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Observation of blue persistent luminescence in amorphous silica annealed by carbon

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ABSTRACT

Intense blue persistent luminescence (PersL) with sufficiently long duration time was firstly observed in SiO_2 particles after calcination with carbon. In indicates that the intense PersL of the optimal SiO_2 sample calcinated with carbon (1:2) at 600 °C can be recorded for about 1 h (0.32 mcd/m^2) and is actually visible for even more than 3 h by the dark-adapted vision in darkness. It reveals that the defects formatted during the calcination with carbon should be associated with oxygen vacancies and they play very important roles as emitters and traps, contributing to the PersL. The depth of the dominant traps in the optimal SiO_2 sample is calculated to be about 0.71 eV, which is in a suitable range for PersL (0.5–0.8 eV).

1. Introduction

Persistent luminescence (PersL) is the phenomenon involving energy traps in materials that are filled during an excitation with ultraviolet (UV) or visible light [1–3]. After the end of excitation, the stored energy is gradually released to emitter centers, which emit light within scores of minutes to hours [4]. The PersL materials have been widely used in safety signs, watch dials, decorative objects, energy, life science and so on [5,6].

At present, researchers have been working to develop efficient PersL materials, and most current works are focused on rare-earth materials [7,8]. However, the rare-earth raw materials are expensive, and these PersL materials are generally synthesized by solid state method at high temperature (>1000 °C). In addition, some PersL materials are doped with some toxic or heavy metal ions such as Ta^{3+}, Pb^{3+}, Bi^{3+}, Cr^{3+}, Cd^{3+} [9,10]. Therefore, it is desirable to develop new PersL materials with the advantages of being low cost, non-toxic, with easy fabrication and excellent PersL properties.

According to these requirements, the SiO_2 is considered to be a good candidate [11]. If we can induce sufficiently long PersL in SiO_2, it would be a great breakthrough and can of course promote relative applications. Recently, some groups have observed the blue photoluminescence (PL) in amorphous SiO_2 and it revealed that the oxygen vacancies created during the annealing process of SiO_2 act as emitters [12]. However, to the best of our knowledge, the sufficiently long PersL ($t > 10$ min) in SiO_2 has not been reported thus far.

In this work, the SiO_2 material was synthesized by a facile sol-gel method [13] and then it was subjected to calcinations with carbon. As a consequence, sufficiently long ($t > 1$ h) blue PersL was clearly observed in the obtained SiO_2 material. It is, of course, a great breakthrough in the PersL field. The as-synthesized SiO_2 sample exhibits the advantages of low cost, non-toxic, easy fabrication and excellent PersL properties. Particularly, the size of SiO_2 particles can be easily controlled. Therefore, this SiO_2 PersL material is potential to be used to label cells for biological and biomedical applications [2,3]. Moreover, the cheap PersL material can also used as pollution settlement detection powder, and other natural markers.

2. Experimental procedures

The SiO_2 raw material was synthesized by a traditional sol-gel method. Solution A was prepared with 19 ml of alcohol, 3 ml of water and 3.6 ml of ammonia (28%). Solution B was prepared with

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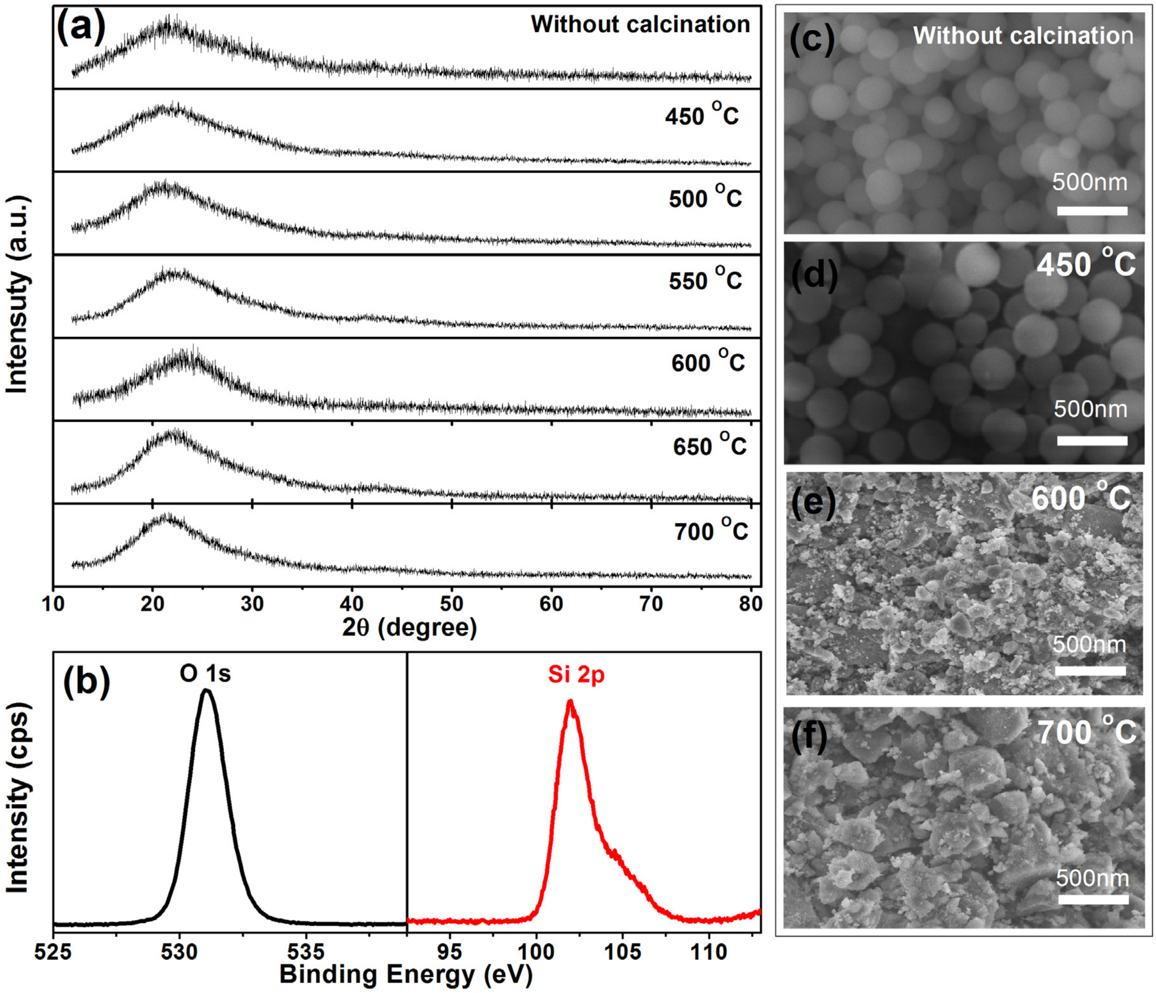

Fig. 1. (a) XRD patterns of the typical SiO_2 samples without calcination and with calcinations by carbon at 450, 500, 550, 600, 650 and 700 °C, respectively; (b) XPS of the typical SiO_2 sample calcinated at 600 °C; (c), (d), (e) and (f) SEM of the typical SiO_2 samples without calcination and with calcinations at 400 °C, 600 °C and 700 °C, respectively.

1.4 ml of tetraethyl orthosilioate (28.0%) and 3.6 ml of alcohol. Firstly, solution A was dropwise added into solution B. The mixed solution was rocked back and forth to prevent gel formation. Secondly, it was stirred for 2–4 h until it appeared milky with no layering, and then it rested for 24 h. The solution was shaken for half an hour by a sonic oscillator, cleaned with the alcohol by a high-speed centrifugal machine and then dried at 60 °C. Then, the SiO_2 samples mixed with different amounts of carbon powders (weight ratio 1:1.5, 1:2, 1:2.5 and 1:3) were subjected to calcinations at different temperatures (450, 550, 600, 650 and 700 °C) for 6 h to obtain the final products.

A Rigaku D/Max-2400 X-ray diffractometer was employed to check the phases of all the samples. PL and PersL spectra were obtained by a FLS-920T spectrophotometer with a 450 W xenon arc lamp (Xe900) as the light source. A PR305 instrument and a FJ-417A TL meter were used to measure the PersL decay curve and thermoluminescence glow curves, respectively. An X-ray photoelectron spectroscopy (XPS) was used for the qualitative analysis of samples. The morphology of the SiO_2 particles was obtained by a scanning electron microscope SEM (S-3400 and S-4800).

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the SiO_2 samples without calcination and with calcination by carbon (weight ratio is 1:2) at different temperatures (T = 450, 550, 600, 650 and 700 °C). The amorphous nature of SiO_2 within the sample is apparent by the broad band in 15–30° and it indicates that the XRD patterns don't exhibit clear variation for the calcinations [14]. Fig. 1(b) gives the XPS spectra of the typical SiO_2 sample after calcination by carbon at 600 °C and the two major peaks at 103.3 and 532.8 eV correspond to the binding energies of Si 2p and O 1s [15,16], respectively. It demonstrates that the as-synthesized samples are amorphous SiO_2. Fig. 1(c)–(f) show the SEM of the typical SiO_2 samples without calcination and with calcination at 400 °C, 600 °C and 700 °C, respectively. It clearly illustrates that the SiO_2 particles with calcination by carbon at 400 °C keep the nano-sphere morphology, and the average particle size is about 200–500 nm. However, when the temperature increases to 600 °C, it shows clear agglomeration.

Fig. 2 shows the PL excitation (λ_{em} = 438 nm) and emission (λ_{ex} = 365 nm) spectra (a) and the PersL emission spectrum (b) of the optimal SiO_2 sample after calcination with carbon (1:2) at 600 °C. The broad excitation band peaked at 365 nm and the emission band, which peaked at 438 nm, can be observed clearly. The PL mechanism of SiO_2 particles is essential different from that of the rare earth doped phosphors and it should be associated with the recombination of F centers (negative oxygen vacancies) with holes [17,20]. Generally, the SiO_2 particles are synthesized by wet chemical methods. It is reasonable to expect that the surfaces of highly hydroxylated silicon, some Si atoms are bonded to more