



# One-step solid-state *in-situ* thermal polymerization of silicon-PEDOT nanocomposites for the application in lithium-ion battery anodes



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## ABSTRACT

The current study presents a one-step solid-state *in-situ* thermal polymerization approach to prepare silicon nanoparticles-polyethylenedioxythiophene (SiNPs-PEDOT) nanocomposites. The structure-related electrochemical performance of the *in-situ* polymerized 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) with SiNPs has been studied for the first time in application to silicon-based lithium-ion battery anodes. Thermal polymerization applied to a solution containing DBEDOT in acetonitrile with suspended silicon nanoparticles resulted in an *in-situ* formed SiNPs-PEDOT nanocomposite. The structure, morphology, and the corresponding electrochemical performance of the *in-situ* SiNPs-PEDOT nanocomposites was studied in comparison to a pure PEDOT as well as to the *ex-situ* polymerized SiNPs-PEDOT nanocomposites using XRD, FTIR, TGA, SEM, TEM, cyclic voltammetry, impedance spectroscopy, and constant current charge-discharge cycles. The XRD, FTIR, and TGA analysis reveal that the *in-situ* polymerization of monomer is not impeded by the presence of the silicon nanoparticles. The SEM and TEM studies reveal a uniform dispersion of SiNPs within *in-situ* polymerized PEDOT matrix compared to *ex-situ* formed SiNPs-PEDOT nanocomposite. In the lithium-ion battery anode, the *in-situ* polymerized SiNPs-PEDOT nanocomposite demonstrates the enhanced lithiation-delithiation kinetics, conductivity, and rate capability in comparison to the *ex-situ* SiNPs-PEDOT nanocomposite.

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## 1. Introduction

Silicon has attracted substantial attention in lithium ion battery research due to its exceptionally high theoretical specific capacitance value ( $4200 \text{ mAhg}^{-1}$ ), which is the highest among all other known anode materials [1,2]. However, widespread application of silicon-based anodes in commercial batteries has been limited by a number of problems. Specifically, the silicon-based anodes, unlike carbon, undergo a 300–400% volume expansion during the lithiation process which causes mechanical deterioration of the silicon nanoparticles resulting in the overall performance decline [3]. Furthermore, the lack of electrical conductivity in silicon creates

the need for a conductive additive, either carbon or a conducting polymer [4]. The solid electrolyte interface (SEI) layer formed on the surface of silicon introduces the challenges such as reduced lithium-ion transport and consumption of the limited supply of lithium, translating it into an irreversible capacity loss.

Traditionally, these challenges have been addressed by using a three-phase system consisting of silicon as an active material, a binder, and an electrical conductor [5,6]. The silicon active phases are usually represented by silicon nanoparticles, nanorods, or nanowires [7,8,9,10,11]. The nanostructural nature of these materials minimizes the expansion damage during lithiation-delithiation [12] by localizing fractures and discontinuities to individual nanoparticles, as opposed to macrostructural components. The binder phase is commonly represented by an adhesive polymer thermoplastic such as polyvinylidene fluoride or polyacrylic acid [13] which is used to improve adhesion of the active silicon-based

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nanocomposite to the current collector and control volume expansion. The drawback of this approach is in minimizing the pathways for electronic transport. To improve the electronic conductivity of the silicon-based anodes, an electrically conducting phase consisting of various types of carbon including graphite, graphene, or nanotubes is commonly used [14,15,16]. This three-phase design has significant disadvantages including “dead weight” of the binding and conducting phases, which, depending on composition, reduces the theoretical specific capacitance of the electrode by up to 50%. The conducting carbon phase has an additional disadvantage of low percolation within the electrode and limited surface contact between the silicon and carbon particles due to the size differences of the individual particles and difficulties in achieving sufficient homogenization at the nanoscale. Therefore only some, but not all of the silicon nanoparticles are in intimate contact with the carbon phase, minimizing the electron conductive pathways at the nanoscale. To improve the silicon-based electrode design, numerous research approaches have recently been directed toward conducting polymers.

Conducting polymers, e.g. polyaniline (PANI) or poly(3,4-ethylene-dioxy-thiophene) (PEDOT) offer several advantages to silicon-based anodes by performing the roles of both binders and conducting phases which drastically reduces the amount of electrode “dead weight”. Conducting polymers also have the advantage of *in-situ* polymerization [1,17,18]. This can be achieved by suspending silicon nanoparticles in a monomer solution which homogeneously disperses around the surface of the silicon nanoparticles forming an electrically conducting polymer matrix. When polymerization is induced either by chemical [17,19] or electrochemical process [1] the polymer chains are formed around the silicon nanoparticles and form a continuous network that links each particle to the adjacent particle resulting in high percolation. The polymer film formed by *in-situ* polymerization also helps to minimize the negative effect of volume expansion by controlling outward growth of the macrostructure during lithiation, thus maintaining the electronic and ionic pathways in the case of an individual silicon nanoparticle fracture.

In a recent study, the superiority of conductive polymers over carbon additives with *in-situ* polyaniline (PANI) proved to have an enormous effect on the performance of Si nanoparticles [17,18,22]. The SiNP-PANI based anodes were able to achieve  $1600 \text{ mA h g}^{-1}$  at a current density of  $1.0 \text{ A g}^{-1}$  for 1000 cycles with almost zero capacity loss [17]. Polyethylenedioxythiophene (PEDOT) was investigated for Si anodes in combination with polystyrene sulfate (PSS) as a result of *in-situ* PEDOT-PSS polymerization [19]. However, this method proved to be ineffective presumably due to the “dead weight” and insulating properties of the PSS. In another study, the *in-situ* PEDOT electropolymerization with silicon nanowires resulted in  $3000 \text{ mA h g}^{-1}$  for 100 cycles at a C/5 rate [1]. However, this method is only applicable for silicon nanowires due to the configuration of the electrochemical set up, in which nanowires must be pre-deposited or grown on a conducting substrate in order to be used as a working electrode. Since nanowires are expensive and not yet practical for commercial battery use, a method of *in-situ* PEDOT polymerization should be developed for silicon nanoparticle-based electrodes.

The goal of the study was to adopt a unique one-step solid-state *in-situ* synthesis [20] for fabrication of silicon nanoparticles-PEDOT (SiNPs-PEDOT) nanocomposite anodes with thermally polymerized 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) resulting in a 2–5 bond linkages of the monomers. The study was further extended to make a comparison between the structure-dependent electrochemical performance of the *in-situ* and *ex-situ* polymerized SiNPs-PEDOT composites for the application in lithium-ion battery anodes.

## 2. Experimental

### 2.1. Synthesis of SiNPs-PEDOT composite

Three different types of electrode materials were synthesized in this study, specifically, a pure PEDOT polymer and two types of SiNPs-PEDOT nanocomposites by *in-situ* and *ex-situ* polymerization. For preparation of a pure PEDOT polymer, the initial monomer mixture was made by dissolving 0.1 g DBEDOT (Sigma Aldrich) in acetonitrile (Sigma Aldrich), followed by 2 h of stirring and 15 min of sonication. The DBEDOT monomer solution was deposited onto an etched copper foil by using a doctor blade and dried overnight in air. In the second *in-situ* approach, 0.1 g of SiNPs (US Research Nanomaterials) were added to the monomer solution, stirred for another 2 h and sonicated for 15 min. The SiNPs-DBEDOT slurry was deposited onto an etched copper foil by using a doctor blade. The deposited layer was dried overnight in air and heated at  $80 \text{ }^\circ\text{C}$  for 48 h in a muffle furnace for the *in-situ* thermal polymerization (Fig. 1). In the third *ex-situ* approach, 0.1 g of SiNP was added to the suspension of the pre-polymerized pure PEDOT powder in acetonitrile followed by 2 h of stirring and 15 min of sonication. The slurry was deposited onto an etched copper foil using the same method and dried overnight in air.

To elucidate the amount of bromine evolving from a 1:1 mixture of PEDOT and SiNPs during thermally induced polymerization, the gravimetric analysis was performed by heating a known amount of the mixture in a vacuum oven while recording the mass values before and after polymerization. For these measurements, the mixture was heated at  $75 \text{ }^\circ\text{C}$  for 2 days to allow for polymerization and another 2 days at  $100 \text{ }^\circ\text{C}$  in vacuum conditions to induce bromine evolution.

### 2.2. Physical characterization

X-ray diffraction analysis was studied by Rigaku Ultima Plus theta-theta X-ray diffraction (XRD) instrument. X-rays of Cu- $k\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) was used to scan the materials in the range of  $5^\circ$ – $90^\circ$  ( $2\theta$ ) with a scan rate of  $1 \text{ }^\circ\text{C}/\text{min}$ . Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) were performed using a SDT Q600 from TA Instruments. Temperature was increased to  $80 \text{ }^\circ\text{C}$  at a ramp rate of  $10 \text{ }^\circ\text{C}/\text{min}$  and held for 8 h while measuring weight loss and heat flow. The SEM images were taken using a Supra 40VP (Zeiss) field emission scanning microscope using an electron beam accelerating at 1 kV potential and a secondary electron (SE2) detector. The materials were further studied using a high-resolution JEOL TEM-2100 HRTEM with an

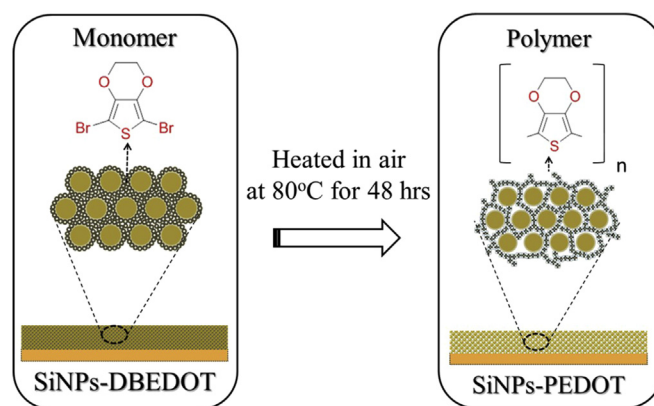


Fig. 1. One step *in-situ* thermal polymerization of SiNPs-DBEDOT on Cu substrate resulting in electrically conducting SiNPs-PEDOT polymer nanocomposite. SiNPs are represented by spheres.

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