

# Stable colloidal dispersion of luminescing silicon nanoparticles for ink-jet printing

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## ABSTRACT

Over the past years, printing technologies have attracted considerable attention due to the possibility of manufacturing low cost printable electronic devices. Therefore, a high industrial demand exists on stabilized dispersions of nanoparticles in aqueous as well as non-aqueous solvents. In this study, we synthesize silicon nanoparticles (Si-NPs) in a gas phase microwave plasma reactor. The surface of Si-NPs is modified with organic ligands using thermally induced hydrosilylation. The particles with modified surface can be readily dispersed in a variety of organic solvents and the dispersion is stable for months. The stable Si-NP ink is used to print structures on glass substrate using ink-jet printing.

**Keywords:** silicon nanoparticles, ink-jet printing, colloidal dispersion, surface functionalization

## 1 INTRODUCTION

From the point of view of cost, availability, non-toxicity and potential for integration into existing technologies, silicon is considered to be a highly desirable material for optoelectronics. However, scientists turned their interest to more complex semiconductors such as GaAs because bulk silicon has poor optical properties due to its indirect band gap. Right after the discovery of efficient light emission from porous silicon, the interest in silicon nanomaterial has drastically increased. Silicon nanomaterial with crystalline structures of size less than 5 nm exhibits enhanced photoluminescence (PL) in the visible regime. The enhanced PL from nanosized silicon is believed to be the result of quantum confinement effects [1, 2]. Variety of techniques have been developed to synthesize nanosized silicon, for example, solid gas reaction [3], liquid phase synthesis [4, 5], reaction in micelles [6, 7], ion implantation of silicon into a SiO<sub>2</sub> matrix [8], gas phase synthesis using CO<sub>2</sub> lasers [9, 10] and radio frequency plasma synthesis [11, 12].

In recent years, printing technology has attracted considerable attention due to low cost printable electronics, such as solar cells [13], transistors [14] and full color displays [15]. For the manufacturing of silicon based electronic and

optoelectronic devices using printing technology, the stable colloidal dispersions of silicon nanoparticles (Si-NPs) is highly desirable. However, the printing of Si-NPs has not received much attention because of the lack of efficient routes to form a stable silicon ink.

In the present work, we synthesize free standing Si-NPs by decomposition of silane (SiH<sub>4</sub>) using a gas phase microwave plasma reactor. The surface of Si-NPs was grafted with organic molecules via liquid phase hydrosilylation. Organically capped Si-NPs form a stable dispersion in many organic solvents. The stabilized dispersion of luminescing Si-NPs was used to fabricate thin films using ink-jet printing.

## 2 EXPERIMENTAL

Si-NPs were synthesized in a microwave plasma reactor by thermal decomposition of silane (SiH<sub>4</sub>). The experimental setup is schematically depicted in figure 1. In the synthesis approach, the precursor (1% SiH<sub>4</sub> in Ar) and dilution gases (Ar and H<sub>2</sub>) were injected coaxially into a quartz glass tube and microwave energy was used to ignite plasma. The plasma causes the pyrolysis of SiH<sub>4</sub> and Si-NPs are formed by nucleation and growth processes. The details of Si-NPs formation have been described elsewhere [16]. The surface etching of Si-NPs was carried out inside a glove box. In a typical experiment, 40 mg of Si-NPs were dispersed into 5 ml of ethanol using mild sonication. Thereafter, a mixture of HF and HNO<sub>3</sub> (10/1 v/v) was added to the dispersion. With this etching procedure, the PL emission of Si-NPs can be tuned across the visible spectrum [17, 18]. After etching, the particles were filtered on a polyvinylidene fluoride (PVDF) membrane filter (pore size 0.1 μm) and washed with ethanol to remove traces of the acids. Subsequent surface functionalization was accomplished by a thermally induced hydrosilylation process [19], where the freshly etched Si-NPs were immersed in alkene and the dispersion was heated at 120°C for 10h. The FTIR spectra of Si-NPs were recorded in diffuse reflectance mode using a Bruker IFS66v/S spectrometer. The PL measurements were carried out at room temperature using a diode-laser as an excitation source operated at a wavelength of 405 nm.

Stable dispersions of functionalized Si-NPs were used to fabricate films on glass substrates using a Dimatix 2800 ink-jet printer.

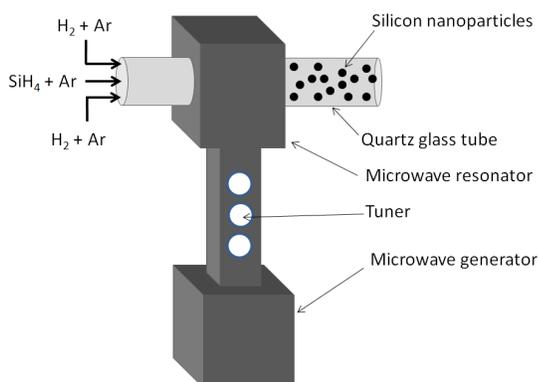


Figure 1: Schematic of the experimental setup for the synthesis of Si-NPs in a microwave plasma reactor.

### 3 RESULTS AND DISCUSSION

The FTIR spectra of as-prepared and freshly etched Si-NPs are presented in figure 2. The spectrum of as-prepared sample (spectrum “A”) displays strongest characteristics from SiOSi stretching mode at  $1068\text{ cm}^{-1}$  and at  $1180\text{ cm}^{-1}$ . Another sharp feature at  $2260\text{ cm}^{-1}$  [20] is observed, which originates from Si-H stretching vibration in  $\text{SiHO}_3$  configuration.

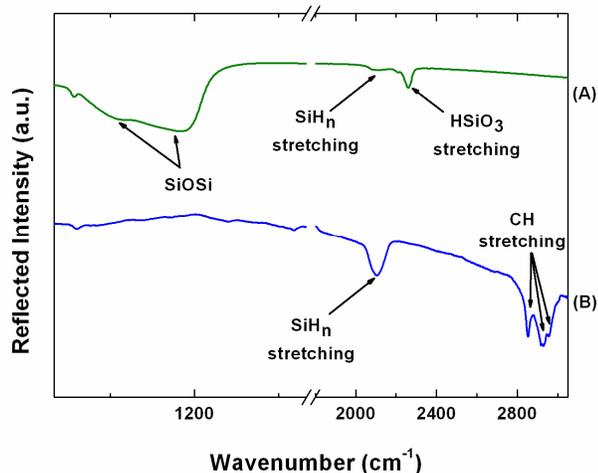


Figure 2: FTIR spectra of as-prepared (spectrum A) and freshly etched Si-NPs (spectrum B).

The oxide signals are present in the as-prepared samples because the material was in contact with air for months. A small intensity of pure  $\text{SiH}_n$  ( $n = 1, 2, 3$ ) stretching vibration around  $2100\text{ cm}^{-1}$  [21] was also observed in as-

prepared samples, indicating that not all Si-H bonds have not been attacked by oxygen. After the etching of as-prepared Si-NPs (spectrum “B”), an intense signal from  $\text{SiH}_n$  vibration was observed and no signature from oxides was noticed. This confirms that the etching process completely removes surface oxides and also terminates the silicon surface with hydrogen. Some sharp aliphatic  $\text{CH}_y$  stretching bands in the region of  $3000 - 2855\text{ cm}^{-1}$  [22] also appeared in freshly etched samples, which might originate from attached ethanol molecules on the silicon surface [23].

The subsequent surface functionalization of freshly etched Si-NPs is carried out using thermally induced hydrosilylation. After functionalization, the NPs were separated from the respective alkene solution by centrifugation, then washed with methanol and dried in vacuum. Figure 3 shows the FTIR spectrum of Si-NPs after grafting of dodecyl molecules on their surface. Together with the characteristic peaks of dodecyl molecules, a small intensity of  $\text{SiH}_n$  stretching vibration can also be seen in the spectrum. This indicates that not all Si-H bonds on the silicon surface were replaced by alkyl groups because the initially attached alkyl groups on the silicon surface provide an increasing steric hindrance for further attachment of organic molecules. The functionalized Si-NPs show very high luminescence compared to as-prepared particles [24]. Additionally, the functionalized particles show stable luminescence for months as the organic ligands on the Si-NPs surface provide an efficient passivation against oxidation.

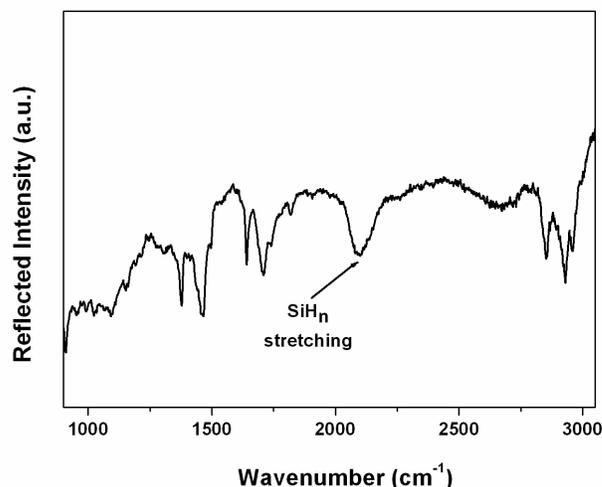


Figure 3: FTIR spectrum of dodecyl terminated Si-NPs.

The functionalized Si-NPs form a very stable dispersion in a variety of common organic solvents because the organic ligands attached on the surface of silicon provide a very good dispersability and long-term stability in organic solvents. The organic dispersions of functionalized Si-NPs can be stored in air for months without any sedimentation of particles. Figure 4 shows the pictures of pure chloroform

(vial “A”) dispersions of functionalized Si-NPs in chloroform (vial “B”) under ambient light (Fig. 4a) and UV illumination (Fig. 4b). The vial with the transparent Si-NPs dispersion shows bright red luminescence upon excitation of Si-NPs with UV light ( $\lambda = 366$  nm), whereas, no luminescence can be seen from the pure solvent.

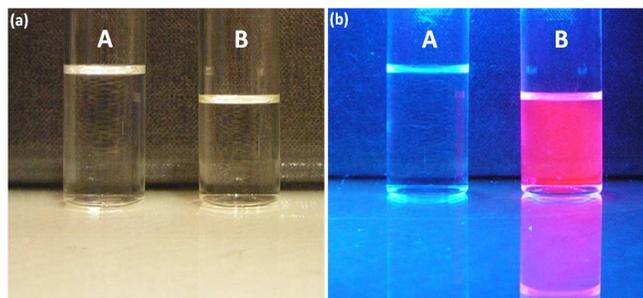


Figure 4: Pure chloroform (vial “A”) and chloroform dispersion of dodecyl terminated Si-NPs (vial “B”) under (a) normal daylight and (b) UV illumination.

In order to produce a stable Si-NP ink with high concentration of luminescing particles and mechanical stability of the printed layer, Si-NPs with diameter around 5nm were etched with HF acid. Thereafter, the surface of freshly etched Si-NPs was terminated with ethyl undecylenate molecules as it provides long-term stability compared to dodecene [25]. The dispersion of ethyl undecylenate terminated Si-NPs also shows very bright luminescence under UV illumination. Figure 5 shows the PL spectrum of ethyl undecylenate terminated Si-NPs at room temperature. The functionalized particles show a broad emission with its maximum around 660 nm.

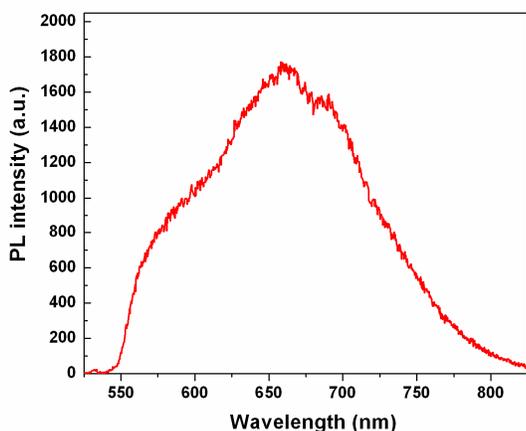


Figure 5: Photoluminescence spectrum of ethyl undecylenate terminated Si-NPs.

We used the stable dispersion of ethyl undecylenate terminated Si-NPs to print multiple transparent layer of a structure on a glass substrate. The printing was carried out at 13 V and a frequency of 3 kHz in a layer-by-layer fa-

shion. Figure 6 shows a Scanning Electron Microscopy (SEM) image of nine layer of a printed structure “G” and a photograph of the respective structure under UV illumination. The luminescence color of the printed structure can hardly be seen under UV illumination because of the high intensity of the reflected UV light, but measurements with high spatial resolution verified that the luminescence spectra of the dispersion and the printed layer are identical.

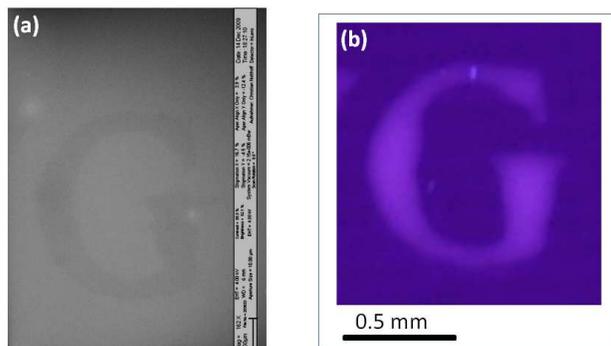


Figure 6: (a) SEM image of printed Si-NPs structure on glass substrate, (b) photograph of the printed structure under UV illumination.

## 4 CONCLUSION

The functionalized Si-NPs form optically clear dispersions in a variety of organic solvents and no sedimentation of functionalized sample was observed over any period of time. The dispersion of highly stable Si-NPs was successfully used to print layers on glass substrate using ink-jet printing.

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