

Water-Soluble, Carboxyl-Modified Silicon Nanoparticles

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ABSTRACT

A practical surface modification of Si nanoparticles was prepared by ultrasound-induced solution synthesis. This speedy rout produces the silicon nanoparticles in the size range from 2 nm to 5 nm and the surface of Si nanoparticles are carboxylated by a simple and timesaving rout. The carboxyl functional groups were directly attached at the nanoparticle surface with covalent bonds between C atoms of organic and Si atoms of the nanoparticle. This organic layer with polar terminated groups keeps Si nanoparticles to stably disperse in aqueous solutions. The carboxyl group of nanoparticles was characterized by FT-IR spectroscopy. The HRTEM images show that the carboxyl-modified Si nanoparticles have spherical shape, predominantly with diameters in the range of 2-4 nm. The emission maximum of PL spectrum for samples exhibited at 475 nm and the FWHM was approximately 130 nm.

Keywords: silicon nanoparticles, water-soluble, surface modification, photoluminescence

1 INTRODUCTION

To understand the complexity and dynamics of biological interaction, it is desirable to monitor the interactions of multiple proteins or cells within an organism [1-5]. Fluorescent tagging of cells and biomolecules with organic fluorophores (e.g., organic dyes and fluorescent proteins) has been used for these purposes. Unfortunately, the use of organic fluorophores for live-cell application is subject to certain limitations. Organic fluorophores tend to have narrow excitation spectra, and often exhibit broad emission bands with red tailing which limits the number of fluorescent probes that can be simultaneously resolved due to spectral overlap [11]. Colloidal semiconductor quantum dots (QDs), such as CdSe-ZnS core-shell QDs, are inorganic fluorophores that are a promising alternative to organic dyes [6-10]. While organic fluorophores are restricted by their narrow excitation spectra, quantum dots can be excited by a single light source in the any wavelength from UV to red. This enables efficient excitation and collection of fluorescent emission. QDs have narrow, tunable emission spectra, and thus emissions from many QDs can be resolved over the same spectral range.

Moreover, in contrast to organic fluorophores, QDs are highly resistant to chemical and metabolic degradation and have a high photobleaching threshold. Also, whereas the organic fluorophores require customized chemistry for conjugation of biomolecules to each fluorophore, a universal approach can be used for conjugating biomolecules to all QDs.

However the use of QDs in biological applications is still limited and primarily confined to in vitro studies [11]. Most original problem of CdSe QDs in biological application is the uncertain stability due to Cd element. Up to date there are no reports to publish an unexpected result of in vitro studies. However, it is dangerous to testify in vivo studies using toxic Cd. Therefore, many researchers are beginning to take an interest in Si QDs because Si would be an ideal material, which is non-toxic, abundant and low cost. There are found few reports referring biological application using Si nanoparticles because it has been known to be indirect materials and poorer emitter. Many of the reported syntheses for group IV QDs have offered a little control of the termination group and most of them were performed at temperatures higher than 500 °C [12-14].

Recently the quantum yield of Si QDs has increased from 1 % to 20 % according to published reports [15]. This is generally accomplished by covering the surface of the QDs with a monolayer of organic material that will be referred to as the termination group. This organic monolayer is important not only for the QDs' stabilization but also for many of the QDs' applications. However, since it is hard to manipulate the surface of QDs with alkyl groups, the alkyl-terminated group IV QDs is limited in their applications.

We will discuss the preparation of silicon nanoparticles of average diameter ~ 3 nm containing biocompatible functionality (hydroxyl and carboxyl group) and how this functionality can be readily manipulated using synthetic methodology. Our method provides organic monolayered nanoparticles formation of high yield (> 60 %) under ambient pressure and at temperature lower than 100 °C. It should be pointed out that the organic molecule attached to the surface of Si nanoparticles by the formation of covalent bonds between carbon and silicon. The one of challenges to using nanoparticles for biological studies is designing hydrophilic nanoparticles that are luminescent, with surface chemistry adaptable to varied biological application. In case of CdSe-ZnS core-shell nanoparticles, it needs to replace

the TOP/TOPO (trioctyl phosphine/trioctyl phosphine oxide) cap with polar terminated groups. The surface of nanoparticles is generally capped with monolayer or multilayer ligand shells have been pursued. The use of phosphine oxides, amines, and thiols as the termination groups for II-VI nanoparticles is common; however, in many cases these termination groups can be displaced. In contrast, the multiplayer method yields nanoparticles that are stable in vitro, but it takes long time as well as it is difficult to control. Therefore, the covalent attached organic layers with polar terminated groups allow stable dispersion of Si nanoparticles in aqueous solutions. It is very important to progress toward biotinylated Si nanoparticles that can be conjugated with streptavidin due to specific binding between biotin and streptavidin.

2 EXPERIMENTS

2.1 Materials and Systems

Chloroacetonitrile (99 %) was purchased from Aldrich and were distilled and kept in a Schlenk storage flask under high purity argon. Reagent-grade ethylene glycol dimethyl ether (glyme, 99.5 %) was dried by stirring with sodium overnight and distilled under argon. Toluene was treated with sulfuric acid at room temperature until the acid layer remained colorless. The acid-treated toluene was washed with distilled deionized water and dried with CaCl_2 prior to distillation over sodium under argon atmosphere. The purified solvents were kept in Schlenk storage flasks under argon.

2.2 Synthesis of Carboxyl Modified Silicon Nanoparticles

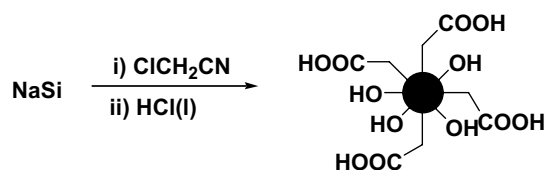
A 50 mg NaSi was added to 50 mL of dried glyme with excess chloroacetonitrile (0.1 mL) under argon atmosphere. The vessel was round-bottomed glassware of 100 mL volume and had side arms for the ultrasonic probe, the gas-purging tube and the thermocouple. The solution was sonicated for 1 h at 85 °C. And then, excess of aqueous hydrochloric acid was added to suspension. During the ultrasonic irradiation, the vessel was tightly closed with the silicon rubber septum so that solvent evaporation was suppressed during full reaction time. After being cooled to room temperature, excess chloroacetonitrile was removed in vacuum. Copious amount of fresh glyme was added and the salts were removed by the centrifugation. The carboxyl terminated Si nanoparticles were transferred to distilled-deionized water.

2.3 Characterization

FT-IR spectra were obtained with a Perkin-Elmer spectrometer. Photoluminescence spectra were made between 340 and 700 nm at room temperature with a He-Cd laser (325 nm) of Kimmon Cl. LTD. Samples were prepared by dispersing silicon nanoparticles in water. High-resolution transmission electron microscopy (HRTEM, Philips CM200) was operated at 200 kV. HRTEM samples were prepared by immersing carbon-coated copper grids dispersion of silicon nanoparticles in organic solvents and drying the solvent off.

3 RESULTS AND DISCUSSION

The hydroxyl-terminated Si nanoparticles represent a good starting material for a variety of synthetic transformations, as hydroxyl groups can be transformed via simple reactions into halides, esters, ethers, aldehydes, and ketones.



Scheme 1: Mechanism for carboxyl-termination process of Si nanoparticles

The carboxyl-terminated nanoparticles were directly prepared from covalent bonding between C atom of organic and Si atom of the nanoparticles surface without the process of hydroxyl termination. A mechanism of carboxyl-termination process is shown in Scheme 1. Sodium silicide was sonicated with excess chloroacetonitrile in absolute glyme for 1 h, and then it was followed to hydrolyze the nitril groups. Carboxyl-terminated nanoparticles were soluble in a large amount of glyme. The mechanism of bonding between Si nanoparticles and organic is not entirely clear. On the basis of our observation, it was proposed that the solubility of sodium silicide could be increased by Cl of acetonitriles, and subsequently occurred the formation of covalent bonding.

The carboxyl terminated Si nanoparticles can be transferred onto carbon coated copper grids for electron microscopy.

In Figure 1, HRTEM image of Si nanoparticles in glyme showed the presence of spherical particles, predominantly with diameters in the range of 2-4 nm.

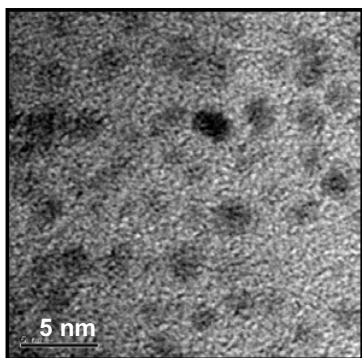


Figure 1: HRTEM image for silicon nanoparticles terminated with carboxyl groups.

The character of alkyl groups at the surface of Si nanoparticles was studied by FT-IR spectroscopy. The band assignments to the functional group are taken from the literature [15]. The FT-IR spectrum exhibited typical features for hydroxyl-terminated Si nanoparticles. The presented spectrum consists of absorption modes around 3300 cm^{-1} according to ν (O-H) stretching and near 1100 cm^{-1} assigned to ν (Si-O) stretching modes, indicating the presence of the hydroxyl group. However, absorption around 620 cm^{-1} corresponding Si-Si deformation modes is obscured.

In Figure 2, for the carboxyl-terminated Si nanoparticles, the C=O stretching at 1621 cm^{-1} and C-O stretching at 1015 cm^{-1} , respectively, indicates the presence of the carboxyl group. The broad band around 3300 cm^{-1} , which is very characteristic of OH, further evidences the carboxyl group on the surface of Si nanoparticles. The OH stretching is typically broad due to hydrogen bonding. However, it is ambiguous if all surfaces of nanoparticles are capped with carboxyl group. On the surface of freshly prepared Si nanoparticles prior to nitrile hydrolysis, it is difficult to find out how many silicon atom of the nanoparticles surface react with organic. Therefore, it is reasonable to suggest that the nanoparticles are terminated with carboxyl and hydroxyl group.

Figure 3 shows PL spectra of Si nanoparticles modified with hydroxyl and carboxyl group. The nanoparticles dispersed in water were excited by 325 nm , He-Cd laser. All intensities were normalized. The emission maximums and FWHMs of the samples are almost same. However, there are slight PL shifts according to each capping molecule.

When compared with the PL of OH capped nanoparticles, it was redshifted as for carboxyl-terminated nanoparticles.

The emission maximum of PL spectra in samples exhibited at 475 nm and the FWHMs are approximately 150 nm . These results mean that both the average size and size distribution are almost same for each samples, and capping molecules did not largely change the optical properties of Si nanoparticles.

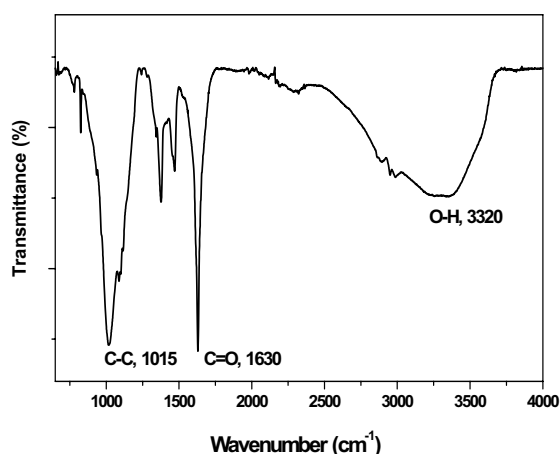


Figure 2: FT-IR spectrum for silicon nanoparticles terminated with carboxyl groups.

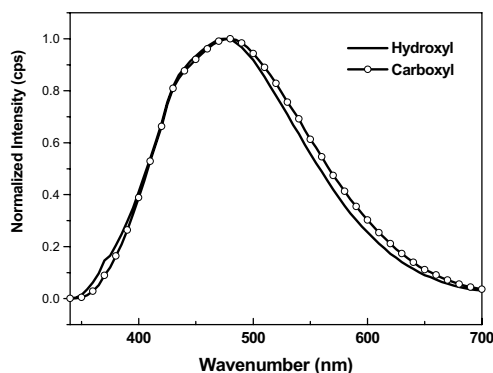


Figure 3: PL spectra of fresh Si nanoparticles with hydroxyl (-) and carboxyl group (o) in water.

4 CONCLUSIONS

We have reported the synthesis of silicon nanoparticles, functionalized with hydroxyl and carboxyl group. The

passivation process is very practical by ultrasound-induced solution routes. The covalent attached organic molecules with polar terminated groups allow not only water-solubility but also stability for months. It is emphasized that the functionalized nanoparticles retain the optical properties of the original Si nanoparticles and the organic molecules at nanoparticles' surface have just a little effect on the optical properties of nanoparticles. Our work will proceed to couple Si nanoparticles to biomolecules.

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