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Supporting information

Controllable synthesis silicon nano-particles by a one-step PECVD-IL method

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Experimental

Four imidazolium based ionic liquids (Cheng Jie Chemical Co. purity ~99%) with various lengths of alkyl-chain (structures are shown in Fig.S1) were used in this work. The ionic liquids were pre-dried in vacuum before the PECVD deposition.

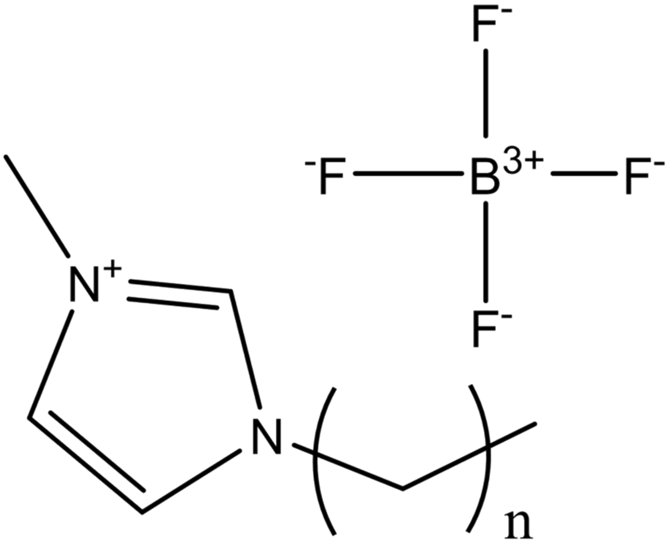
The synthesis of SiNPs by PECVD-IL method was carried out in a home-made cluster RF-PECVD apparatus. For each experiment, about 2.5 mL ionic liquid was added into a metal petri-dish (5.0 cm diameter, 0.5 cm height) that was placed on top of the substrate holder to collect the SiNPs. SiH_4 (~5%) diluted in H_2 was applied as the reaction gas. The vacuum level was maintained at 133 Pa for all sample deposition processes.

For the comparison, samples were prepared by hot-wire CVD (HWCVD) process. Tungsten wire (Alfa Aesar, Purity>99.95%, 0.5 mm in diameter and about 15 cm in length) was used as hot-wire which was fixed 4.0 cm above the substrate. The temperature of hot-wire was monitored by a two-color infrared pyrometer (Raytek, MR1SCCF) and was kept at 1700 ℃ for all samples. The deposition pressure of the HWCVD process was set at 20 Pa.

For transmission electron microscopy (TEM) measurements, the as deposited IL was pre-treated in an ultra-sonic machine before diluted in ethanol. The solution was then dripped on a carbon-coated copper grid for the TEM measurements. A TEM (Hitachi HT 7700, operating at 100 kV) was used to analyse the morphology of the SiNPs synthesized using the PECVD-IL method. The size distribution of the SiNPs was obtained by measuring ~300 SiNPs in randomly chosen area of several micrographs. High-resolution TEM images were obtained on a TECNAI F30 S-Twin (FEI Company) with an accelerating voltage of 300 kV. The crystallographic analysis of the SiNPs was based on PDF ICDD 75-0841 database.

Figure S1

Structural formula of ionic liquid applied in this research.



Ionic Liquid	Abbreviation	n
Ethyl-MIm-BF$_4$	EMIm-BF$_4$	1
Butyl-MIm-BF$_4$	BMIm-BF$_4$	3
Hexyl-MIm-BF$_4$	HMIm-BF$_4$	5
Octyl-MIm-BF$_4$	OMIm-BF$_4$	7
Decyl-MIm-BF$_4$	DMIm-BF$_4$	9

Figure S2

Optical photograph of OMIm-BF4 ionic liquid after PECVD treatment, and the scheme of SiNPs within IL.

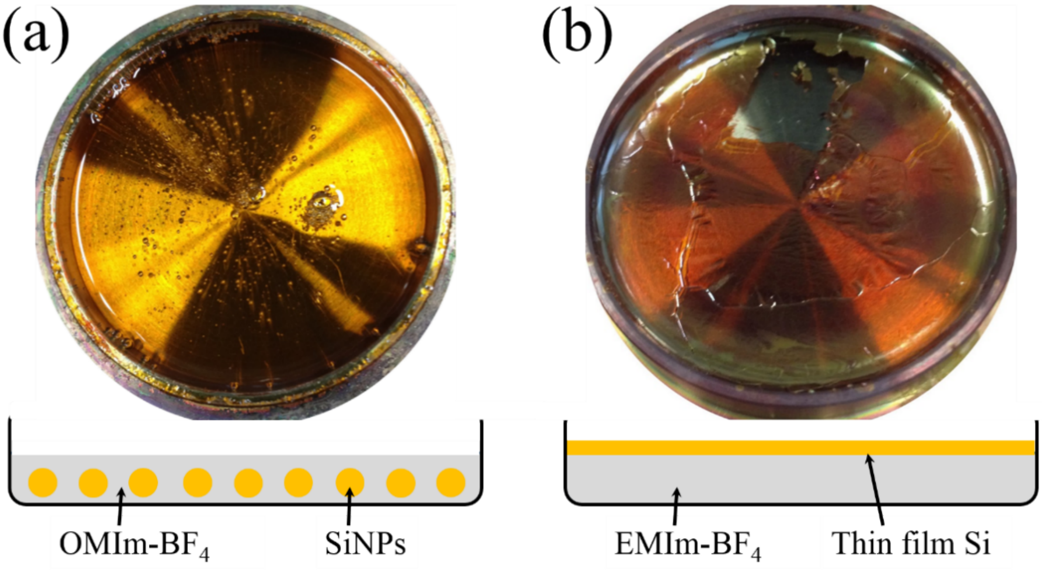


Figure S3

SEM images of thin film Si deposited on glass substrate, with RF power at 150 W.

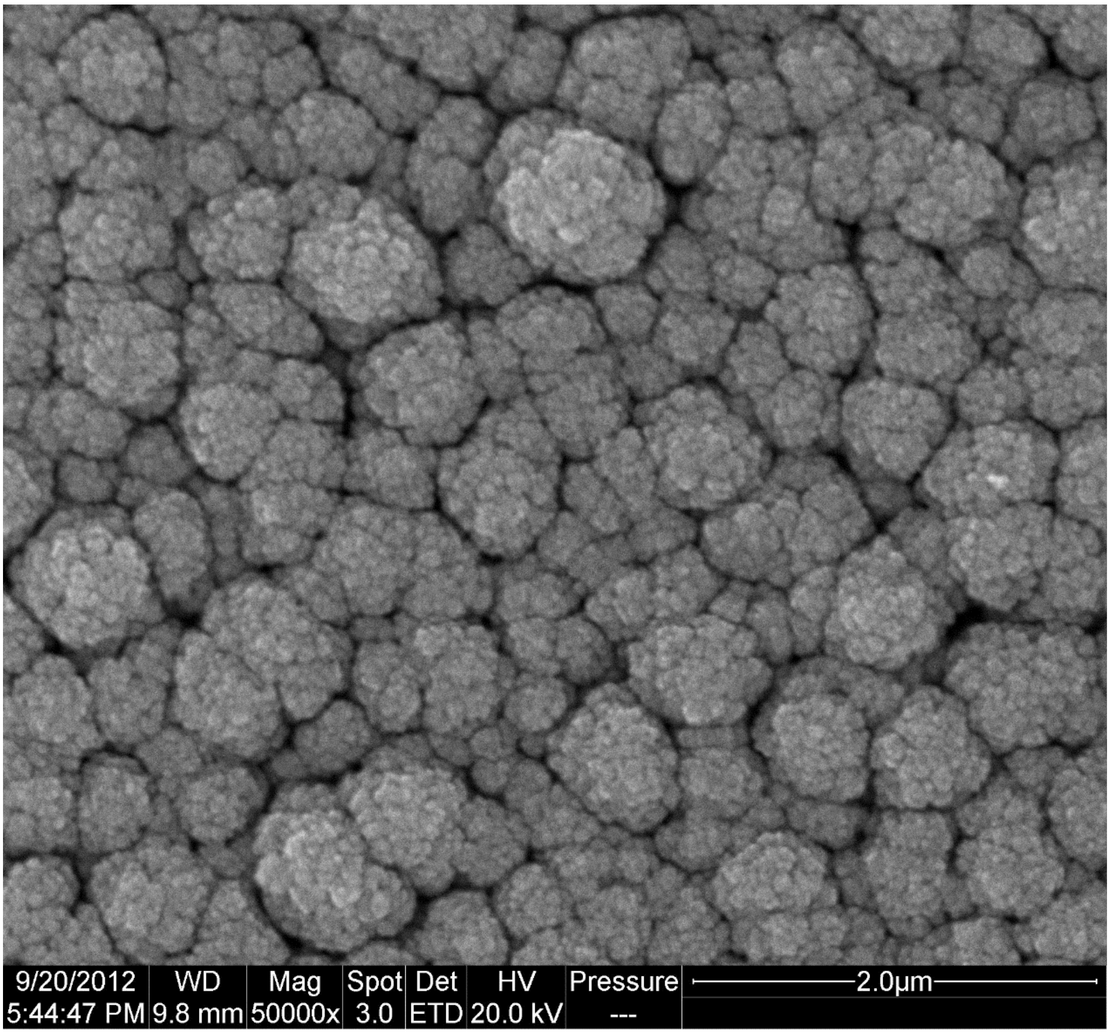
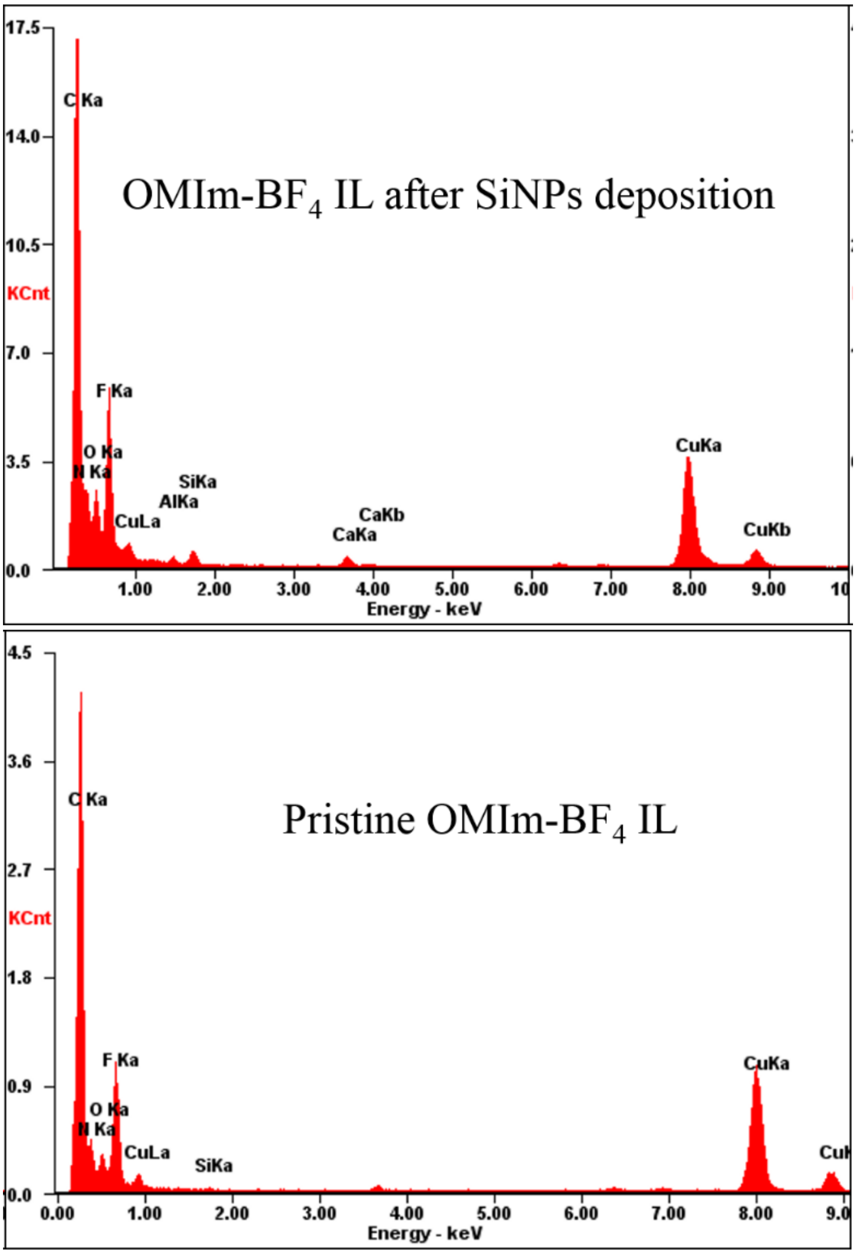


Figure S4

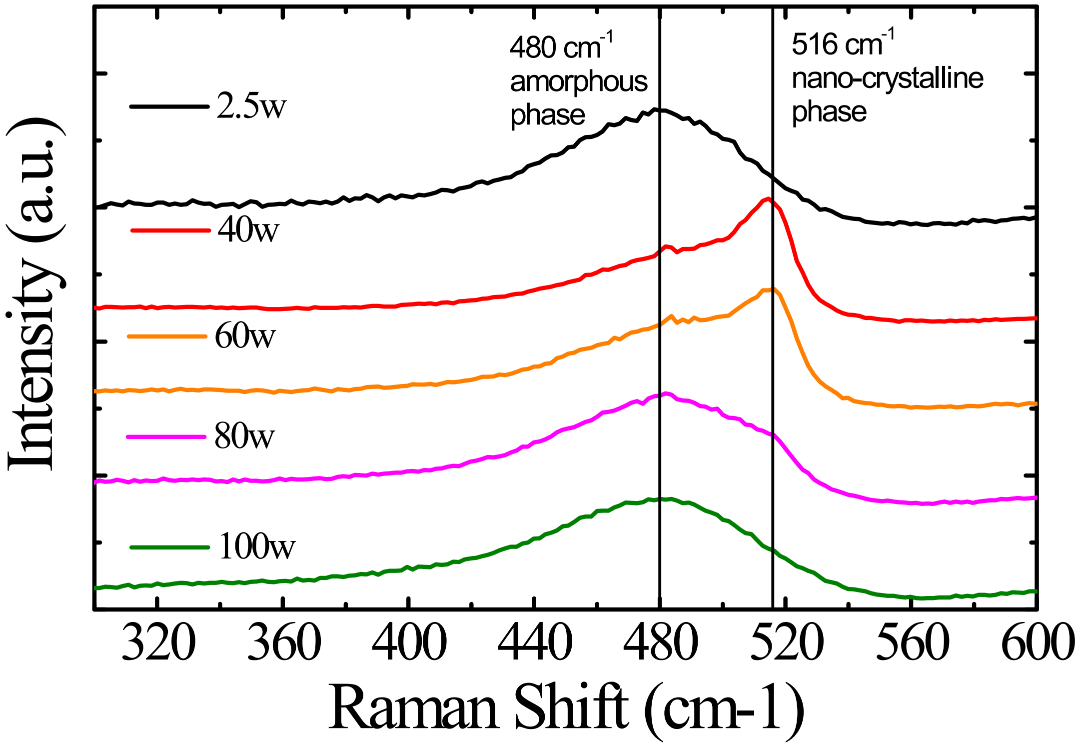
For EDX analysis, the sample was 5 times diluted in ethanol and passed through a 220 nm syringe filter, the solution was then dropped on Cu mesh for TEM observation.



EDXA results obtained from TEM showed confirmed signal of Si, this result suggested that Si was actually deposited into the ILs and therefore the SiNPs was synthesized. Meanwhile the signal of C, F, N were attibutted to the OMIm-BF$_4$ ionic liquid, other signals were obtained from sample holder.

Figure S5

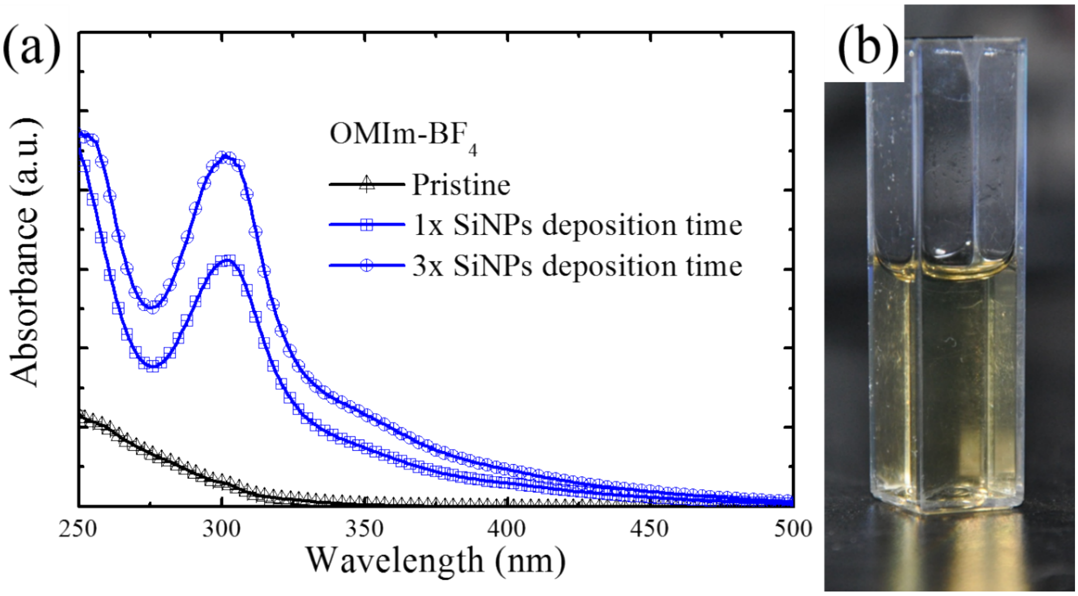
Raman spectra were collected using Renishaw inVia Raman Spectrometer excited by a solid laser (exciting wavelength is 532 nm), the spectra resolution is 1.5-2.0 cm-1.



The Raman spectral of thin film Si fabricated by PECVD under various RF power, our result indicate the thin film Si was amorphous under a low RF power of 2.5 W and increased prominently as RF power increased to 40 W. As the RF power further increased, the crystallinity of thin film Si was gradually decreased and pure amorphous thin film Si was obtained when RF power was increased to 100 W.

Figure S6

UV-Vis spectral of SiNPs were obtained on Varian Cary 5000 spectrometer, the as deposited IL was diluted 100 times in ethanol and solution was injected into a quartz cuvette for measurement, empty cuvette was used for baseline measurement.

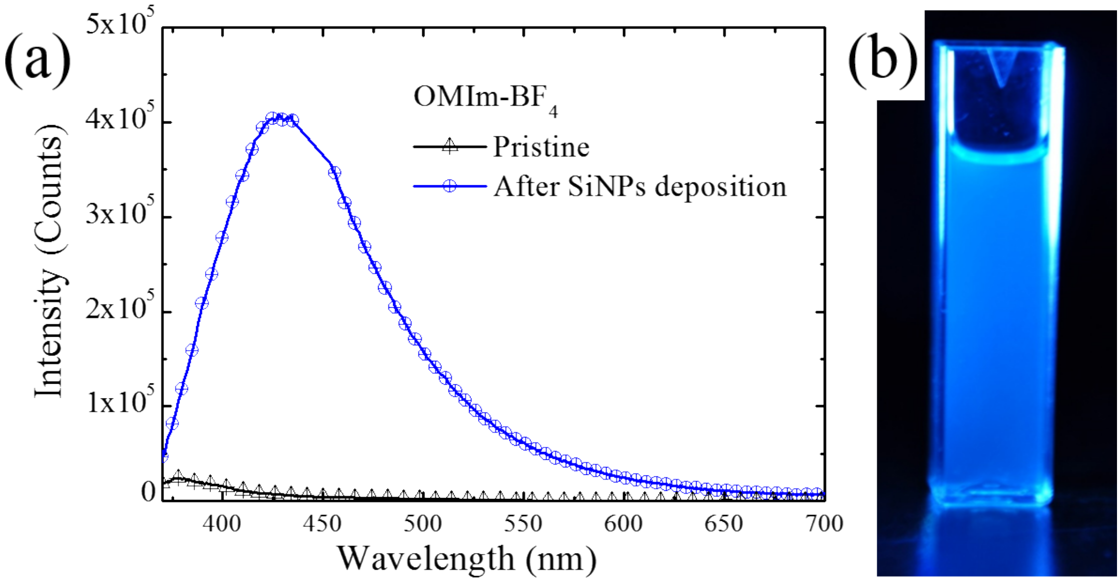


(a) Comparison between the UV-Vis spectral of pristine OMIm-BF4 ionic liquid and which after SiNPs deposition.

(b) Photograph of a sample for UV-Vis measurement.

Figure S7

Steady-state photoluminescence (PL) spectral were obtained on an FLS920 fluorescence spectrometer (Edinburgh Instruments) in air at room temperature. A 450 W Xe lamp was used as the excitation source. A 400 nm low-pass filter and a 370 nm high-pass filter were installed on the optical path of incident light and emissive light, respectively.

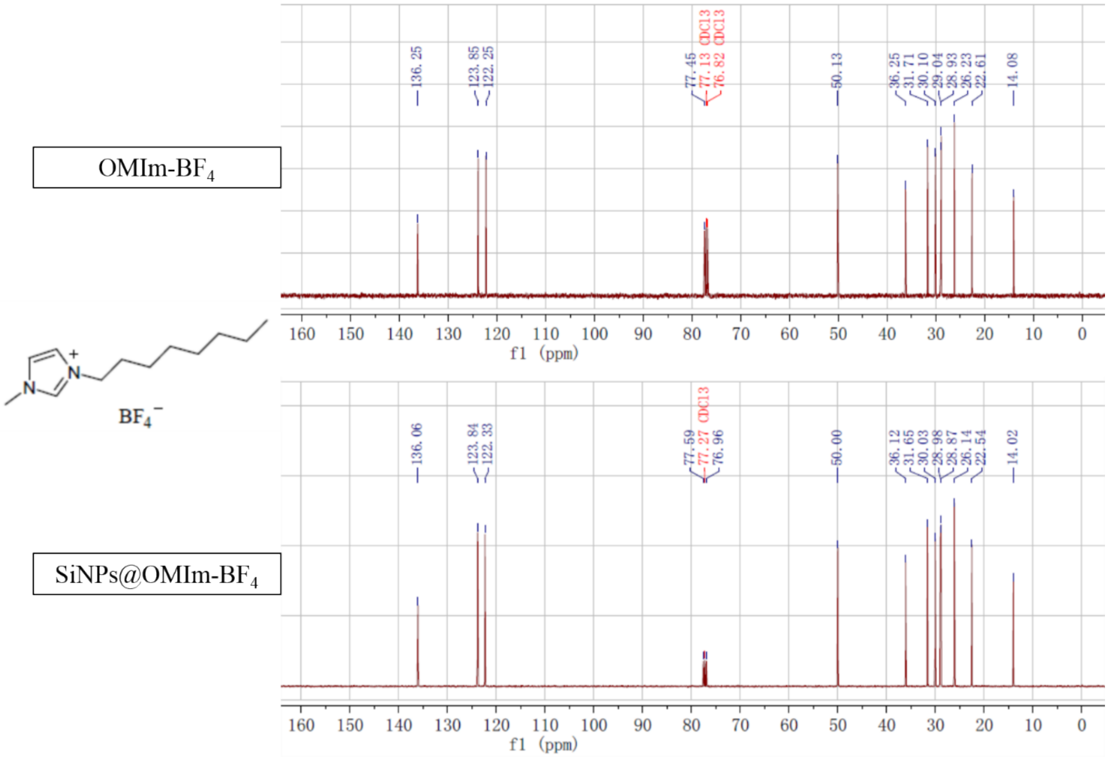


(a) Comparison of photoluminescence spectral between the pristine OMIm-BF$_4$ ionic liquid and which after SiNPs deposition.

(b) Ionic liquid after SiNPs deposition showing strong photoluminescence under 325 nm UV light illumination.

Figure S8

The NMR spectral were recorded on a Bruker 400MHz NMR spectrometer, with samples diluted in $CDCl_3$. The chemical shifts for ^1H NMR were recorded in parts per million (ppm) downfield from tetramethylsilane (TMS) with $CDCl_3$ (7.26 ppm) as the internal standard. The chemical shifts for ^{13}C NMR were recorded in parts per million (ppm) downfield using the central peak of $CDCl_3$ (77.16 ppm) as the internal standard.



Comparison between the ^{13}C-NMR spectral of pristine OMIm-BF4 ionic liquid with which after SiNPs deposition.

Figure S9

Size distribution and fitted gauss distribution of SiNPs synthesized with various distance between RF electrode and IL substrate (d_e) by PECVD-IL method.