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Silver nanoparticles decorated stain-etched mesoporous silicon for sensitive, selective detection of ascorbic acid

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ABSTRACT

Novel silver nanoparticles decorated porous silicon (AgNPs-PSi) was fabricated via stain etching of Si, followed by simple immersion plating of Ag and applied successfully for enhanced electro-oxidation and quantification of ascorbic acid (AA). The newly developed nanocomposite consists of mesoporous Si (<20 nm) decorated by crystalline 15–50 nm AgNPs. Remarkable sensing performance was achieved with high sensitivity (1.279 μA μM cm^{-2}), fast response time (<5 s), wide linear range (20–600 μM: $R^2 = 0.9933$), low limit of detection (0.83 μM at S/N = 3) and excellent anti-interference and repeatability behavior. The current Ag-PSi modified glassy carbon electrode was further applied to a commercially available vitamin C supplement with satisfactory detection result.

1. Introduction

Porous silicon (PSi) is generally fabricated by electrochemical anodization of Si in hydrofluoric acid-based solutions and the produced porous films could offer many advantages for chemical and biosensing applications [1–3]. The rationale of using PSi in sensors is basically related to its huge surface area with open, reactive porous structures, electrical-optical characteristics and controllable surface modification and functionalization [4]. However, the standard anodization procedure is not appropriate to produce PSi nanopowder, characterized by much larger porosity-to-weight ratio, which would be beneficial to further modify the working electrodes for various sensor-related fields [5,6].

Ascorbic acid (AA) is widely used in various food-drinks related industries and essentially plays indispensable role in humans' physiological processes [7]. The development of rapid, sensitive approach for accurate detection of AA is therefore of considerable importance. Among several sensing methods, the electrochemical technique is highly nominated owing to simplicity in operation, sensitivity and rapid response. However, the effective sensing of AA at bare working electrodes is often hindered by highly-induced overpotential and electrode fouling effect [8]. With an ultimate objective to minimize such existing drawbacks, a novel AA amperometric sensor based on AgNPs decorated PSi modified glassy carbon electrode (GCE) is developed. Due to enhanced electrooxidation reaction of AA, the current modified electrode exhibited high sensitivity, selectivity, rapid response with acceptable detection result toward a commercial vitamin C tablet.

2. Experimental

Silicon powder (1 g; average diameter 40 μm) was dispersed in 10 mL of 48% HF and 40 mL pure water, with a dropwise addition of 2.5 mL, 70% HNO_3 under continuous mild stirring at room temperature [5]. Nitrogen oxide vapor was observed and stain etching process was completed in 15 min. The resulting PSi particles were filtered, washed with water, and left for natural drying.

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To produce AgNPs-PSi, a simple immersion plating procedure was applied in which 0.5 g of as-formed PSi powder was re-dispersed in 80 mL, 0.1 M HF, with the addition of 5 mL of 0.05 M $AgNO_3$ dropwise under stirring. The as-formed AgNPs-PSi was collected by filtration and drying. Further details of materials characterization, electrode modification and electrochemical measurements are provided in Supplementary Information (SI).

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.matlet.2018.09.076.

3. Results and discussion

The XRD patterns of Fig. 1(A) reveal a series of sharp peaks at 2θ = 28.5°, 47.16°, 56.1°, 69.16°, 76.5° and 88.0°, assigned respectively to (1 1 1), (2 2 0), (3 1 1), (4 0 0), (3 3 1) and (4 2 2) lattice planes of Si (JCPDS No. 27-1402) [9], with no impurity-related phases. For Ag-PSi, additional peaks at 38.17^0, 44.33^0, 64.3^0 and 77.5° are indexed respectively to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of Ag (fcc) [5]. Raman spectra, Fig. 1(B), indicate well defined peak at ~510 cm^{-1} related to optical-phonon scattering at the center of Si Brillouin zone confirming the presence of nanocrystalline Si in both samples [10]. Such a peak is slightly red-shifted due to reduction in lattice constant of PSi compared to c-Si [11]. A broad peak at ~308 cm^{-1} is associated with transverse acoustic (TA) vibrational mode [10], while the one at 924 cm^{-1} corresponds to scattering of transverse optical phonons [12].

TEM images, Fig. 1(C,C1), reveal high density random pores with sizes <20 nm. The PSi matrix is homogenously decorated with spherical 15–50 nm Ag nanoparticles, Fig. 1(D,D1). The SAED pattern of PSi shows discontinuity of crystalline Si probably due to formed voids, Fig. 1(C2), whereas the spotty rings, Fig. 1(D2), are due to poly-crystalline character of AgNPs. The EDX analysis showed Si peak characteristic for PSi, Fig. 1(C3), with C and Cu peaks originating from Cu grid. Fig. 1(D3) shows three peaks characteristic for Ag along with the main original Si peak. The textural properties of PSi and PSi-AgNPs obtained by N_2 sorption isotherms, along with the pore size distribution are further presented in Fig. S1. It is worthy to mention that there is no contradiction between above XRD and SAED results of PSi. An amorphous Si phase in PSi specimen has been early confirmed by micro-Raman spectroscopy [13] and XPS measurements [14]. Additionally, Ogata et al. [15], have detected a dual structure in PSi by XRD and TEM analysis. The XRD exhibited a crystalline phase, whereas TEM observation showed an amorphous-like image. The associated SAED pattern revealed a halo pattern with faint spots and rings,

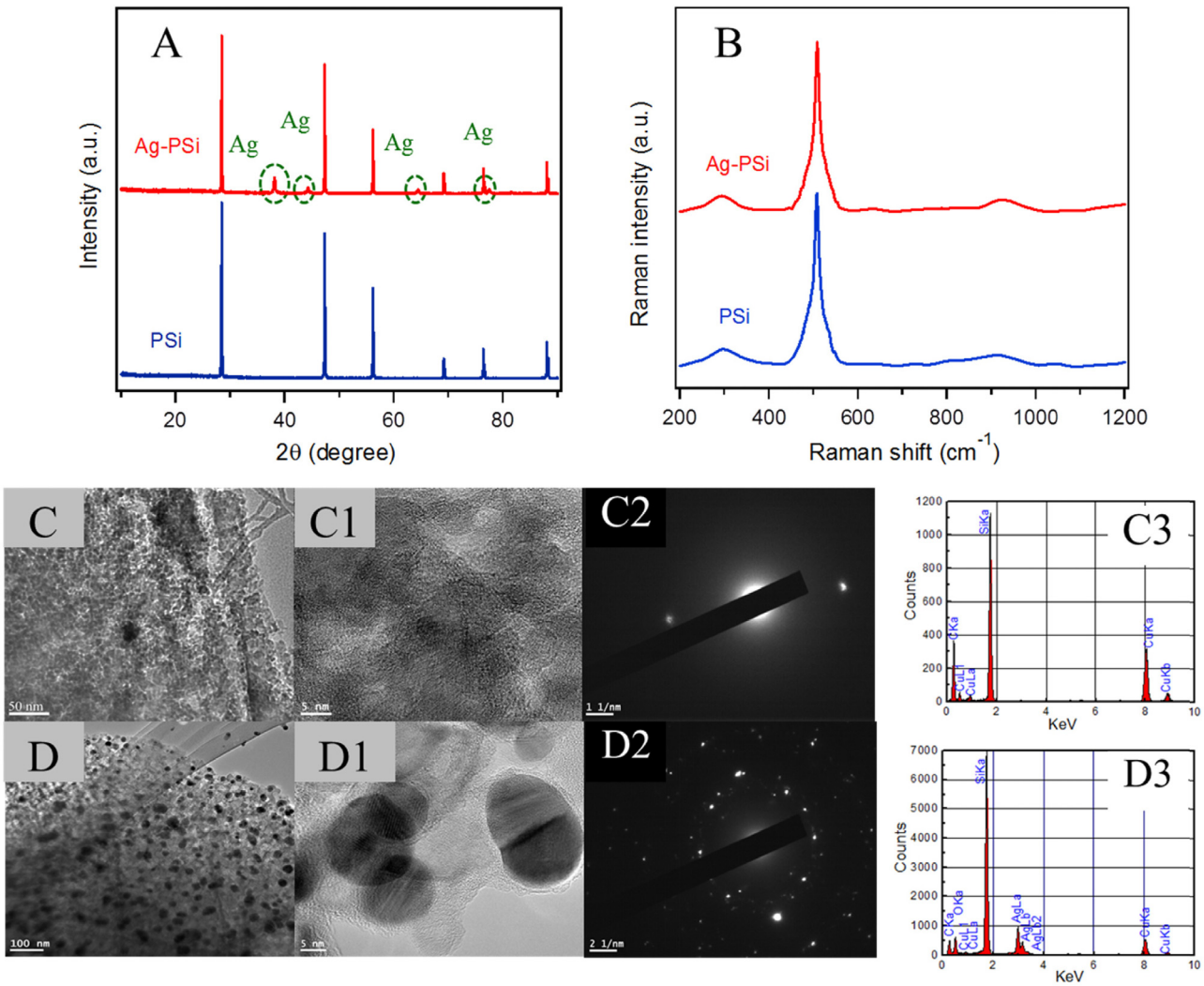

Fig. 1. (A) XRD patterns; (B) Raman spectra. (C), (D): TEM images of PSi and PSi-AgNPs; (C1), (D1): HRTEM images, (C2), (D2): SAED and (C3), (D3): EDX analysis.