Broadband Light Absorption by Silver Nanoparticles Decorated Silica Nanospheres

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1. Synthesis of SiO₂ nanospheres

Monodispersed silica spheres having a uniform diameter distribution have been fabricated using a pioneering method reported by the Stöber et al. [1]. In the Stöber method, spherical silica nanoparticles of different sizes ranging from 50 nm to 1.5 μm were prepared through the hydrolysis of tetraalkylorthosilicate, e.g. tetraethylorthosilicate (TEOS), in a basic solution of water and alcohol, e.g. ethyl alcohol. Fig. S1 shows the structural characterization and size distributions of SiO_2 NPs prepared with methanol.
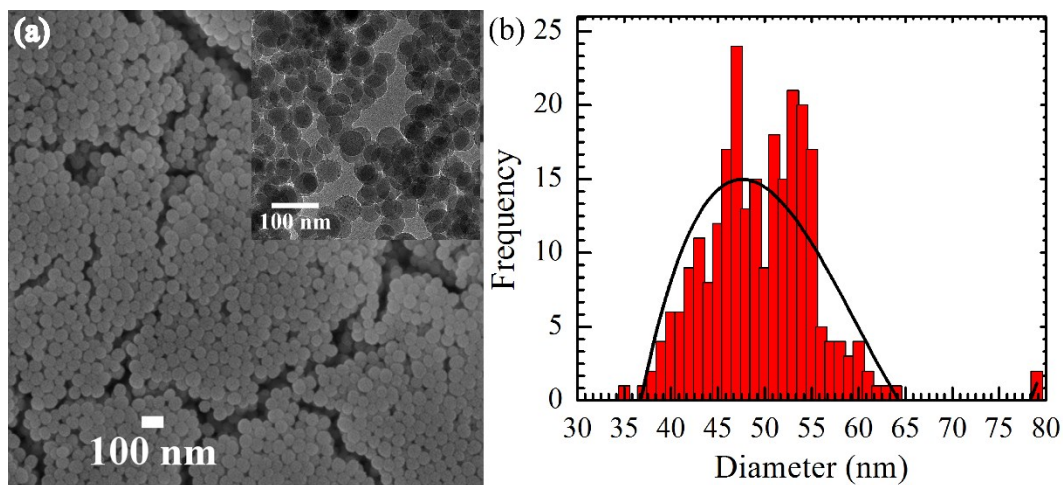

Fig. S1 (a) SEM and TEM characterization of SiO_2 NPs prepared with methanol and (b) histogram for the size distribution of nanoparticles. Histogram displayed a polinomial fit.

2. Synthesis of Ag NPs decorated SiO$_2$ nanospheres

Preparation of SiO$_2$@Ag NPs decorated nanospheres using SnCl$_2$.2H$_2$O

Fig. S2 illustrates the method for the decoration of Ag NPs on SiO$_2$ NSs using Sn^{2+} modification. In this synthesis method, silica nanospheres were mixed with SnCl$_2$.2H$_2$O aqueous solution for 1 h and then the mixture were centrifuged at 8000 rpm for 30 mins to remove unabsorbed Sn^{2+} and redispersed in 30 ml DI water. SnCl$_2$.2H$_2$O aqueous solution contained citric acid to avoid hydrolyzation of SnCl$_2$. In a typical synthesis recipe, 1 g SnCl$_2$.2H$_2$O and 0.9 g citric acid were added into 50 ml DI water. The pH for the solution was about 2.3. Then, 25 ml aqueous solution of silica nanospheres with concentration about 10mg/ml were added into the SnCl$_2$ solution and mixed for 1 h with gentle magnetic stirring. Finally, 30 ml Sn^{2+} modified silica colloids were added into 30 ml ammoniacal 0.05 M AgNO$_3$ solution and stirred for 30 mins. Silver nuclei decorated silica spheres were obtained through centrifugation at 8000 rpm and redispersed in 30 ml di water. To get the Ag NPs decorated silica nanospheres 2 ml 0.01M NaBH$_4$ aqueous solution were added as reducer.

Fig. S2 Schematic illustrations for the decoration of SiO$_2$ NSs with Ag NPs by modifying the silica surface with Sn^{2+}.

To increase the size of Ag NPs a second step called particle growth step was employed. For the particle growth step, two solutions were prepared and these are: solution A (prepared by mixing 0.12 g AgNO3, 0.1g Tri sodium citrate, and ammonia in a mixture of 20 ml DI water and 20 ml ethanol), solution B(prepared by mixing 20 ml ethanol and 1 ml formaldehyde solution). 5 ml of seed solution was diluted to 10 ml by adding 5 ml ethanol and then 10 ml Solution A was added under vigorous magnetic stirring. Finally, 2 ml of solution B was added under vigorous stirring for 5 mins. The final Ag NPs decorated SiO$_2$ NSs were collected through centrifugation at 7000 rpm and washed twice before re-suspending in DI water. The average diameter of the decorated Ag NPs were about 12 nm for sample S2 (Fig. S3).
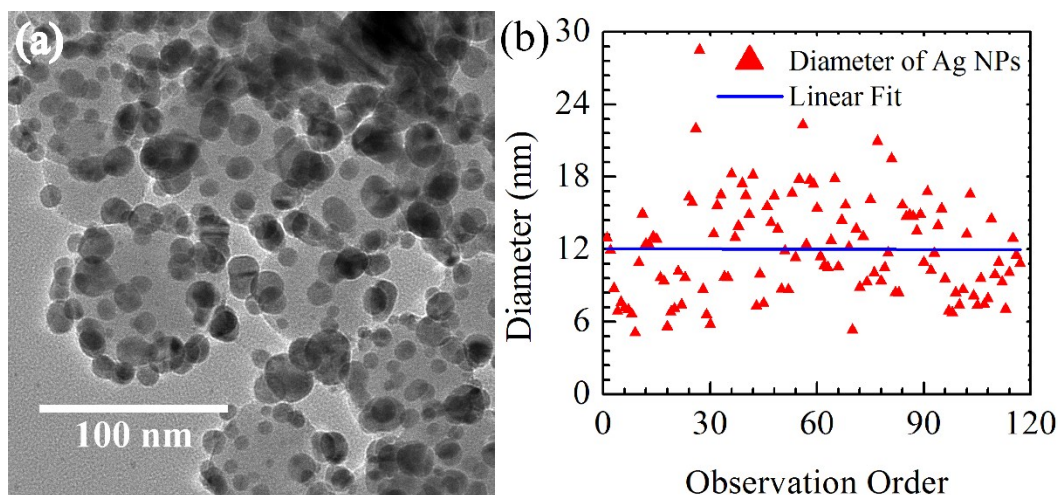
Fig. S3 (a) TEM image of the Ag NPs decorated SiO$_2$ NSs after particle growth step for sample S2 and (b) shows the corresponding size distribution of decorated Ag NPs.

Preparation of SiO$_2$@Ag NPs decorated nanospheres through APTES modification.

APTES functionalization on the surface of silica nanospheres: Amino-functionalized silica nanospheres were prepared by using a modified Stöber method [2]. In this method, 100 mg of SiO$_2$ NPs were dispersed in 100 ml DI water through ultrasonication and then 20 ml of this silica solution was mixed with 200µL of 28% aqueous ammonia solution under vigorous magnetic stirring. Finally, 1 ml of a 10% (V/V) APTES aqueous solution was added and the mixed solution was then stirred for 24 h under vigorous magnetic stirring. The suspension was centrifuged at 7000 rpm for 30 mins and washed with DI water for five times. Silica particle with APTES modified were resuspended in DI water through ultrasonication and 50µL of 0.1 M HCl was added to avoid agglomeration.

Ag NPs decoration: 5 ml of APTES modified silica particles solution were added to 15 ml of ammoniacal 0.05 M AgNO$_3$ solution and stirred for 5 mins for homogeneous co-ordination and then 100µL 0.01 M NaBH$_4$ solution was added for the reduction process to form Ag NPs. Finally, Ag NPs decorated silica nanospheres were centrifuged at 7000 rpm for 30 min and washed 2 times with DI water.

Preparation of SiO$_2$@Ag NPs decorated nanospheres through Cobalt (II) Nitrate hexahydrate modification.

In a typical experimental procedure, 0.25 g Cobalt (II) Nitrate hexahydrate was dissolved in 25 ml DI water and then 25 ml of aqueous silica solution (0.02 g/ml) was added under vigorous magnetic stirring and left for 30 mins for homogeneous co-ordination. Then 100 ml solution prepared by dissolving 0.038 g citric acid and 0.06 g NaBH$_4$ was then rapidly injected in to the solution a very light greenish color appeared. Finally the solution was centrifuged at 8000 rpm twice and re-dispersed in 100 ml DI water.

In order to decorate with Ag NPs, 10 ml of cobalt modified SiO_2 NSs was mixed with 50 ml solution of citric acid and $NaBH_4$ (0.038 g citric acid and 0.06 g $NaBH_4$ were dissolved in 200 ml of DI water). After several minutes when the bubble ceased to release from the reaction between the surpluses $NaBH_4$ with water, a 20 ml of 0.025 M $AgNO_3$ solution was added under gentle stirring. After 5 mins of stirring, 200 µL of freshly prepared $NaBH_4$ was added for the complete reduction. A deep green color appeared (S4) and the products were collected by centrifugation at 8000 rpm for 30 mins.

Preparation of SiO_2@Ag NPs decorated nanospheres through EDTA modification.

APTES modified SiO_2 NSs were modified with EDTA for the functionalization with negatively charged carboxylic group[3]. Amino-functionalized SiO_2 NSs were prepared by using a modified Stöber method [2]. In this method, 100 mg of SiO_2 NPs were dispersed in 100 ml DI water through ultrasonication and then 20 ml of this silica solution was mixed with 200µL of 28% aqueous ammonia solution under vigorous magnetic stirring. Finally, 1 ml of a 10% (V/V) APTES aqueous solution was added and the mixed solution was then stirred for 24 h under vigorous magnetic stirring. The suspension was centrifuged at 7000 rpm for 30 mins and washed with DI water for five times. Finally dried at 105°C for 4 h.

In order to obtain EDTA modified SiO_2 NSs, 0.25 g of APTES modified SiO_2 NSs were mixed with a solution of 0.25 g EDTA in 20 ml ethanol and acetic acid (1:1) and stirred at 76°C for 16 h. The suspension was centrifuged at 7000 rpm and washed twice and dried at 100°C for 1 h.

In a typical experimental procedure for the ring like arrangement of Ag NPs on EDTA modified SiO_2 NSs, two solution was prepared. Solution 1: 0.15 g cobalt (II) Nitrate hexahydrate was dissolved to 15 ml of DI water and solution 2: 0.12 g $NaBH_4$ and 0.076 g citric acid were dissolved in 200 ml of DI water and left for aging until bubbles disappear. EDTA modified SiO_2 NSs were dispersed in solution 1 through ultrasonication for 30 mins. Then 100 ml of solution 2 was added rapidly under gentle magnetic stirring. Finally, 50 ml of 0.025 M ammoniacal $AgNO_3$ was rapidly and stirred for 15 min before adding 5 ml of 0.01M $NaBH_4$ solution for the complete reduction. Resultant ring like Ag NPs decorated SiO_2 NSs (Fig. S4) were collected through centrifugation at 7000 rpm for 15 mins and washed twice with DI water.
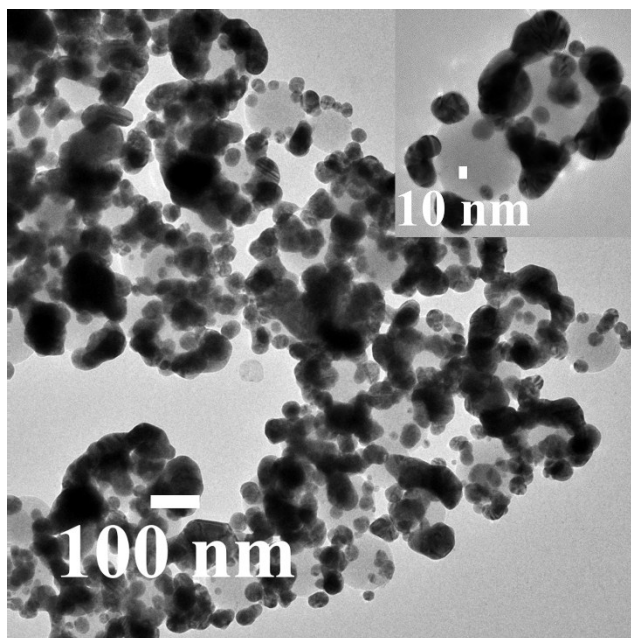
Fig. S4 TEM image of ring like Ag NPs decorated SiO$_2$ NSs.

Preparation of SiO$_2$@Ag NPs decorated nanospheres through Hydrothermal Loading.

Fig. S5 shows the Schematic illustrations for the hydrothermal decoration of SiO$_2$ NSs with Ag NPs. This method, firstly, involves the preparation of stock solution by dispersing 100 mg SiO$_2$ in 30 mL of ethanol. Then, a silver solution was prepared by adding 0.1g of AgNO$_3$ into water-ammonia solution (2.5 mL DI water and 0.2 mL ammonia). Afterwards, 1g PVP was added into 13 mL of the stock solution. To this suspension, 2.7 mL of AgNO$_3$ (0.22mM) were added drop wise under magnetic stirring and maintained 30 mins to allow a homogeneous coordination of the silver ions with the amine surface moieties. The mixed solution (15 mL) was transferred into a Teflon-lined stainless steel autoclave (20 mL) and heated at 120°C for 12 h in an electric oven.
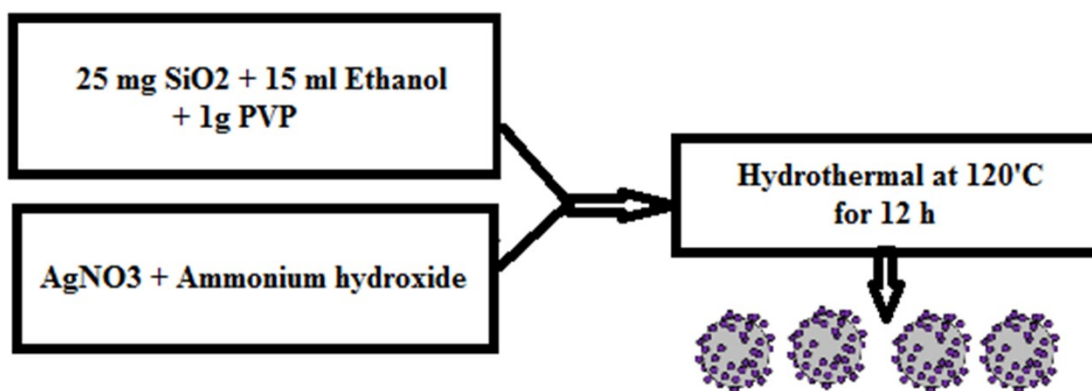

Fig. S5 Schematic illustrations for the hydrothermal decoration of silica nanospheres with Ag NPs.

3. 3D-FDTD modelling to calculate SPR line spectra

SPR line spectra due to the response of Ag NPs decorated silica spheres to a plane wave excitation was evaluated with the finite-difference time-domain (FDTD) method using Lumerical FDTD Solutions v8.5.4. The geometries considered here varies with silica core radius, number of Ag NPs on the silica surface, and the size of Ag NPs. The Ag NPs were considered to be spherical on top of silica sphere. The modeled geometry was placed in water environment with refractive index 1.33 and illuminated by a plane wave. All the simulation were performed with the modeled silica core as 33, 38, 38.5, 45, 46, 50, 55 nm radius sphere and the radius of Ag NPs to be 1.5, 2.5, 3, 3.75, 4, 4.5, 5, 6, 7, 8, and 21 nm. All simulations were performed with a mesh size of 0.5 nm and subjected to a plane-wave illumination at 250 different wavelengths between 300 nm and 1600 nm. The materials property data for silver reported by Palik [4] was used and the refractive index of SiO_2 was approximated as 1.45 and taken constant over the wavelengths.

In order to calculate extinction efficiency (Q_{ext}) that evaluates the nanoparticle's ability to concentrate light in the interior of the surrounding environment, for example water, following equation has been used relating extinction cross-sections with the Q_{ext}.

$$Q_{ext} = \frac{Extinction\ Cross-\sec tions}{\pi(R_c + 2 \times R_{Ag})^2}$$ ………………………. (eq. S1)

Where R_c is the radius of the silica core and R_{Ag} is the radius of the Ag NPs on the surface of the silica nanospheres. Fig. S3 shows the SPR line spectra obtained by the finite-difference time-domain (FDTD) method for the experimental sizes. Table S1 summarizes all the details of the experimentally synthesizes sizes of Ag NPs decorated silica nanospheres and the peak position at maximum extinction efficiency obtained from UV-vis-NIR absorption spectra and 3D-FDTD method.
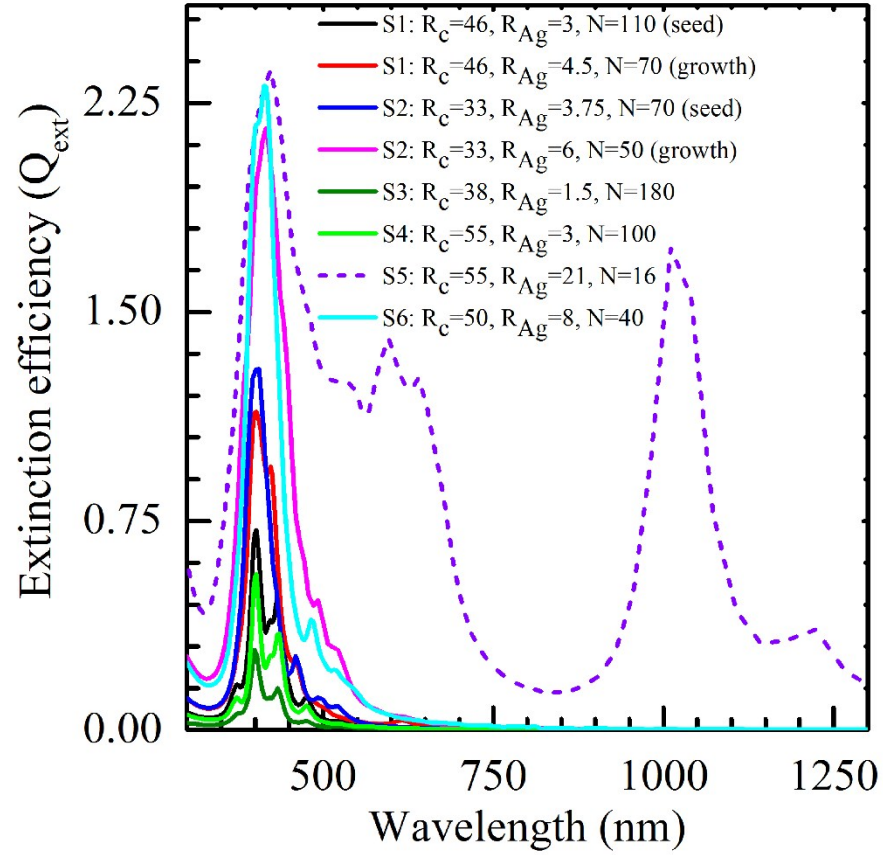
Fig. S6 Calculated extinction spectra of N silver NPs decorated on silica nanospheres obtained by 3D-FDTD study for experimental sizes. A single nanosphere decorated with Ag NPs was surrounded with water of refractive 1.33.

Table S1: Experimental and 3D-FDTD calculated positions of the SPR peak for the as-synthesized structure.

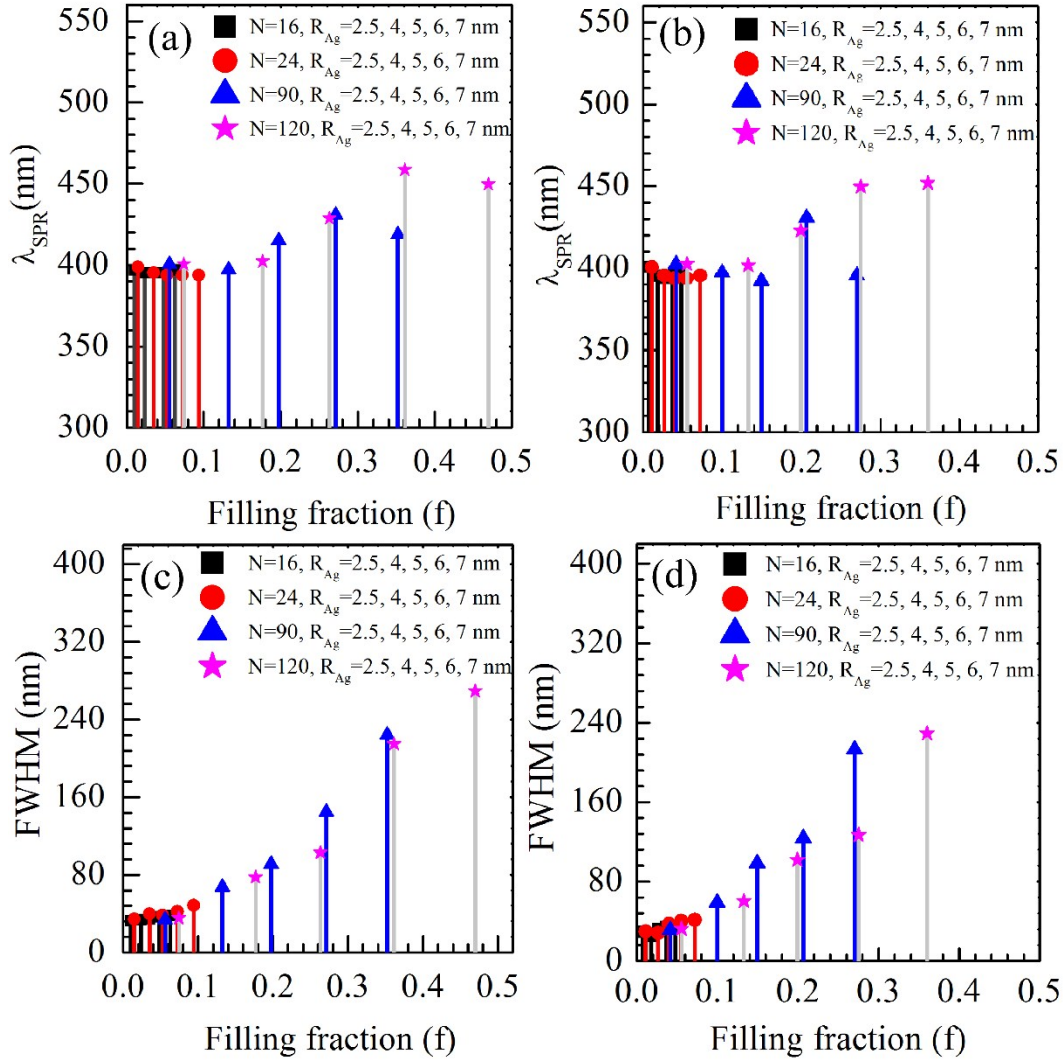| Samples	N	R_avg (nm)	R_c (nm)	Calculated filling factor(f)	Calculated SPR peak position (nm)	Maximum extinction efficiency (Q_ext)	Experimental SPR peak position (nm)
S1(seed)	110	3	46	0.0686	401.253	0.719	409
S1(particle)	70	4.5	46	0.0924	401.253	1.142	403
S2(seed)	70	3.75	33	0.1211	405.528	1.296	396
S2(particle)	50	6	33	0.1957	415.277	2.159	426
S3	180	1.5	38	0.0432	399.163	0.288	394
S4	100	3	55	0.0446	399.038	0.545	406
S5	16	21	55	0.1985	422.691	2.368	423
S6	40	8	50	0.1260	413.109	2.312	421

Fig. S7 Calculated positions of the SPR peak for the maximum extinction efficiency as a function of the filling fraction. Every color represents five different sizes of Ag NPs for a specific N and R_c that causes an increase in the filling factor. (a) Represents the changes in SPR peak position with filling factor for R_c=38.5 nm. (b) Represents the changes in SPR peak position with filling factor for R_c=45 nm. (c) Shows the FWHM that can be achieved with R_c=38.5 nm for a filling factor. (d) Shows the FWHM that can be achieved with Rc=45 nm for a filling factor.

Reference

1. Stöber, W., A. Fink, and E. Bohn, Controlled growth of monodisperse silica spheres in the micron size range. Journal of colloid and interface science, 1968. **26**(1): p. 62-69.
2. Watanabe, S., et al., Flow Synthesis of Plasmonic Gold Nanoshells via a Microreactor. Particle & Particle Systems Characterization, 2015. **32**(2): p. 234-242.
3. Repo, E., et al., Removal of Co (II) and Ni (II) ions from contaminated water using silica gel functionalized with EDTA and/or DTPA as chelating agents. Journal of hazardous materials, 2009. **171**(1): p. 1071-1080.
4. Palik, E.D., Handbook of optical constants of solids. Vol. 3. 1998: Academic press.