In situ Synthesis of Chiral AuNCs with Aggregation-Induced Emission Using Glutathione and Ceria Precursor Nanosheets for Glutathione Biosensing

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Chemicals and Materials.

Cerium(III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$), ammonium bicarbonate and sodium hydroxide were received from Alfa Aesar Co., Ltd., Aladdin Industrial Corporation and Xilong Scientific Co., Ltd; respectively. Gold(III) chloride trihydrate ($HAuCl_4.3H_2O$) and glutathione(GSH) were received from Energy Chemical Co., Ltd. 20.0 mg of the as-synthesized cerium carbonate $Ce(CO_3)_2$ NS were dispersed in 2.0 mL distilled water by ultrasonication for preparing a colloidal stock solution of (10 mg/mL).

Instruments.

Photoluminescence (PL) and Circular Dichroism (CD) spectra of the NCs samples were recorded by a HITACHI F7000 and Bio-logic MOS-450 photospectrometer; respectively. High Resolution Transmission Electron Microscopic (HRTEM) images of AuNCs and $Ce(CO_3)_2$ NS were obtained using on a JEOL JEM-2100 microscope biased at 200 kV. Atomic Force Microscope (AFM) and Scanning Electron Microscope (SEM) images of $Ce(CO_3)_2$ NS were taken on a BRUKER Multi Mode 8 and JEOL JSM-7800F, respectively. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Fisher Scientific K-Alpha+ spectrometer. X-ray powder diffraction (XRD) patterns were recorded on a PANalytical B.V. Empyrean X-ray diffractometer with Cu Kαradiation(λ= 0.154056 nm).

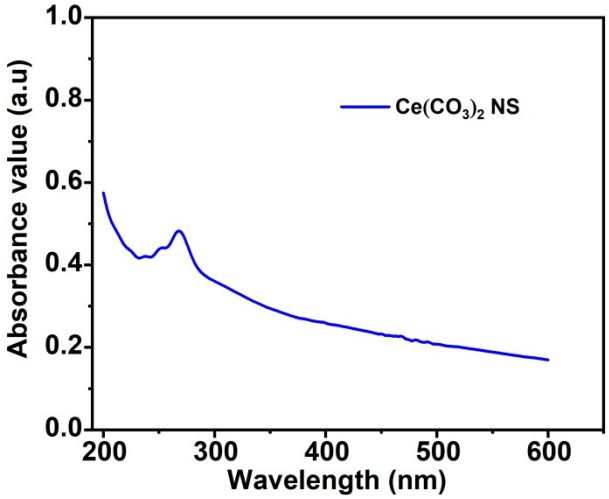

Figure S1. Absorption spectrum of $Ce(CO_3)_2$ NS solution.

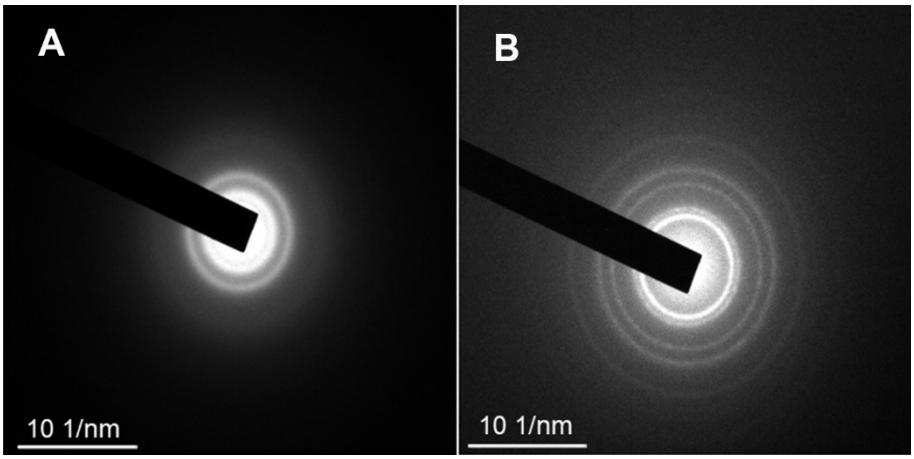

Figure S2. SAED images of insitu synthesized Au0@Au(I)-SG NCs (A) and $Ce(CO_3)_2$ NS (B)

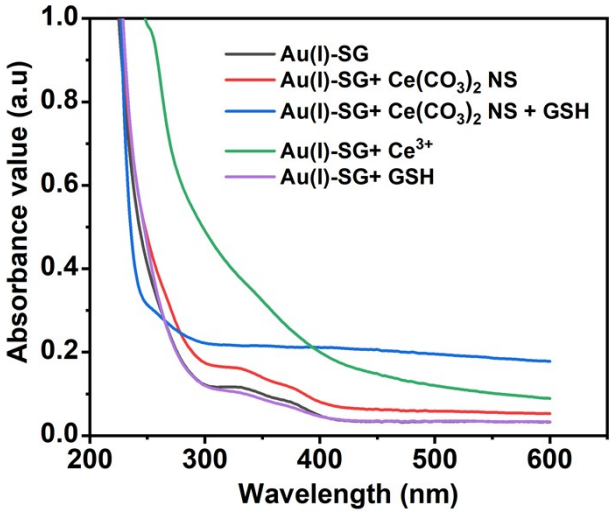

Figure S3. Absorption spectra for solution of Au(I)-SG oligomers in the absence (black line) and presence of Ce^{3+} ions (green line), or GSH (light magenta line) and absorption spectra for solutions of the conjugate probe of Au(I)-SG/$Ce(CO_3)_2$ NS in the absence (red line) and presence of GSH (purple line).

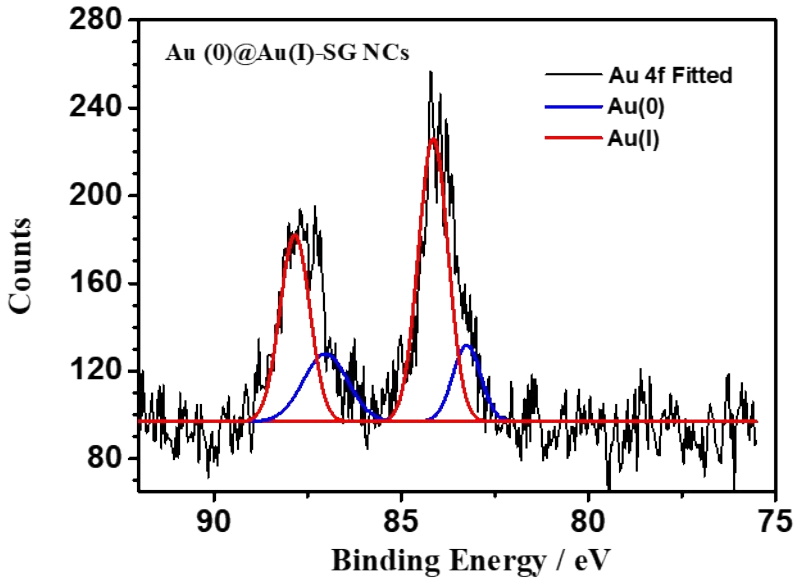

Figure S4. The Au ($4f_{7/2}$) spectrum of the as-synthesized luminescent Au(0)@Au(I)−SG nanoclusters

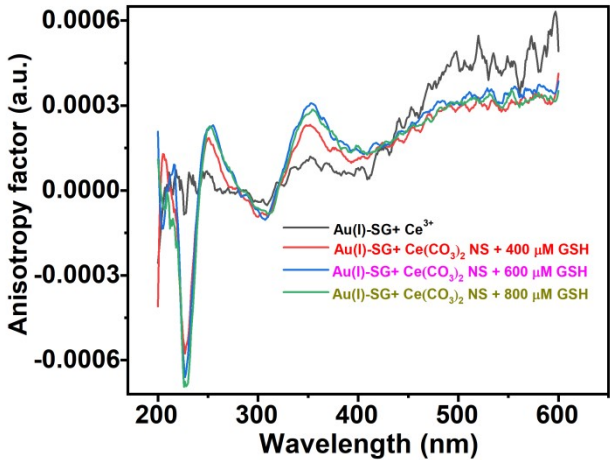

Figure S5. Anisotropy factor spectra for solution of Au(I)-SG oligomers in presence of 50 µM Ce^{3+} ions and solutions of the conjugate probe of Au(I)-SG/$Ce(CO_3)_2$ NS in presence of GSH (400, 600, 800 µM).

Table S1. XPS data of the synthesized $Ce(CO_3)_2$ NS

Name	Peak BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N)	Atomic %
C1s-Ce4s	284.8	14082.06	3.04	85384.39	1197.29	40.95
O1s	531.07	73645.64	3.19	246206.39	1427.36	48.82
Ce3d	884.41	66153.56	6.74	782059.17	298.78	10.22

Table S2: Repeatability and reproducibility results for GSH sensing using Au(I)-SG/$Ce(CO_3)_2$ NS probe

GSH amount (µM)	% Recovery [a] ± % RSD	
	Intra-day precision	Inter-day precision
200	99.13 ± 1.90	98.84 ± 2.31
500	99.98 ± 1.75	101.35 ± 2.84
1000	100.50 ± 1.82	100.90 ± 2.62

[a] refers to average value of three assays.

Table S3. Comparison of AIE-based probe for GSH sensing with some previous methods.

Technique	Applied Materials*	Linear range (μM)	LOD (μ	Ref.
Colorimetry	AgNPs	0-400	4.11	[1]
Colorimetry	Coumarin derivatives	0 -180	6.84	[2]
Colorimetry	Cu^{2+}/Imidazole derivatives	7.5-37.5	2.98	[3]
Colorimetry	Cytidine-AuNCs	0-400	10	[4]
Colorimetry	NDP	$0\text{-}80\times10^3$	178	[5]
Chronoamperometry	AuNPs-PEDOT/ GCE	0.5-10	0.1	[6]
CV	AuNPs/Al_2O_3.TiO_2 NPs /GCE	5-50, 100-750		[7]
DPV	PDI−SH/ CPE	$(0.5\text{-}5)\times10^3$	17	[8]
CV	Graphene modified-SPCE	1-100	8.01	[9]
HPLC-ED	Reversed C18- HPLC	5.1–325.4	2.3	[10]
Fluorimetry	Au(I)-SG/$Ce(CO_3)_2$ NS	0-1000	1.02	Our work

* AgNPs, NDP, AuNPs, PDI-SH, GCE, PEDOT, CPE and SPCE represent silver nanoparticles, naphthalene derivate containing piazselenole, gold nanoparticles, thiolated perylene diimides, glassy carbon electrode, poly(3,4)ethylene dioxythiophene, carbon paste electrode and screen printed carbon electrode; respectively.

Table S4. Comparison of AIE-based probe for GSH sensing with other previous luminescent approaches.

Technique	Applied Materials*	Linear range (μM)	LOD (μM)	Ref.
ECL	GO/CdTe QDs	24-214	8.3	[11]
ECL	CdSe/ZnS QDs	10-180	1.5	[12]
CL	Peroxidase/luminol-H_2O_2	0.75-30	0.75	[13]
Fluorimetry	N-GQDs/MoS_2	400-4000	2.47	[14]
Fluorimetry	MnO_2/UCNPs	N/A	0.9	[15]
Fluorimetry	TAT-probe	0-12	5.15	[16]
Fluorimetry	DTFN	0-500	1.03	[17]
Fluorimetry	AuNCs/MnO_2 NS	0-500	4	[18]
Fluorimetry	TP-N	0-50	1.53	[19]
Fluorimetry	N,S-CDs@Cu^{2+}	10-150	3.74	[20]
Fluorimetry	NP-BO-HEM	0-200	1.37	[21]
Fluorimetry	Au(I)-SG/Ce$(CO_3)_2$ NS	0-1000	1.02	Our work

* GO, QD, GQDs, UCNPs, TAT-probe, DTFN, TP-N and CDs, refer to, graphene oxide, quantum dots, graphene quantum dots, upconversion nanoparticles, two-photon biothiols probe, dual-targeting fluorescence nanoprobe, phthalazinetrione derivative, 2-(benzo[d]thiazol-2-yl)-4-hydroxyphthalazin-1(2H)-one hydrate-dimer, and carbon dots, respectively.

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