Preparation and photoelectrochemical properties of porous silicon/carbon dots composites

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Abstract. Porous silicon/carbon dots composites were prepared by electrolyzing and deposition with two graphite rods working as electrodes. The porous silicon was prepared by metal assisted chemical etching of silicon powder and then added into the ultra-pure water electrolyte. The structure and morphology of porous silicon, carbon dots and porous silicon/carbon dots composites were characterized by SEM, XRD, UV-vis and PL et al. At the same time, we have tested the electrochemical performance of porous silicon / carbon dots composites electrode. The results show that the fluorescence property of the composites is better than porous silicon and carbon dots. After the deposition of carbon dots, the photoluminescence intensity of porous silicon increased around 1.4 times and the decrease of luminescence efficiency of the complex is only around 6.8%. And it shows excellent broadband light reflectivity from 200nm to 700nm, consistently below 20%.

1. Introduction

Silicon is a hot research field, which is the basic material of photoelectric integration. However, silicon is an indirect bandgap semiconductor, which itself can only emit very weak infrared light. Different from silicon body materials, porous silicon possesses a large number of ultra-fine nano-silicon grains and silicon nanowires and highly efficient photoluminescence characteristics in the visible region at room temperature. Porous silicon materials have also attracted great interest in the specific applications of chemical and biological sensing as its large internal surface area [1]. The main problem of porous silicon luminescence is instability. In fact, the newly prepared porous silicon is passivated by hydrogen, and its exposure to ambient air will cause the gradual modification of the hydrogenated surface by oxidation. It may change the structure of the Nc-Si surface and then affect its optical properties, which will lead to the attenuation of fluorescence intensity. In order to improve the photoluminescence of porous silicon, it is necessary to change the composition of porous silicon surface. Many researchers paid a great deal of attention on the surface passivation, such as carbon passivation, nitrogen passivation and iron passivation [2]. Li used n-butamine as carbon source by the way of radiofrequency glow discharge to prepare carbon film, which can passivate porous silicon. The PL and EL strength of the treated porous silicon were enhanced and their luminescence stability was characterized [3]. Yu improved the luminescent properties of porous silicon by electrochemically
passivating porous silicon using the deposition of Al on the surface to form a more stable chemical bond Si-Al than Si-H [4].

Carbon dots (C-Dots) is a new type of carbon nano-material with a size of less than 10 nm, which is first discovered by Xu et al [5]. Compared with the traditional organic dye and the semiconductor quantum dot, the carbon dots not only have the advantages of stable optical property and easy realization of surface functionalization, but also the characteristics of biocompatibility and cell toxicity and the like [6-7]. The carbon dots are widely favored by the excellent fluorescence effect and the alternative semiconductor dots. There are two methods for synthesizing the carbon dots at present: one is the bottom up, including a combustion method, a thermal solution, the like, and a top-to-bottom synthesis method by breaking the carbon precursor [8-9]. And then the polymer surface is passivated so as to effectively emit light, mainly including electric arc discharge, electrochemical oxidation and hydrothermal method and the like [10-12]. The carbon dots can be excited under near-infrared light (NIR), and fluorescence is emitted in the NIR spectral region. The carbon dots have a wide application prospect, including biological imaging [13], drug delivery [14], gene delivery [15-16] and photocatalysis [17], and the like. C-Dots can be used together with semiconductors as electron absorbers and can suppress electron-hole recombination or generate electron–hole pairs. Kang designed a C-Dots/C3N4 composites system of metal-free photolysis water catalyst [18]. Liu prepared a complex of noble metal nanoparticles with C-Dots and studied its catalytic activity for the oxidation of cyclohexane [19]. Zhang reported heterogeneous conjunctiva prepared by simple layer-by-layer assembly techniques of C-Dots and CDs. This structure facilitates the separation of photogenerated electrons and holes, which in turn effectively prevents exciton re-binding [20]. Kang et al. prepared the composites (C-Dots/NiFe-LDH) of C-Dots and Ni-ferroic hydrotalcite by hydrothermal method and studied their catalytic effect on water oxidation in strong alkaline solution [21]. Using carbon film to passivate porous silicon was investigated extensively. At present, few studies have tried to passivate porous silicon with carbon dots, so we try to compound them to explore the properties of this new material. The results show that this combination can effectively passivate the porous silicon, which has good light response and little effect on the light absorption performance of the porous silicon.

In this paper, the porous silicon/carbon dots composites were prepared by electrolyzing and deposition with two graphite rods working as electrodes, and the method of preparing porous silicon is metal assisted chemical etching of silicon powder [22-23]. The silicon powder used is metallurgical grade silicon powder, which is rich in source with a low cost. Moreover, the porous silicon prepared by this method not only has high yield, but also excellent performance and good adsorption. The morphology, composition and optical properties of the prepared materials were characterized and the electrochemical properties of the materials were tested in our research.

2. Experimental section

2.1. The preparation of porous silicon
The porous silicon was prepared by metal assisted chemical etching of silicon powder. The corrosion solution consists of 4mL 0.25mol/L AgNO3 solution, 10mL HF solution and 36mL deionized water in the PTFE reaction container. It was added at first and then 2g silicon powder. Then let it react for half an hour under stirring. The next, we centrifuged the react solution and washed it with deionized water three times. Finally, we made it dry at 40°C, and keep it in a sealed container.

2.2. Synthesis of Porous silicon/carbon dots composites
The porous silicon/carbon dots composites were prepared by electrolyzing and deposition with two graphite rods working as electrodes. The porous silicon added into the ultra-pure water electrolyte. The porous silicon/carbon dots composites solution was obtained by electrolysis for 120h using a direct current power supply applied 30V at the poles under continuous magnetic stirring. The original colorless electrolyte gradually changed into a dark solution. The dark solution was then filtered and
the final prepared solution was sonicated for another 2h. Dried and preserved at a temperature of 40°C to obtain porous silicon/carbon dots composites micro-nanoparticles.

2.3. Preparation of electrode for testing
The 50mg composite powder was dispersed in the mixture of appropriate amount of anhydrous ethanol and 5ul of 5% Nafion solution. Then the solution was evenly dripped onto the clean FTO glass. After the solution is all coated on the FTO glass, let the alcohol volatilize naturally to the surface close to drying, put into the oven to dry, used as a working electrode.

2.4. Sample characterization
The microstructure and morphology of porous silicon/carbon dots composites were characterized by scanning electron microscopy (SEM, PHILIPS-TMP, Netherlands), with the accelerating voltage of 10.00kV. The composition of the sample was analyzed by X-ray diffraction (XPert PRO MPD, Netherlands). The fluorescence properties of the composites were characterized by fluorescence spectrophotometer (LS55, PerkinElmer, American). The excitation wavelength was 320nm, the scanning speed was 1200nm/min, and the excitation slit was 1.0nm. The characteristic absorption peak of composites was tested by UV-vis spectrophotometer (U-3010, Hi-tachi, Japan). The intercalation width was 2nm and the scanning speed was 300nm/min. The photoelectric measurements were performed in a custom-made electrochemical cell with a 3.6cm² window using an electrochemical workstation (PGSTAT204, Netherlands). And 50mg composite powder were mixed with anhydrous ethanol and Nafion solution and coated on FTO glass to fabricate working electrode, Ag/AgCl (filled with saturated KCl solution) electrode as the reference electrode and a platinum electrode as counter electrode. A 500W Xe lamp was used to provide 1 sun illumination to the sample. The electrolyte is 0.1M Na₂SO₄ aqueous solution.

3. Results and discussions
3.1. Physical and photochemical properties of Porous silicon/carbon dots composites
Figure 1 shows the XRD pattern of the porous silicon and the as-prepared porous silicon/carbon dots composites. The diffraction peaks are very obvious, indicating that the crystallinity is great. It can be learned from the XRD spectrum of curves that characteristic diffraction peaks appear at 28.5 (111), 47.4° (220), 56.5° (311), 69.2° (400), 76.6° (331), 88.0° (422)position and the intensities are in agreement with the diffraction data of the monocristalline silicon standard spectrum (JCPDS card 27-1402) [24]. A clearly broad diffraction peak appears near 2θ=26.5° of the complex, which is consistent with the (002) carbon crystal plane. It is the amorphous morphological characteristic peak of carbon. And it indicates that the obtained carbon dots are mainly amorphous carbon structure without complete and continuous crystal structure, which is consistent with the results of SEM atlas analysis. Compared with the XRD of porous silicon, the porous silicon/carbon dots composites show an obvious diffraction peak of carbon dots, which indicates that we successfully composite carbon dots on the surface of porous silicon achieving the results we initially wanted.

Figure 2 is the SEM morphology of the synthesized samples. Figure 2a shown the pure carbon dots. The graphite rods are peeled off into tiny carbon dots. As shown in the figure, the carbon dots are approximately spherical, uniform in distribution and size, and it might have a strong agglomeration effect. Figure 2b is the SEM image of porous silicon. It could observe from the figure that there are dense pore structures on the surface of silicon particles, and the microstructure of porous silicon is uniform, and the silicon matrix between pores shows a spongy structure. Figure 2c and Figure 2d are the SEM images of porous silicon and carbon dot composites. There are a large number of particulate matters in the gap on the surface of porous silicon. Carbon dots are mixed into the pore structure of porous silicon to form the desired porous silicon/carbon dots micro-nanocomposites. The SEM morphology results show that carbon dots are adsorbed on the surface of porous silicon, and the synthesis of porous silicon / carbon dots composites is a great success.
Figure 1. XRD patterns of porous silicon and porous silicon/carbon dots composites.

As can be seen from the Figure 3, the fluorescence emission spectrum of the porous silicon and the porous silicon/carbon dots composites have been obtained when the excitation wavelength is 320nm and the scanning speed is 600nm/min. They all produce stock shifts. The maximum fluorescence intensity is obtained in the vicinity of the emission wavelength of 640nm. As the emission wavelength increases, the fluorescence intensity is firstly increased and then is weakened gradually. And the fluorescence performance of the composites is better than the pure porous silicon. The results show that the photoluminescence intensity of porous silicon can be effectively improved by the deposition of carbon dots, which is around as 1.4 times as porous silicon.

Ten days later, we examined the fluorescence properties of porous silicon and complex again. The results showed that the luminescence efficiency of both is reduced after ten days. We can find that the
The decrease of luminescence efficiency of the complex is only around 6.8%. And it was significantly lower than the decrease of porous silicon which is around 39.3%. It indicated that when carbon dots are deposited, the luminescence efficiency and luminescence stability of the complex are greatly improved compared with the porous silicon.

Figure 3. Fluorescence emission spectrum of the porous silicon and the porous silicon/carbon dots composites.

Figure 4 shows the UV-vis reflectivity spectra of porous silicon and porous silicon/carbon dots composites. The porous silicon shows excellent broadband light reflectivity about 10% from 200nm to 700nm. It was indicated that the reflectivity of porous silicon/carbon dots composites is slightly larger than porous silicon. In the visible region, the reflectivity of them tend to be consistent, which is around 10%. As considering the excellent luminescence properties and stability of the composites, the sacrificial effect on performance is not too great. The increase of reflectivity after the addition of carbon dots may be due to the attachment of carbon dots to the surface of porous silicon, which have relatively high reflectivity.

Figure 4. UV-vis reflectivity spectra of porous silicon and porous silicon/carbon dots composites.
3.2. Electrochemical Characteristics of Porous silicon/carbon dots composites

In order to investigate the photoelectrochemical property of the porous silicon/carbon dots composites photocathode, we tested the linear sweep voltammetry using the electrochemical workstation. Figure 5 shows the linear sweep voltammetry plots of the porous silicon/carbon dots composites photocathode. In order to eliminate the large error of electrode potential caused by polarization current, we choose a three-electrode system. The sample served as the working electrode, Pt wire coil served as the counter electrode and the Ag/AgCl served as the reference electrode in Na₂SO₄ solution. As the negative bias increases, the current density increases gradually. We can find that the curve does not change linearly, which is consistent with the properties of porous silicon as semiconductor material. It can be seen from the figure that under the illumination condition, adding the same negative bias voltage, the current appears increases. When the overpotential is about -0.6V, the current density difference reaches the maximum, close to 0.04mA/cm². The cathodic currents of the sample electrode had a significant improvement beyond -0.2V, which is the peak potential of the reduction reaction.

![Linear sweep voltammetry plots of the porous silicon/carbon dots composites photocathode.](image)

4. Conclusions

In conclusion, we have developed a new porous silicon/carbon dots composites material with excellent photoelectric properties. The porous silicon/carbon dots composites exhibit high luminescence efficiency and great stability relatively. The photocatalytic efficiency of it is almost 1.4 times higher than that of porous silicon, and the decrease of luminescence efficiency of the complex is only around 6.8%. And it shows excellent broadband light reflectivity from 200nm to 700nm, consistently below 20%. Besides, the current density can increase around 0.04mA/cm² when the overpotential is about -0.6V, reaches the maximum, close to 0.04mA/cm². More importantly, the composite material is fabricated by some simple and cost-effective methods. Considering the abundance of the materials and the scalable production, this approach is promising for the fabrication of Si-based photoelectrodes.

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