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Preparation of silica nanoparticles from waste silicon sludge

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ABSTRACT

In order to reduce the release of hazardous waste silicon sludge (WSS) into the environment, we report a novel method to transform the WSS into silica nanoparticles and simultaneously to separate abrasive silicon carbide (SiC) particles. Alkali dissolution and acid precipitation processes were utilized to prepare silica nanoparticles effectively. The alkali dissolution process was carried out by sodium hydroxide to produce sodium silicate solution, from which SiC was separated by filtration. Afterward, the silica nanoparticles were prepared by acid precipitation method using hydrochloric acid. Box–Behnken design (BBD) was used to optimize the process variables affecting the dissolution efficiency, namely, mass ratio of NaOH and WSS, reaction temperature, and reaction time, and to determine the optimum conditions for the reaction process. Ultraviolet-visible spectrophotometer was used to measure the silica concentration in the solution. Characterized by XRD, FTIR, TEM, and BET surface area analysis, the silica with average pore size (10.52 nm), high specific surface area (430.9 m^2/g) was obtained, and the particle size was about 20–45 nm.

1. Introduction

Silicon is the most widely used material in semi-conductor and photovoltaic industries [1–3]. As per current status, the consumption of silicon wafer currently accounts for more than 70% of the cost for solar cells [4–6]. However, in silicon wafer manufacturing for solar cells, a great amount of hazardous kerf loss silicon with tiny silicon particles is produced, resulting in serious environmental problems [7]. The kerf loss silicon is in the form of slurry that consists of pure fine particles of silicon, silica, abrasive silicon carbide (SiC) particles, metal impurities from cutting wire, polyethylene glycol solution, and additives for better particle suspension. In view of the growing demands for low-cost silicon wafer and emission limits for hazardous materials, the recovery of kerf loss silicon is an important task for the semiconductor and PV industries [8].

The polyethylene glycol solution in the slurry is currently separated by centrifugal process and reused in silicon ingot slicing process. As far as the recovery of SiC abrasive is concerned, the purification methods including electrophoresis [7], magnetization [9], and froth flotation technologies [10] have been applied. It is easy to recycle SiC owing to the large particle size and low acceptable purity [11]. In general, the industrial waste silicon sludge (WSS), composed of silicon, SiC, and silica, were generated after separating the larger SiC, polyethylene glycol solution, and additives in the kerf loss silicon. However, to obtain the high pure silicon particles from WSS is a difficult task. Because of the particle diameter, silica nanoparticles have large-scale industrial applications, such as thermal insulators, emulsifiers, catalysis, composite fillers, and biological sciences [11–17].

The properties of thixotropy, thickening, dispersion, improving the intensity of rubber tearing, toughness and wear-resisting, increasing the clarity of the print guarantee that silica nanoparticles can be used in fields of rudder products, printing ink, paint and coating, sunscreen cream, paste products, manufacturing refrigerator shell, computer keyboard, etc.

The silica nanoparticles are generally prepared using vapor-phase reaction, sol-gel and thermo-decomposition methods [18–20]. Nevertheless, preparing silica nanoparticles from WSS has not been reported in previous papers.

A novel method to transform silicon into silica nanoparticles and simultaneously to separate particles of SiC in WSS has been reported in this paper (Fig. 1). The following chemical equations explain the process of preparing silica:

$$2NaOH + nSi + (2n-1)H_2O = Na_2O \cdot nSiO_2 + 2nH_2\uparrow \quad (1)$$

$$2NaOH + nSiO_2 = Na_2O \cdot nSiO_2 + H_2O \quad (2)$$

$$Na_2O \cdot nSiO_2 + 2HCl = nSiO_2 + 2NaCl + H_2O \quad (3)$$

Process variable optimization by the conventional method is very time consuming, expensive, and laborious. Response surface methodology

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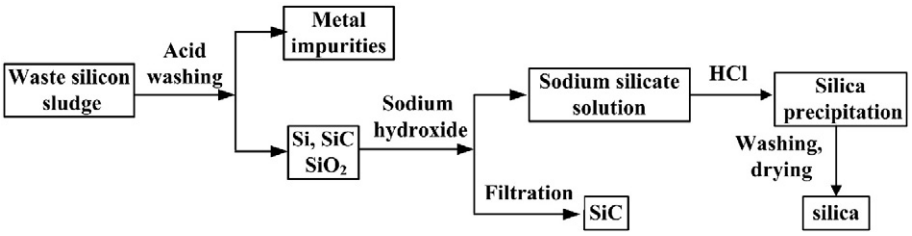

Fig. 1. Schematic representation of the procedure.

(RSM), an efficient statistical tool to solve multi-variable problems, sets the response of system as functions of one or more factors, using graphics and polynomials to display the function relation and select the optimum conditions of experimental design.

Box–Behnken design (BBD) was used to optimize the process variables affecting the dissolution efficiency, namely, mass ratio of NaOH and WSS, reaction temperature, and reaction time. Compared with orthogonal experimental method, BBD uses regression fitting of the relation between the factors and response value to get the response surface analysis diagram and contour map, which can help us distinguish optimization area and screen optimal conditions. In general, BBD is expressed by second-order polynomial to optimize variables.

The silica nanoparticles were characterized by XRD, FTIR, TEM, and BET surface area analysis. The separated SiC particles were simultaneously characterized by XRD and SEM.

2. Materials and methods

2.1. Materials

The WSS, obtained from Haobo Science & Technology Inc. (Jiangsu, China), consisted of 53 wt% Si particles, 17 wt% abrasive SiC particles, 29 wt% silica, and 1 wt% metal impurities. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Jiangtian Chemical Reagents Co. (Tianjin, China). All chemicals (analytical grade) were used without further purification.

2.2. Acid washing

Acid washing was used to remove the metal impurities prior to preparing silica from WSS. WSS samples (10 g) were dispersed in 30 mL distilled water, and the pH was adjusted to 5 using 36% HCl. These dispersions were stirred for 3 h, centrifuged and then the WSS residues washed with 50 mL water were used for preparing silica.

2.3. Experimental design

Response surface methodology has been used to conduct and plan experiments in order to extract the maximum amount of information in the fewest number of runs [21–23]. A 15-run BBD was employed to optimize the process variables (mass ratio, reaction temperature, and reaction time) and to investigate the effects of these variables on the dissolution efficiency of the silicon and silica from WSS pre-washed by HCl.

Table 1
Factors and levels for experimental design using Box–Behnken method.

Variables	Level		
	−1	0	1
Mass ratio (X_1)	1.4	1.6	1.8
Temperature(°C, X_2)	100	110	120
Time (h, X_3)	2	3	4

In Table 1, these three variables were designated as X_1, X_2, and X_3 and prescribed into three levels, coded +1, 0, and −1 for high, intermediate, and low values, respectively. The test variables were coded according to the following equation:

$$x_i = \frac{X_i - X_0}{\Delta X} \quad i = 1, 2, 3 \tag{4}$$

in which x_i is the coded value of the independent variable, X_i is the corresponding actual value, X_0 is the actual value at the center point, and ΔX is the increment of X_i corresponding to a variation of 1 unit of x.

The mathematical relationship between the response (dissolution efficiency) and these variables can be described by the following second-order polynomial equation:

$$Y = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i=1}^{3} \sum_{j=1}^{3} \beta_{ij} X_i X_j \tag{5}$$

Y is the response. The parameter β_o is the model constant, β_i is the linear coefficient, β_{ii} is the quadratic coefficient, and β_{ij} is the interaction coefficient.

The quality of fit of the polynomial model equation was expressed by the coefficient of determination R^2. ANOVA was performed, and the effects and regression coefficients of linear, quadratic, and interaction terms were determined. The model evaluated the effects of independent variables on the response.

2.4. Silica preparation

Each experiment was performed by dissolving a certain amount of sodium hydroxide in 20 mL deionized water and then 0.5 g WSS was added. The mass ratio of NaOH and WSS, temperature, and time were adjusted according to the experimental design. The reaction process was carried out under constant stirring rate of 800 rpm (DF-101S, Shanxi, China). After the reaction, the resultant slurry was cooled to room temperature, filtered in the condition of vacuum, and washed with 40 mL deionized water. The nonreactive SiC was left on the filter paper.

The concentration of silica in the solution was measured using UV spectrophotometer (752, Shanghai, China) and the weight percent of the dissolved silica in the solution was calculated.

The sodium silicate solution was titrated with 20% HCl under 80 °C to pH 5 along with constant vigorous stirring. Silica gels started to precipitate slowly and were set for 10 h at room temperature. Deionized water was added to the gels, which were then broken to make slurries. The slurries were centrifuged for 15 min at 2000 rpm, and the clear supernatants were discarded. The washing step was repeated to remove impurities. The clean silica was transferred into a beaker and dried at 60 °C for 12 h. The product was stored in a vacuum desiccator for further characterizations.