Applied Catalysis B: Environmental 236 (2018) 338–347

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Mesoporous implantable Pt/$SrTiO_3$:C,N nanocuboids delivering enhanced photocatalytic H_2-production activity via plasmon-induced interfacial electron transfer

Ioannis Tamiolakis[a], Dong Liu[b], Fang-Xing Xiao[b], Jian Xie[c], Ioannis T. Papadas[d], Teddy Salim[c], Bin Liu[b], Qichun Zhang[c,e], Stelios A. Choulis[d], Gerasimos S. Armatas[a,*]

[a] University of Crete, Department of Materials Science and Technology, Heraklion 71003, Greece
[b] Nanyang Technological University, School of Chemical and Biomedical Engineering, 62 Nanyang Drive, Singapore 637459, Singapore
[c] Nanyang Technological University, School of Materials Science and Engineering Singapore 639798, Singapore
[d] Cyprus University of Technology, Department of Mechanical Engineering and Materials Science and Engineering, Limassol 3041, Cyprus
[e] Nanyang Technological University, Division of Chemistry and Biological Chemistry, School of Physical and Mathematics Science, Singapore 637371, Singapore

ARTICLE INFO

Keywords:
Strontium titanate
Nanoparticles
Mesoporous materials
Hydrogen production
Photocatalysis

ABSTRACT

Band edge engineering of semiconductor nanostructures is one of the most appealing approaches to enhance light absorption, carrier separation and, ultimately, solar to fuel conversion efficiency. In this study, we devise a facile polymer-assisted sol-gel chemical method to prepare highly porous, crystalline implanted $SrTiO_3$ (STO) nanoparticles and demonstrate their performance for photocatalytic hydrogen generation from water. X-ray scattering, electron microscopy, and nitrogen physisorption data corroborate that the as-made catalysts comprise 100-nm-sized nanocuboid particles containing a highly internal porous structure (BET surface area ~176 $m^2\ g^{-1}$) with uniform mesopores (ca. 5.8 nm in diameter). Interestingly, a partial substitution of N and C for O is attained in STO lattice with this synthetic protocol, according to the elemental analysis, and infrared (IR) and X-ray photoelectron spectroscopy (XPS) studies. Compared to STO:C,N, the STO:C,N mesoporous decorated with Pt nanoparticles (ca. 3 nm) present unique attributes that allow for an impressive improvement of up to 74-fold in photocatalytic H_2-production activity. By combining UV–vis/NIR optical absorption, photoluminescence, Raman and electrochemical impedance spectroscopy, we show that this improved performance arises from the unique nanostructure, which provides massive surface active sites, and the proper alignment of defect states and conduction band-edge position of the STO:C,N semiconductor with respect to the interband transitions of metal, which permit efficient plasmon-induced interfacial electron transfer between the Pt–STO:C,N junction.

1. Introduction

Exploiting solar-to-chemical energy conversion by semiconductor-based photocatalysis is a promising means for addressing future energy demands. This approach is based on the generation of bound electron-hole pairs (excitons) in a photochemically active material through sunlight absorption. The photogenerated electrons and holes can subsequently participate in redox reactions, such as water splitting and pollutant degradation [1]. To this end, a growing interest in developing highly-active nanostructured semiconductors has evolved in recent years. Among various morphologies, three-dimensional (3D) nanoporous semiconductors are considered as a class of very promising candidates for photocatalysis due to their high accessible surface area, large exposure of active sites and small dimension of the framework constituents. These characteristics could enable fast mass-transport kinetics and short electron to the surface pathway, suppressing the rapid recombination of photogenerated carriers in the particle core, and thus facilitating a high rate of photocatalytic reactions [2,3].

Over the past years, a large number of semiconductor materials have been investigated to catalyze the generation of molecular hydrogen from water. Among them, strontium titanate ($SrTiO_3$, STO) is a key player that is still gaining increased attention in the fields of water splitting and CO_2 fixation catalysis [4]. The unique properties of STO stems from its high charge-carrier mobility along the (001) layered structure (TiO_2 slabs), low concentration of defect sites in the crystal lattice, and excellent chemical stability [5,6]. Moreover, the small exciton binding energy of the STO perovskite, as a result of its large dielectric constant (ε = 300), has been proposed to play a key role in its

---

[*] Corresponding author.
E-mail address: garmatas@materials.uoc.gr (G.S. Armatas).

https://doi.org/10.1016/j.apcatb.2018.05.036
Received 20 March 2018; Received in revised form 9 May 2018; Accepted 12 May 2018
0926-3373/

photocatalytic performance, leading to a large dissociation of excitons. This means that the majority of photoexcited carriers escape initial recombination and are available as free electrons and holes for consecutive redox reactions. However, notwithstanding these advantageous attributes, STO is a wide band gap semiconductor (E_g = 3.1–3.3 eV) which requires ultraviolet light ($\lambda < 380$ nm) for operation; it corresponds only to a 3–4% fraction of the solar spectrum. An effective strategy to overcome the intrinsic limitations of STO is to extend its light absorption into the visible region by incorporating metal (like Rh, Cr, Sb) [7,8] or nonmetal (like C, N, F, S, I) [9–11] impurities into the structure. Even though metal doping can narrow the band gap of the material by creating localized midgap d states, it may also form phase impurities acting as recombination centers for photogenerated electron-hole pairs [12]. Consequently, this process might repress the carrier conductivity and therefore, in-turn, deteriorate the photocatalytic performance. On the contrary, non-metal doping has been shown to be more advantageous in this direction. N^{3-} ions, for example, can be partly substituted for oxygen (O^{2-}) in the oxide lattice, introducing localized N 2p levels at 0.3 to 0.5 eV above the valence band maximum (VBM) of STO, and more importantly, without contributing to the electron-hole pair recombination process [13]. Besides, the p electronic states can overlap sufficient with the O 2p orbitals of the semiconductor, narrowing the band gap. Nevertheless, N dopants, which are typically stabilized inside the titanate lattice via an electron transfer from the high-energy Ti^{3+} states to the partially occupied N 2p orbitals [14], are susceptible to N_2 release during the catalytic reactions [15]. Also, implantation with nitrogen is typically associated with the formation of oxygen vacancies into the structure through introducing localized Ti^{3+} 3d states at about 0.5–1 eV below the conduction band minimum (CBM) of STO [16]. These discrete midgap energy levels, however, might lower the reduction potential of the excited electrons for hydrogen evolution or become trapping sites for interband electron–hole relaxations, impairing the effectiveness of doping. Recently, codoping with trivalent rare-earth (La^{3+}, Eu^{3+}) and Cr^{3+} cations at the Sr^{2+} sites has been demonstrated to compensate the formation of oxygen vacancies in STO and improves photocatalytic efficiency [17].

So far, a variety of well-defined STO nanoparticles with a broad range of morphologies, from nanorods to nanowires and to nanocubes, have already been prepared. Synthetic methods to produce these materials include high-temperature solid-state reaction of precursor salts, sol-gel polymerization, and solvothermal treatment [18–20]. To the best of our knowledge, however, none of these nanomaterials are porous, and their surface area is due to the voids between the particles. In order to develop highly efficient photocatalysts, exploring new design strategies based on the critical requirements of well-defined electronic structure and high density of surface active sites is a pressing issue. Here, we report the synthesis of novel STO nanoparticles with a large intrinsic mesoporosity through a facile two-step synthetic method involving a polymer-assisted sol-gel chemical method followed by a low-temperature solvothermal process. We show that the resulting materials consist of nanocuboid particles, which express a large internal surface area available for reaction, while they can be readily n-type doped by carbon and nitrogen substitutions. By combining optical absorption, photoluminescence and electrochemical impedance spectroscopy results, we also provide insight into the photoelectrochemical behaviour of the unmodified and Pt-loaded implanted STO nanoparticles. The results indicate that the effectiveness of our catalyst in enhancing hydrogen production under UV/Vis-light illumination is determined by the efficient separation and migration of photogenerated carriers through the matched energy levels of the midgap states of C,N-codoped STO and interband transitions of Pt nanoparticles.

2. Experimental

2.1. Materials

Polyoxyethylene-*b*-cetyl ether (Brij 58) block copolymer ($HO(CH_2CH_2O)_{20}C_{16}H_{33}$, $M_n \sim 1124$), titanium(IV) chloride (99.9%), hexachloroplatinic(IV) acid hydrate ($\geq$98%, $H_2PtCl_6 \cdot xH_2O$), ethylenediamine ($\geq$99%), acetic acid ($\geq$99.5%) and absolute ethanol (99.8%) were purchased from Sigma-Aldrich. Titanium(IV) propoxide ($\geq$98%, TPP) was supplied by Merck. Strontium nitrate (> 99%, $Sr(NO_3)_2$) was purchased from Alfa-Aesar.

2.2. Synthesis of mesoporous STO and STO:C,N nanoparticles

In a typical synthesis, 0.75 g of polyoxyethylene-*b*-cetyl ether (POE (20)-*b*-C16) block copolymer was dissolved in a mixed solvent of ethanol (2 mL), water (1 mL) and HNO_3 (1 M aqueous solution, 0.1 mL). In a separate vial, 0.38 mmol of $TiCl_4$ and 1.39 mmol of TPP were dissolved in 2.5 mL of anhydrous ethanol at 5 °C, and the as-formed clear solution was slowly added to the block copolymer solution under vigorous stirring. After 5 min of stirring, 1.77 mmol of $Sr(NO_3)_2$ was added, and the resulting suspension was then further stirred at 5 °C for 1 h. Then, 10 mL of 1 M NaOH solution were added dropwisely to the reaction mixture (within a ~3 h period), and the obtained suspension was transferred to a 50 mL Teflon-lined autoclave and heated at 80 °C for 18 h. Finally, the white product was collected by filtration, washed thoroughly with 1 M acetic acid and water, and dried at 60 °C overnight. The template was removed by calcination in nitrogen for 4 h at 260 °C and then for 3 h at 400 °C, using a heating rate of 0.5 °C min^{-1}. Mesoporous C/N-codoped $SrTiO_3$ nanoparticles (ut-STO:C,N), obtained as a light gray powder, were also prepared using a similar procedure, but without the addition of the template.

2.3. Photochemical deposition of Pt on STO:C,N

The Pt-loaded STO:C,N nanoparticles were synthesized through a photochemical reduction method. In a typical procedure, 100 mg of as-prepared STO:C,N nanoparticles were dispersed by vigorous stirring in a aqueous solution (10 mL) containing 20% (v/v) of methanol. Then, a nominal amount of H_2PtCl_6 dissolved in water (1 mg mL^{-1}) was added to the above suspension under stirring, and the resulting mixture was purged with argon for 30 min. The reaction mixture was then irradiated under magnetic stirring for 1 h under 300 W Xe lamp at room temperature. The grey products were isolated by filtration, washed with deionized water several times, and dried at 60 °C overnight. Utilizing this method, we were able to produce Pt-decorated STO:C,N materials with 1, 1.5 and 2 wt% of Pt content. For comparison, Pt-decorated STO (Pt/STO) and ut-STO:C,N (ut-Pt/STO:C,N) catalysts with 1.5 wt% Pt loading were also prepared using unmodified STO and untemplated STO:C,N, respectively, as supports. The Pt content in each Pt-loaded catalyst was confirmed by energy dispersive X-ray spectroscopy (EDS).

2.4. Photocatalytic hydrogen evolution

The photocatalytic experiments for hydrogen production were carried out in an air-tight Pyrex glass reactor with a 300 W Xe arc lamp. In a typical experiment, 20 mg of catalyst was dispersed in 50 mL of water/methanol solution (8:2 v/v) under stirring, and the resulting mixture was purged with argon for more than 30 min to completely remove the air. The reaction mixture was then irradiated under magnetic stirring at 20 °C, using a cooling water system. The evolved gas was analyzed using a gas chromatograph (Shimadzu GC-2014) equipped with a thermal conductivity detector (TCD).