Supplementary Information

1. ***Experimental***

1.1.1 *Synthesis of hollow silica nanoparticles NPs.*

The precursor of sol-gel silica is fresh made 1.0 M $Si(OH)_4$ solution which was made by adding tetramethyl orthosilicate to a 1 mM HCl solution. To synthesize hollow silica NPs, 50 uL of polystyrene beads suspension (2.64% by weight) 200 uL of 0.1% poly-L-lysine water solution and 25 uL 1.0 M were added to 1.0 mL pH7.4 phosphate buffer (1X) followed by adding 25 uL of the $Si(OH)_4$ solution and the mixture was stirred 15 min. Core-shell NPs were collected by centrifugation and washed by water. Polymer cores were removed by calcining particles 18 h at 500 °C. Figure 1 shows SEM and TEM images of hollow silica NPs and an average diameter of 85±10 nm was gained from SEM image.

1.1.2 *Surface adsorption coating of PSFF polymer on hollow silica NPs.*

To coat PSFF on plain hollow silica NPs 3 mg of silica NPs were suspended in 0.3 mL toluene and 0.3 mg of PSFF was added the suspension and mixture was stirred 4 hours before spinning down the NPs and washing with toluene, ethanol and water. The PSFF coated NPs were resuspended in 3 mL of pH7.4 PBS buffer for explosive detection.

1.1.3 *Covalent attachment of PSFF polymer on the surface of hollow silica NPs.*

The procedure of coating $(MeO)_3Si$-PSFF on plain silica NPs was the same as coating of PSFF except that absorption time was 8 hours.

1.1.4 *Covalent attachment of octadecyl moieties on the surface of hollow silica NPs and following adsorption of PSFF polymer.*

To coat octadecyl groups on plain hollow silica NPs, 3 mg of silica NPs were suspended in 1 mL of toluene and 60 uL of octadecyl(triethoxy)silane was added to the suspension. The mixture was stirred overnight at room temperature. After washing with toluene the NPs were coated with PSFF using the same procedure of coating PSFF on plain silica NPs in 1.1.2.

1.2 *Available surface on hollow silica NPs*

A BET measurement showed that the calcined hollow silica NPs had a typical mesoporous structure with a surfaced area of 400 m^2/g. The degree of covalent surface modification possible was quantified using 3-aminopropyl(trimethoxy)silane (APTS) to modify the surface of silica. The density of 3-aminopropyl groups on the surface of NPs serves as a measure of the available reactive surface of silica NPs. Modification of 3-aminopropyl groups was induced by adding APTS into a suspension of hollow silica NPs in absolute ethanol and the mixture was stirred for 1 h followed with washing with ethanol and drying in vacuum at room temperature. The quantification of amino group was carried by forming a cleavable crosslink between each amino group and N-succinimidyl 3-(2-pyridyldithio) propionate (SPDP), and after washing away excess reagent the disulfide bonds were cleaved by dithiothreitol (DTT) to releases 2-pyridylthiol, whose absorbance was measured at 343 nm[1]. Several measurements yielded a density of 1.20×10^{20} primary amines per gram of silica NPs. Dividing 1.20×10^{20} by the average surface area of silica NPs (400 m^2/g) gave a density of amino groups by area of

3.0×10^{17} primary amines per square meter.

The mass of single silica NPs was evaluated with following equation:

$$\mathbf{M} = \frac{Mc - V \times c}{N \times V}$$

M (mg) is the mass per hollow silica NP; Mc (mg) is the mass of the core-shell polystyrene-silica NPs before calcination; V (mL) is the volume of polystyrene (PS) beads suspension used in synthesis reaction; c (mg/mL) is the concentration of PS beads provided by producer (26.4 mg/mL); N (/mL) is the number concentration of PS beads provided by the supplier (9.07×10^{13} beads per mL). Here we assumed that 100% of PS beads were coated by uniform silica shells. Using this equation the mass of single hollow silica NP is 2.60×10^{-13} mg and the surface area of this hollow silica NP is 1.04×10^{5} nm^2 using the BET data. The calculated mass of a hollow nanoshell using the experimentally measured (from SEM and TEM images) diameter of 85 nm and a 10 nm thick wall of silica gel (using a density 2 g/cc for Polysciences solid silica gel microspheres) can be calculated as 3.5 x 10^{-13} mg, which is in good agreement with the experimentally measured value.

For comparison with the porous hollow silica shell, we calculated the area of a hypothetical smooth hollow shell with a diameter of 85 nm and a 10 nm thick solid wall. The surface area of this smooth hollow shell (sum of area of inner and outer surface) and the quantities of amine groups estimated on this smooth hollow shell and porous hollow shell are given in Table 2.

1.3 *Density of PSFF on hollow silica NPs*

The density of PSFF on hollow silica NPs is the quantity of PSFF polymer chains per unit area of silica surface. It is calculated with following equation:

$$\mathbf{D} = \frac{\frac{Mp}{Mw} \times A}{Ms \times 400}$$

D (m^{-2}) is the density of PSFF on silica NPs; Mp (g) is the mass of PSFF absorbed on silica NPs; Mw is the molecule weight of PSFF from GPC testing; A is Avogadro constant; Ms (g) is the mass of silica NPs used to absorb PSFF; 400 (m^2/g) is the surface area of silica NPs from BET testing. The results of calculation are in Table 3.

Table 1 Molecular weights of PSFF

Entry	M_n (NMR)	M_w (GPC)	$(M_w/M_n)^a$	n^a
PSFF	17 000	20 000	2.3	47

[a] Measured using GPC data.

Table 2 Quantity of amine groups on hollow NPs

Nanoparticles	Surface area (nm^2)	Quantity of surface amine group per nanoparticles
Porous silica shell	1.04×10^5	31200
Smooth shell[a]	3.6×10^4	4360

[a]Calculated using SEM determined size of 85 nm for outer shell diameter and 65nm for inner shell diameter.

Table 3 Density of PSFF on silica NPs[a]

Nanoparticles	PSFF coated plain silica NPs	PSFF coated C_{18} modified silica NPs	Silane-PSFF coated plain silica NPs
D (PSFF/m^2)	3.84×10^{15}	1.35×10^{15}	2.63×10^{15}
D (PSFF/nm^2)	3.84×10^{-3}	1.35×10^{-3}	2.63×10^{-3}

[a]Calculation assumed n = 47 for PSFF.

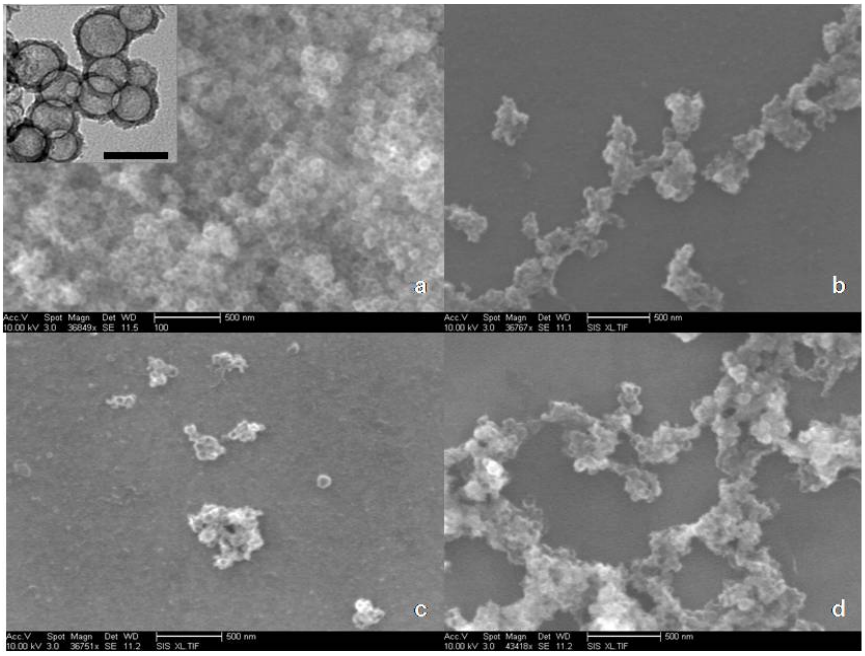

Figure. 1 SEM pictures of silica NPs (a), PSFF coated NPs (b), PSFF coated C_{18} modified NPs (c) and silane-PSFF coated NPs (d). All scale bars in SEM pictures are 500 nm. Inserted figure in a is TEM image of hollow silica NPs, scale bar is 100 nm.

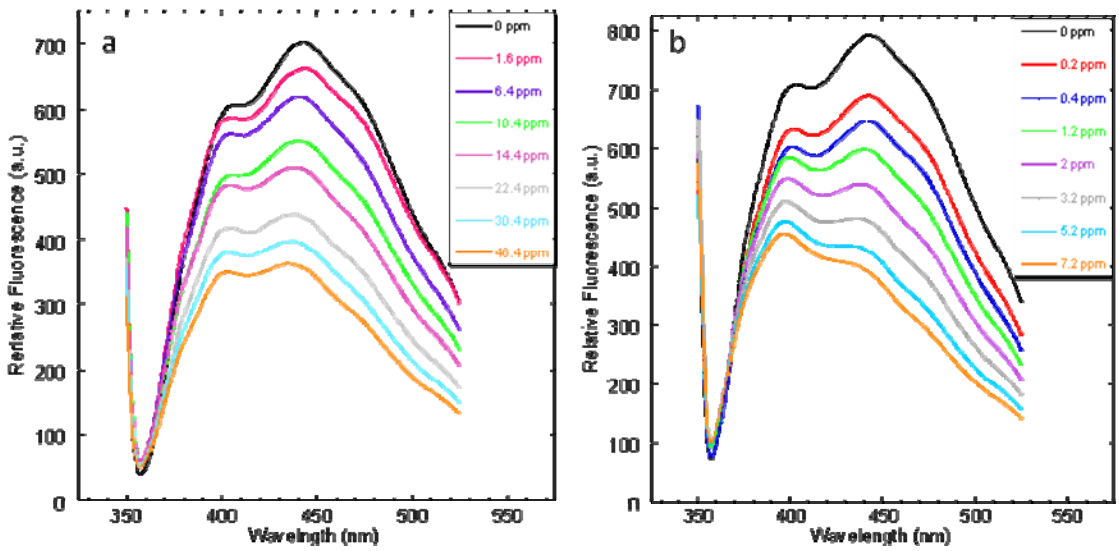

Fig. 2 Fluorescence quenching of PBS suspension of PSFF coated plain NPs (a) and PSFF coated C18 modified NPs (b) in the presence of TNT. The concentration of NPs is 0.1 mg/mL by the mass of silica nanospheres.

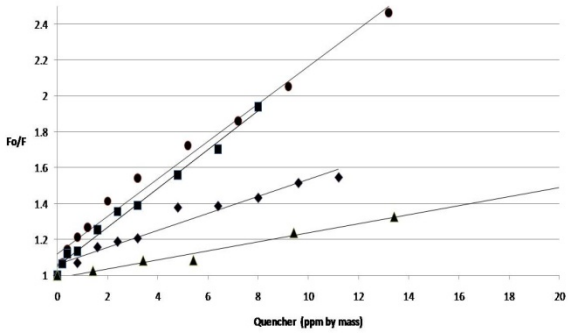

Figure. 3 Stern-Volmer plots of luminescence quenching of PSFF coated NPs suspended in water at varying percentages (ppm by weight) TNT and RDX. Legend: (PSFF adsorbed plain spheres with TNT ▲, PSFF coated C_{18} modified spheres with TNT ●, silane-PSFF coated plain spheres with TNT ■, silane-PSFF coated plain spheres with RDX ◆.

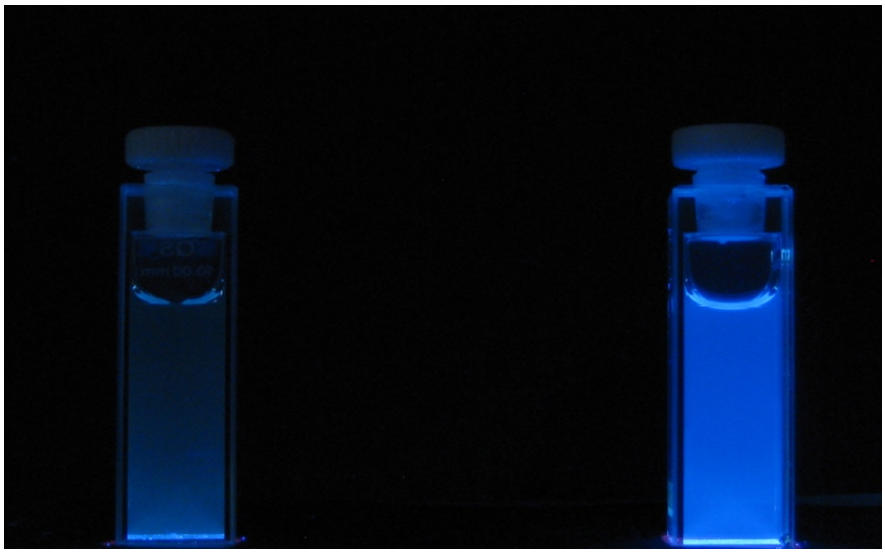

Figure. 4 Suspension of Silane-PSFF coated NPs (0.05 mg/mL, right) in PBS quenched by 40 ppm TNT (left) vs no added TNT (right) when irradiated with a UV lamp from below.

Reference

1. M. Ghasemi, M. Minier, M. Tatoulian, F. Arefi-Khonsari. *Langmuir* 2007, 23, 11554.