitate was separated and washed with deionized water until the supernatant was close to neutrality. The obtained slurry was re-dispersed in a 100 ml of the mixture solution of acetic acid and ethanol (volume ratio: 5:95) and then stirred at room temperature for 24 hours to remove CTAB. The final product was washed with deionized water for several times and then dried in air at room temperature. Carbon dots-silica hybrid mesoporous sphere without Ag NPs (named as CDSiMs) was prepared with the same procedure except for the introduction of Ag(NH$_3$)$_2^{2+}$ and its absolute QY was ~47% (excited at 360 nm).

1.3 Characterization

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were recorded with JEOL JEM-2100 microscope operating at accelerating voltage of 200 kV. The IR spectra of the product were measured by the Hitachi Fourier transform infrared (FT-IR) spectroscopy with the resolution of 4 cm$^{-1}$ and scan times of 49. Shimadzu UV-1601 spectrophotometer had been used to measure UV-Vis spectra. Fluorescence spectra were recorded with F-4500 fluorescence spectrophotometer. Time-resolved PL spectroscopy was performed with a time-correlated single photon counting (TCSPC) module (Edinburgh Instruments F900) and a temporal resolution 4ps. Pulse laser (~375 nm) with an average power of 1 mW operating at 40
MHz with duration of 70 ps was used for the excitation of Ag-CDSiMs or CDSiMs. The sample was prepared by pressing the corresponding powders into wafer. The X-ray diffraction (XRD) pattern was recorded with a Rigaku DMax-RB X-ray diffractometer with the Cu Kα radiation ($\lambda=1.5418\text{Å}$) operated at 40 kV and 40 mA at the scanning speed of 0.01°/s. X-ray photoelectron Spectroscopy (XPS) analysis was carried out on ESCAlab250xi electron spectrometer from Thermo Scientific with Al-Kα radiation and spot size of 650 μm. Their binding energy was corrected with the C1s of 284.8 eV. N$_2$ adsorption-desorption measurements were performed on a Micrometrics ASAP 2020 instrument and the pore size distribution was calculated from the desorption branch of the sorption isotherms with the Barret-Joyner-Halenda (BJH) method. Before measurements, the samples were dried in vacuum at 100 °C for 6 h. The size of silane functionalized carbon dots was measured with Dynamic Light Scattering (DLS) on a Dynapro NanoStar (Wyatt, USA). The absolute QY of CDSiMs was measured by Edinburgh FLS 920 fluorescence spectrophotometer with integrating sphere.


2. Results

Fig. S1 a) TEM images of Ag-CDSiMs with lower magnification; b) size distribution histogram of Ag NPs in Fig. S1a)

Fig. S2 HRTEM image of Ag NPs in Ag-CDSiMs

Fig. S3 XRD spectra of CDSiMs and Ag-CDSiMs
Fig. S4 Large magnification TEM images of Ag–CDSiMs (a) and CDSiMs (b)

Fig. S5 Photograph of CDSiMs (left) and Ag-CDSiMs (right) aqueous solution (1g/L) under ~365 nm

Fig. S6 High-resolution XPS spectrum of Ag3d.
Fig. S7 XPS survey spectra of CDSiMs and Ag-CDSiMs

Fig. S8 TEM images: a) Ag-SiMs prepared with Ag(NH$_3$)$_2^+$ and TEOS as a co-precursor; b) Ag-SiMs prepared with Ag(NH$_3$)$_2^+$, TEOS and methyl alcohol as co-precursor; c) Ag-SiMs prepared with Ag(NH$_3$)$_2^+$, TEOS and AEAPTMS as co-precursors.