Supporting Information

Luminous polystyrene upconverted nanoparticles to visualize the traces of nanoplastics in a vegetable plant

Bushra Maryam^a, Muhammad Asim^b, Li jiaxuan^a, Hamna Qayyum^c, Xianhua Liu^{a*}

- a. School of Environmental Sciences and Engineering, Tianjin University, Tianjin 300072, China
- b. Key Laboratory for Green Chemical Technology of the Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072 China
- c. National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, 230029, China

*Corresponding Author

Xianhua Liu – School of Environmental Sciences and Engineering, Tianjin University, Tianjin 300072, China

Email: <u>lxh@tju.edu.cn</u>

Contents

Text S1: Characterizations of Materials	.3
Text S2: Plant culture and luminous upconverted PS particles exposure	.4
Text S3: Luminous upconverted PS nanoparticles stability	.5
Text S4: Physiological indicator effects after PS-NPs exposure	6
Scheme S1: Synthesis illustration of LUC-nano and PS@LUC-nano	.7
Figure S1: TEM characterization of LUC-nano.	.8
Figure S2: TEM characterization of PS@LUC-nano.	.9
Table S1: Interplanar spacing (d-spacing) calculated by XRD planes	10
Table S2: Binding energy of LUC-nano and PS@LUC-nano by Dmol3 code1	11
Figure S3: Stability of PS@LUC-nano in Hoagland and plant media solution1	12
Table S3: Time dependent effects of PS-NPs on growth parameters of <i>B. rapa</i> 1	13

Text S1: Characterizations of Materials

In this study, detailed analyses of the samples were performed using a variety of sophisticated instruments. High-resolution transmission electron microscopy (HR-TEM) images were captured using a JEM-2100F microscope. This microscope was also equipped with an energy dispersive spectrum (EDS) system for elemental analysis. The dynamic light scattering (DLS) method was used to measure the size of PS-NPs using a Malvern Zetasizer (Malvern, UK). The average hydrodynamic diameter of the PS@LUC-nano particles dispersed in pure water were determined by DLS using a Malvern Zetasizer Nano-ZS90. The crystallographic structure of the samples was investigated through X-ray diffraction (XRD) using a D/MAX-2500 diffractometer, which operates with Cu Ka radiation at a voltage of 40 kV and a current of 40 mA, and a scanning rate of 10°C per minute. X-ray photoelectron spectroscopy (XPS) measurements were conducted with a PHI-1600 spectroscope, employing Al Ka radiation. The binding energies obtained were calibrated against the C1s peak of contamination carbon, which is typically observed at 284.8 eV. Fourier transform infrared spectroscopy (FTIR) measurements were performed in transmission mode at normal incidence, using a Bruker VERTEX 70 spectrometer at ambient conditions. Lastly, the materials' photoluminescence emission spectra were analyzed using an F97XP fluorescence spectrophotometer (manufactured by Shanghai Lengguang, China). This equipment was equipped with a 980 nm NIR laser, serving as the source of excitation.

Text S2: Plant culture and luminous upconverted PS particles exposure

Firstly, *Brassica rapa* var. *perviridis* seeds were sterilized with 75% ethanol and washed thrice with distilled water. Initially the seeds were allowed to germinate in sterilized coco peat media and placed in an artificial chamber in dark conditions and adequate amount of water was added frequently to maintain moist condition which is necessary for seed germination. After five days, the uniform seedlings selected and transferred into a wide mouth glass container containing 50% Hoagland growth solution (1000 mL) and placed in incubator (growth chamber) at 22°C with illumination (250 μ mol m⁻² s⁻¹), a 12:12-hours (hrs) light: dark photoperiod and 60% relative humidity. After seven days, 100 μ g/L of PS@LUC-nano was introduced into 1000 mL of 50% Hoagland growth solution. The *B. rapa* var. *perviridis* plants were then placed in flasks containing this solution, with three plants in each group, for a duration of 10 and 20 days. The experiment was repeated three times to avoid errors.

Text S3: Luminous upconverted PS nanoparticles stability

The stability of the synthesized luminescent PS nanoparticles was determined in Hoagland solution and plant solution (a solution that simulated the conditions inside the plant cell environment) by exposing the luminescent PS nanoparticles $(5,000 \ \mu gL^{-1})$ to 50% Hoagland solution and nutrient solution containing 2.5 mM Ca $(NO_3)_2$, 1 mM MgSO₄, 2.5 mM KNO₃, 0.1 mM K₂HPO₄, 5 mM NaCl, 50 μ M glucose, 25 μ M oxalic acid, 12.5 μ M serine and 5.0 μ M sodium iron chlorophyllin. The luminescent PS nanoparticles were dispersed in solutions initially adjusted to pH 6.5. The solution was centrifuged to separate the filtrate and nanoparticles after 21 days of exposure, and the particles were subsequently oven dried for 12 hrs at 60°C. The structure of particles inside the plant and hydroponic solution was examined by TEM and luminesce stability of filtrate and nanoparticles was analyzed by photoluminescence emission spectra at excitation wavelength of 980 nm.

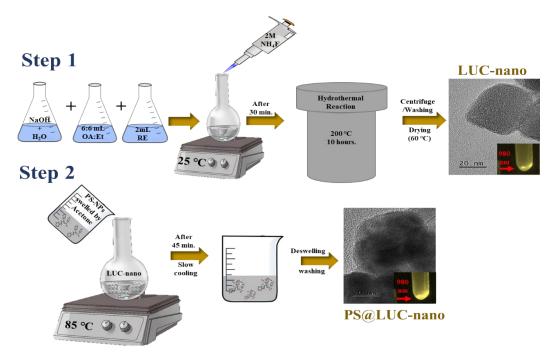
Text S4: Physiological indicator effects after PS-NPs exposure

A separate plant culture experiment was performed to investigate the potential effects of pristine PS-NPs (50 nm particle size, 100 µg/L concentration) exposure on physiological indicators in the *Brassica rapa* var. *perviridis*. Plants cultured in 50% hoagland solution were randomly selected to be exposed to pristine PS-NPs at concentration of 100 µg/L against control conditioned plant (CK). Three independent replicates were used for each treatment. After harvesting at 10 and 20 days, the plants were gently removed from the flask, and were rinsed with deionized water thoroughly. The fresh weight and fresh yield (consumable or eatable portion of vegetable) of the spinach plants were measured immediately considered as fresh biomass. Sample were dried in oven at 70°C for 24 hrs to measure dry biomass and dry yield of spinach plant. Water content of plant was measured by formula:

 $WC = W_{fresh} - W_{dry} / W_{dry} \times 100$

Root length, stem length, and leaf length and width was measured by measuring scale. Stem diameter was measured by vernier caliper and leaf area (A) was measured by Montgomery equation (ME), that is:

$$A = c(L \times W)$$



Scheme S1: Synthesis illustration of LUC-nano (step 1) and PS@LUC-nano (step 2).

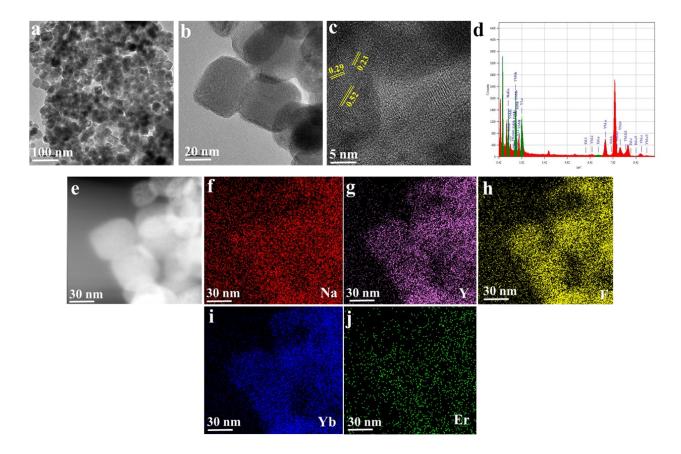


Figure S1: TEM characterization of LUC-nano. (a) (b) TEM images, (c) interplanar spacing, and (d) EDX elemental graph, (e) EDX elemental mapping of, (f) Na, (g) Y, (h) F, (i) Yb, and (j) Er.

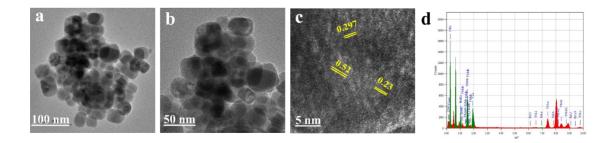


Figure S2: TEM characterization of PS@LUC-nano. (a), (b) TEM images, (c) interplanar spacing, and (d) EDX elemental graph.

Peak	2theta	theta	d=nλ/2sinθ
100	17.250342	8.625171	5.13637066
110	29.986	14.993	2.97756832
200	30.97	15.485	2.88516905
111	38.9329	19.46645	2.31144436
201	43.64	21.82	2.07241527
211	53.76	26.88	1.70373846

Table S1: Interplanar spacing (d-spacing) calculated by XRD planes.

Table S2: Binding energy of LUC-nano and PS@LUC-nano calculated by firstprinciples through Dmol3 code.

Structure	Binding energy/eV
α-NaYF ₄ :Yb ⁺³ ,Er ⁺³	-5.5919
PS@NaYF ₄ :Yb ⁺³ ,Er ⁺³	-12.6848

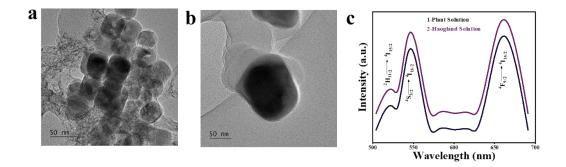


Figure S3: Stability of PS@LUC-nano in (a) Hoagland solution, (b) plant media solution, (c) Luminescent up-conversion emission spectra of centrifuged particles from plant solution and Hoagland solution.

Table S3: Time dependent effects of PS-NPs on growth parameters of *B. rapa* var. *perviridis* followed by exposure with 100 μ gL⁻¹ 50nm PS particles in 50% Hoagland solution for 10 and 20 days. Data are presented as Mean \pm SD (n=3), with p-values <0.05 using one-way analysis of variance (ANOVA).

Parameters	10 Days		20 Days	
rarameters -	СК	PS-NPs	СК	PS-NPs
Root length (cm)	10.1±1	6.0±1	13.1±1	7.0±1
Stem length (cm)	$1.99{\pm}0.1$	1.73±0.1	2.63 ± 0.1	2.23 ± 0.2
Stem diameter (cm)	0.31 ± 0.08	0.15 ± 0.03	0.45 ± 0.08	0.21±0.03
Leaf length (cm)	4.03±1.1	2.11±0.5	5.33±1.1	3.34±1.1
Leaf width (cm)	2.14±0.9	1.01 ± 0.05	3.11±0.9	$1.96{\pm}0.8$
Leaf Area (cm ²)	8.62±0.1	2.13±0.2	16.57±0.1	6.54±0.1
Leaf count (number)	4±0.5	2±0.5	5±0.5	3±0.5