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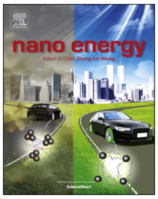

Full paper

Structural and compositional control in copper selenide nanocrystals for light-induced self-repairable electrodes

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ABSTRACT

In nature, self-healing can be induced by sunlight for damage and wound repair, and this phenomenon is very important to living species for prolonging their lives. This self-repairing feature is obviously highly desirable for non-biological materials and manmade systems. In this paper, we demonstrate, for the first time, that battery electrodes can be self-repaired when exposed to sunlight. Here, we show that the optical, and photoelectrochemical (PEC) properties can be controlled by varying structural and compositional parameters of copper selenide nanocrystals (NCs). Cation to anion ratio in copper selenide ($Cu_{2\pm x}Se$) NCs can be controlled over a wide range of 1.3–2.7 by simply changing the reaction temperature and impurity. Light-induced self-repairable behavior is demonstrated with electrochemical (EC) and PEC performances of electrodes made with stoichiometric copper selenide NCs. This nature-inspired, self-repairing behavior can be applied to batteries, supercapacitors, and photo-electrochemical fuel generators.

1. Introduction

Today, an average person throws away eight batteries per year thus millions of batteries are wasted imposing an immeasurable, adverse effect on our environment [1]. In nature, self-repairing is an important feature for living species, where wounds are self-healed to restore physiological functions and extend the life of an organism. Sunlight is an important self-repairing activator in plants and animals, where photons are absorbed through electronic absorption of some molecular chromophores or photoacceptors, which turns on intensified physiological activities to repair wounds [2]. Inspired by this phenomenon, it is highly desirable to incorporate self-reparability features in energy harvesting, e.g. electrochemical cells, as well as in energy storage devices, e.g. batteries and capacitors, to prolong their lifetime. Electrochemical reactions at electrode-electrolyte interfaces in batteries result in the structural and compositional changes in electrode material due to the irreversible redox reaction that causes degradation in device performance over the course of a number of cycles and ultimately resulting in its failure [3,4]. Therefore, self-reparability features require structural and compositional control of the electrode material over many cycles to ensure its prolonged operation.

Recently, copper chalcogenides have attracted extensive research due to their fascinating physical, chemical, and semiconducting properties driven by their chemical composition and crystalline structure, which are tailorable through intelligent control of synthesis conditions [5–10]. Copper selenide (Cu_2Se) is an important chalcogenide material with a wide range of applications in thermoelectric and photovoltaic-based energy harvesting [11–13], in photocatalytic degradation of dyes for water purification, in the fabrication of electrodes for batteries [14,15], and in photo-ablation therapy [16]. Due to their metal-like behavior, copper selenide nanocrystals (NCs) have strong localized surface plasmon resonance (LSPR) absorption tunable by their size, shape, and chemical composition [17,18]. Strong and widely tunable LSPRs in near and mid-infrared spectral regions make copper selenide an ideal candidate for solar energy harvesting, photodetector and plasmonic sensing applications.

Elemental composition is a decisive parameter for copper selenide NCs that control their crystalline structure and electronic behavior [19] and hence self-repairable capability. For example, bulk and stoichiometric copper selenide (Cu_2Se) is a zero bandgap material with metal-like behavior [20]. However, copper-deficient $Cu_{2-x}Se$ is an intrinsic p-type semiconductor with direct and indirect bandgap energies in the range of 2.1–2.3 eV and 1.2–1.4 eV, respectively [14,19,20]. Non-stoichiometry in $Cu_{2\pm x}Se$ NCs affects their electronic properties and significantly alters their crystalline structure and cation exchange properties [21–23]. Not only composition, but the arrangement of atoms in a given structural phase is also a crucial parameter to control electronic, thermal, and chemical properties of copper selenide [20–23]. For

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example, Pb^{+2} ions selectively react with different planes of cubic and hexagonal stoichiometric Cu_2Se NCs in cation exchange reactions [24]. Owing to these magnificent characteristics, compositional and structural control in copper selenide NCs is highly desirable for their specific scientific and technological applications, which poses a general challenge for researchers to discover new synthesis methodologies.

Typical methodology discovery is conducted with conventional solution chemistry, where either the concentration of chemical precursors is varied [25], or post-processing techniques, such as cation exchange or thermal annealing, are used to control chemical composition or crystallinity/phase of materials [24,26,27]. In the former case, the amount of required precursor needs to be calculated and measured precisely for a given chemical composition. However, the latter involves multiple additional time-consuming steps that increase the possibility of contamination and environmental exposure. For example, annealing of the sample at a high temperature for phase conversion might oxidize it and limit its device applications.

In this work, we report reaction temperature and impurity-induced structural and compositional control in gram scale synthesis of $Cu_{2\pm x}Se$ NCs for light-induced self-repairable electrodes for electrochemical cells. The reaction temperature is varied from 200 to 260 °C to tune the copper to selenium ratio from 1.8 to 2.5 while retaining their α-crystalline phase. Doping of silver is also used to control compositional properties as well as the crystalline structure of copper selenide NCs. At a given reaction temperature (230 °C), 1% w/w doping of Ag transfers stoichiometric (α-Cu_2Se) copper selenide NCs to non-stoichiometric (α-$Cu_{2.7}Se$) selenium deficient NCs of the same crystalline phase, while 2% doping of silver causes compositional and phase transformation to produce non-stoichiometric β-phase of copper selenide (β-$Cu_{1.3}Se$) NCs. Stoichiometric α-Cu_2Se and non-stoichiometric β-$Cu_{1.3}Se$ NCs are tested for EC and PEC performance. Interestingly, we observed light-induced self-repairable behavior for an electrode made with copper selenide NCs having Cu/Se ratio close to its stoichiometric value. In the dark, an electrode made from stoichiometric copper selenide NCs shows a decrease in anodic current density as well as a decrease in the value of oxidation potential with the number of cycles (degradation). However, under illumination with a solar simulator, it re-attains its initial state of current density and oxidation potential (i.e. light induced self-repairing under solar light) after the same number of cycles.

2. Experimental section

2.1. Synthesis of copper selenide nanocrystals

2.1.1. Materials

Copper oxide (CuO; 99.95%), selenium oxide (SeO2; 99.97%), silver oxide (AgO;99.97%), sodium hydroxide (NaOH; 99.97%), polyvinylpolymide (PVP; MW 8000), and ethylene glycol (EG) were purchased from Alfa Aesar and were used without further purification.

2.1.2. Synthesis procedure

Deionized water and a mixture of deionized water, PVP and EG mixture were used as solvents for the synthesis of different samples. In a typical synthesis procedure for samples S1–S3, 1.6 g CuO and 1.11 g SeO_2 powders were added into 36 ml water followed by ultrasonic dispersion for 30 min to make the first solution. In a separate glass vessel, 0.8 g of NaOH was dissolved into 100 ml of deionized water to make a 0.2 M solution. Both solutions were transferred into 150 ml teflon-lined stainless-steel autoclave and maintained at a constant reaction temperature (150–260 °C) for 24 h followed by natural cooling. Products were separated by centrifugation, washed 2–3 times sequentially with water and ethyl alcohol, dried at 60 °C in an air oven and finally stored in dried and cleaned glass vials for further characterizations and applications. For samples S4-S7, mixture of 0.5 g polyvinylpyrrolidone (PVP) into 36 ml of EG was used as a solvent in place of deionized water for making the first solution. PVP was used as a stabilizer and growth terminator that controls size of particles and reduces their aggregation/agglomeration. For samples S8 and S9, we added 1% w/w (16 mg) and 2% w/w (32 mg) of AgO powders, respectively into reaction mixtures and maintained them at 230 °C temperatures for 24 h. We did not use a larger amount of Ag doping due to the possibility for the synthesis of highly non-stoichiometric copper selenide NCs. Table 1 shows the experimental parameters used and the final products obtained for samples S1–S9.

Table 1
Synthesis parameters and compositional and structural phase of as-produced final products.

Sample Name	Solvent	Ag doping w/w (%)	Reaction temperature (°C)	Product
S1	Water	0	200	CuO
S2	Water	0	230	CuO
S3	water	0	260	CuO
S4	Water/EG/PVP	0	150	CuO
S5	Water/EG/PVP	0	200	α-$Cu_{1.8}Se$
[a,b]*S6*	*Water/EG/PVP*	*0*	*230*	*α-Cu_2Se*
S7	Water/EG/PVP	0	260	α-$Cu_{2.5}Se$
S8	Water/EG/PVP	1	230	α-$Cu_{2.7}Se$
[a]*S9*	*Water/EG/PVP*	*2*	*230*	*β-$Cu_{1.3}Se$*

[a] Samples tested for PEC performance.
[b] Sample with photo-repairable property.

2.2. Characterizations of as-synthesized copper selenide nanocrystals

Crystalline properties of as produced powder samples having micro as well as nano-crystals were measured using PANalytical X-ray diffractometer with λ = 1.5406 A° line from Cu-Kα source. As produced powder samples (0.25 mg/ml) were ultrasonically dispersed into double distilled water and obtained solutions were used for UV–visible-IR measurements using PerkinElmer Lambda-900 double beam spectrophotometer in the spectral range of 250–2500 nm. Films were drop-casted on ITO coated glass slides from the corresponding dispersions used for optical measurements. Crystallinity and phase of as-prepared films were also measured using the same X-ray diffractometer. X-ray measurement from powder samples would have major diffractions from micro-crystals, while those measured from films have diffractions from nanocrystals. Zeiss Auriga and PhenomWorld Scanning electron microscopes (SEMs) were used for surface morphology, while an Energy Dispersive X-ray absorption (EDAX) spectrometer attached with SEM was used for elemental analysis and mapping of the nanoparticles deposited on ITO coated glass slides. Three different spots on the same particle and five different particles of the same sample were used to get the average elemental composition of each sample.

2.3. Photo-electrochemical and light induced self-reparability measurements

Electrochemical measurements in dark and under solar light illumination were done in a conventional three-electrode system using an electrochemical workstation (Biological, Model VMP3). A platinum wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes respectively. The working electrodes were fabricated using drop cast deposition of acetone dispersed (1 mg/ml) powders on a 15 mm × 15 mm ITO coated glass substrate with 100 nm thickness of conducting ITO layer. Weight of the ITO coated glass was measured before and after coating to measure the amount of copper selenide powders on electrodes using a microbalance (Radwag RS 60/