論 文 の 内 容 の 要 旨

論文題目　Synthesis of photoluminescent silicon nanoparticles by plasma-CVD
（プラズマCVDによる蛍光シリコンナノ粒子の合成）

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Chapter 1 (Introduction)

Photoluminescent semiconductor nanoparticles can show excellent optical properties compared with organic dyes or fluorescent proteins. There is increasing attention being focused on nanoscale materials in the fields of optoelectronics and biolabeling. Chalcogenide (e.g. CdSe, PbSe) semiconductor nanoparticles have been the subject of much fundamental and applied research. However, the presence of heavy metals and the consequent toxicity of these materials has restricted their application. In the past years, photoluminescent nanometer-scale silicon was reported and has been closely studied based on its potential novel optical properties. Synthesis of silicon nanoparticles (Si-NPs) have also been reported by different methods, like solid, liquid or gas phase reactions. However, particle synthesis with full-color of photoluminescence (PL) is still a challenge. Of those methods, gas phase synthesis has the advantages of rapid and continuous production. However, the main precursor for gas phase synthesis is silane, and the preparation has to be followed by surface modification using wet chemistry to ensure stability of the resultant nanocrystals. It is worth examining other precursors for the synthesis of Si-NPs to assess their practicality. Furthermore, due to the outstanding optical property and low cytotoxicity, Si-NP shows promising application for bio-imaging agent and the *in vitro*/*vivo* imaging is undergoing. However, there is not yet sufficient understanding of the properties of Si-NPs as selective bio-labels. There is therefore a need for new simple synthetic routes to water-dispersible Si-NPs and for further study of the fundamental properties of these NPs as bio-labeling probes.

In this thesis, we will focus on synthesis and application of photoluminescent Si-NPs. RF-plasma was used to decompose $SiBr_4$. Firstly, the research background and current progresses are introduced (Chapter 1). The synthesis procedure was listed after the general introduction and the synthesized product was characterized from the aspect of surface component, size, crystallinity, optical properties and stability (Chapter 2). The parameters in

terms of particle formation, which may affect crystal size and optical properties, were discussed in Chapter 3. In Chapter 4, cell-imaging application of Si-NPs was investigated after surface modification process to obtain water-dispersible Si-NPs. Finally, conclusion and future prospects are given in Chapter 5.

Chapter 2 (Synthesis of silicon nanoparticles using plasma-CVD)

Si-NPs were synthesized from rf (13.56 MHz radio frequency) plasma. In brief, the precursor material was introduced into the chamber via an Ar gas carrier passing through liquid $SiBr_4$. H_2 was also introduced as a reducing agent along with the inert argon carrier gas. The plasma power density was fixed at 1.25 W/cm^2. The flow rate of $SiBr_4$ and H_2 were 1–3 and 20 sccm respectively. To obtain tunable PL colors, the total pressure in the chamber was controlled in 2–4 Torr. Nanoparticles exhibiting blue emission, which were obtained at 3 Torr, were used for characterization. The synthesized particles are considered to be surface oxidized and the surface Si–O–Si bonding was confirmed by FTIR. High magnification images of crystals and the electron-diffraction patterns are observed from TEM.

The optical properties were investigated. UV-vis absorption shows a shoulder near 360 nm, whereas the PL spectrum shows emission with a peak at 470 nm when excited at 340 nm. The optical stability is another important issue which directly relates to the applications. We took a number of PL measurements using a single sample over half a year. From the integrated peak areas of the PL spectra, we found that the PL intensity declined by 20% in the first 14 days and then remained almost constant for the following 200 days. We consider that the observed PL stability is caused by the protected surfaces of the silicon nanoparticles. The photostability of the nanoparticles-ethanol suspension was also checked. The PL retains 80% of the initial intensity after 3 hours irradiation. This result is quite important for cell-imaging applications, especially for those long-term measurements such as observation of the cell division. The quantum yield was also measured by compared with Rhodanmine 6G under the same excitation wavelength and showed as high as 24%.

Chapter 3 (Formation mechanism of silicon nanoparticles with different fluorescent colors)

The synthesis parameters were investigated to reveal the key factors for particles formation. Plasma power was firstly examined. As increasing of the power, increasing of the

crystallinity was observed in our system. When the power during synthesis is set at 50 W, the products are amorphous silicon. Whereas the synthesized particles show clear electron diffraction pattern observed from TEM when power increases up to 250 W. Raman was also used to macroscopic analyze the crystallnity of the sample. In addition, the particles synthesized at low power condition show higher Br residue content, which would be one of the reasons for amorphous silicon formation.

In addition to the power effect, pressure, which includes partial pressure and total pressure, was found direct affect the color of PL. In the synthesis condition with low total and partial pressure, the size of crystal can be as large as ~20 nm. After HF/HNO_3 mixed acid etching, the sample shows a red PL under UV irradiation. Whereas high pressure condition form nanoparticles with visible blue to green PL. TEM analysis also suggested that the red PL sample (~5.4 nm) has larger size than the blue one (~1.8 nm). The nucleation theory is considered to be one of the reasons, the higher partial pressures the smaller critical sizes in supersaturation condition.

Chapter 4 (Practical application of fluorescent silicon nanoparticles: cell-imaging)

The study of intracellular compartments is an important area of biological chemistry. Among intracellular organelles, endoplasmic reticulum (ER) plays a critical role in protein synthesis and transport in a cell. Once the function of ER is interfered, some serious diseases, such as diabetes and Alzheimer's disease, would be caused. Therefore direct visualization of ER to understand how ER acts in a certain environment is quite important both scientifically and practically. As introduced before, fluorescent Si-NPs are expected as a new, less toxic bio-label for long-term observation. Similar to other inorganic semiconductor nanoparticles, the intrinsic surface of silicon is hydrophobic which limits the water-dispersibility for the further biological applications. Thus, the surface modification process for water-dispersible is quite important to Si-NPs.

For the surface modification, we select using block copolymer (F127) as non-covalent bond coverage. F127 is a kind of surfactant with hydrophobic and hydrophilic blocks. Nanoparticles after modification with F127 show water-dispersibility. TEM image of Si-NPs dispersed in water after F127 modification showing that Si-NPs formed aggregates with small size (20–40 nm). We also measured size distribution by DLS, which is in agreement with the

size of aggregates observed from TEM results. Zeta potential was measured and it reveals that copolymer-coated Si-NPs have a neutral surface charge in water. The F127-modified Si-NPs also show good photostability, retaining 80% of the initial PL intensity after UV irradiation for 3 hours. Furthermore, UV irradiation did not induce any increase in aggregation size of dispersed Si-NPs.

Then we studied the utility of our block copolymer functionalized Si-NPs for cell imaging. We firstly measure the cell viability in terms of the concentration of Si-NPs. The result shows our Si-NPs are low-toxic. A concentration of 0.1 mg/ml was used for cell imaging, with which cytotoxicity to human umbilical vein endothelial cells (HUVECs) was negligible. In the low-magnification microscope images of the cells, we confirmed that HUVECs were successfully labeled. High-magnification microscopy revealed that a network structure in the cell is selectively labeled. To test our hypothesis, HUVECs were co-stained with Si-NPs and ER-tracker red (a commercial molecule used to selectively labels the ER). The intracellular localization of ER-tracker red and F127-modified Si-NPs is almost identical, thus F127-modified nanoparticles do selectively label the ER in live HUVECs. As recently reported by Kabanov *et al.*,[1] hydrophobic poly-propylene oxide (PPO) block contained copolymer plays an important role for the specific pathway via caveolae mediated endocytosis transfer to the mitochondria through ER. This is one of the main reasons that our F127-modified Si-NPs selectively localize at ER, because the F127 also contain PPO block.

General conclusion

This thesis reported synthesis and application of silicon nanoparticles, which were obtained from plasma decomposition of $SiBr_4$. The size and optical properties of the as-synthesized nanoparticles were characterized. The PL colors can be tuned by changing the pressure during synthesis. Furthermore, the particle formation and possible PL mechanism was also discussed. Surface modification of the nanoparticles was done with the assistance of block copolymer F127. The water dispersed nanoparticles show excellent optical stability and small aggregation size after modification. The surface modified nanoparticles can be used to selectively label the endoplasmic reticulum in live cells with low cytotoxicity.

Reference

G. Sahay, V. Gautam, R. Luxenhofer, A. V. Kabanov, *Biomaterials* 2010, **31**, 1757.