Thermochemical method of synthesizing stemmed nanoflower TiO$_2$/eC$_3$N$_4$ heterojunction structures with enhanced solar water splitting

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Abstract

TiO$_2$ nanoflower array linking to stem on a Ti foil is synthesized by thermochemical digestion of titanium at 80 °C by hydrogen peroxide and hydrofluoric acid solution. TiO$_2$ nanoflower comprised of the anatase TiO$_2$ which encased Ti metal core as seen by transmission electron microscopy (TEM), x-ray Photoelectron Spectroscopy based depth profiling, x-ray diffraction (XRD) analysis, and energy dispersive x-ray based elemental mapping. The TEM, selected area electron diffraction, and XRD analysis of air annealed TiO$_2$ nanoflower show presence of anatase (101) and anatase (200) crystals of about 35 nm size. The Photoelectrochemical activity in water splitting is assessed for heterojunction formed by the TiO$_2$ nanoflower with exfoliated carbon nitride (eC$_3$N$_4$), and the same is compared with heterojunction of TiO$_2$ nanotubular array and eC$_3$N$_4$. It was found from linear sweep voltammetry and electrochemical impedance spectroscopy that the synthesized stemmed-nanoflower TiO$_2$ offers superior PEC activity towards water splitting when used in heterojunction with eC$_3$N$_4$ as compared to that of TiO$_2$ nanotube with eC$_3$N$_4$.

1. Introduction

Titania is a versatile material used in solar energy-based applications like solar cells, solar CO$_2$ reduction, and photoelectrochemical water splitting. TiO$_2$ in the anatase phase has a bandgap of 3.2 eV [1] and can be photo-excited using UV solar radiation [2]. Usually, doping of TiO$_2$ or fabricating a heterojunction with TiO$_2$ may be a necessity to lower the band gap and enhance the separation of the photo-generated electrons and holes. The modification of crystal lattice is not as straightforward as it may appear [3–9], and it is the reason why the Z-scheme of formation of heterojunction has taken dominance over the crystal doping in terms of the scientific research efforts. The Z-scheme theorizes that addition of an appropriate sensitizer, which forms a heterojunction with anatase TiO$_2$, not only sufficiently reduces the heterojunction band gap but also improves the separation of the photo-generated electrons and holes [10, 11].

In past few years, a surge in research, regarding the use of transition metal dichalcogenides such as MoS$_2$ [12–14], 2d polymeric organic semiconductors like graphene [15], its allied variants [16–18], and graphitic carbon nitride (gC$_3$N$_4$) [19–21] as the Z-scheme sensitizers, has been observed. Out of all, gC$_3$N$_4$ has gathered attention as a metal-free photocatalytic sensitizer for heterojunction with anatase TiO$_2$ because of former’s simple and facile preparation, appropriately placed band edges (CB at $-1.3$ eV and VB at $+1.4$ eV, vs. NHE, pH 7.0) and a smaller band gap of 2.7 eV. Even then, the use of gC$_3$N$_4$ in its bulk deposited form suffers from weak, non-synergistic charge carrier mobility. While in bulk form, a large number of graphitic layers deposited one over another actively hinders the electron-hole separation, the exfoliated form at the juncture of anatase TiO$_2$ is extremely useful in eradicating the difficulty in charge carrier migration [22]. The efficiency of heterojunction depends on contact area, particle size and interface length [10]. Therefore, various attempts are being made by creating nanotubular [23–25], nanocolumnar [26–29], and other
structures of TiO$_2$ to increase the heterojunction surface area and decrease the particle size. While the nanoparticles may be synthesized energy efficiently and the deposited films can be sensitized well, these structures bring in the electronic resistance and the recombination of the photogenerated pair of electron and hole [34]. It is so because the semiconductor nanoparticle forms an interface at the conductive substrate itself, and the interface may work as the recombination surface.

On the other hand, the nanotubular structures provide a reduction in electronic resistance due to the inherent metallic core within the semiconductor walls. However, the nanotubular structure poses a threat of pore-clogging when sensitized with the 2d sensitizers [35]. Here, a branched and hierarchical stemmed-nanoflower TiO$_2$ not only allows more physical access to the 2d sensitizers as compared to the nanotubular arrays but also facilitates efficient charge separation through the interconnected interfaces of different characteristic lengths [36–38]. The stemmed structure provides larger surface area with a higher number of active sites retaining the direct electron pathways [39]. However, there are limited studies regarding the synthesis of such multi-branched, stemmed-nanoflower TiO$_2$ structure, which essentially contains a metallic core fixed at the metallic base inside and flower like structure outside [27, 39, 40]. The prominent drawbacks of the earlier works include non-branching [27], asymmetrical branching [39] and use of high temperature in TiO$_2$ nanostructure formation [40]. Also, earlier studies were hesitant to explore the possibility of the use of low temperature and more significantly, the recovery of the exhausted fluoride used for etching purpose.

In the present work, we report a single step, HF/H$_2$O$_2$ solution based thermochemical method to synthesize a branched, stemmed nanoflower TiO$_2$ structure. Further, it is shown that the photoelectrochemical (PEC) water splitting activity of the TiO$_2$/eC$_3$N$_4$ heterojunction is superior when stemmed-nanoflower TiO$_2$ structure is used instead of nanotubular TiO$_2$ structure along with eC$_3$N$_4$. The electrochemical impedance spectroscopy (EIS) studies suggest that the improvement in PEC activity is due to the reduced reactance between TiO$_2$ nanoflower photoanode and the electrolyte. Finally, we put forth a method by which the spent HF can be re-used.

2. Material and methods

2.1. Synthesis of the titania nanostructures

The titanium metal foils (250 µm thick, 99.5%, Alfa Aesar) were cut into 20 mm × 20 mm size and cleaned through ultra-sonication, sequentially in acetone, ethanol, propan-2-ol (IPA), and deionized water (DIW). The cleaned Ti foils were placed vertically in polypropylene vials which already contained the 20 ml volume of the 100 mM solution of hydrofluoric acid (HF, 40%, Merck) in hydrogen peroxide (H$_2$O$_2$, 30% Fisher Scientific). After this, the polypropylene vials were kept at 80 °C for 2 h to prepare yellow powder of gC$_3$N$_4$. The as-obtained powder was vacuum annealed at 500 °C for 2.5 h to allow the dehydration of the crystals.

2.2. Synthesis of the exfoliated-gC$_3$N$_4$ (eC$_3$N$_4$)

The sensitizer eC$_3$N$_4$ was obtained by exfoliating the bulk synthesized gC$_3$N$_4$ in IPA. Firstly Melamine (98%, Sigma Aldrich) was heated in air at 550 °C for 2 h to prepare yellow powder of gC$_3$N$_4$. The as obtained gC$_3$N$_4$ powder was ground and 3 mg of it was dispersed into 1 ml of IPA (99.8%, Merck), and the dispersion was ultra-sonicated for 10 h at room temperature. The unexfoliated particles were removed through centrifugation at 3000 rpm for 10 min. The supernatant white suspension containing eC$_3$N$_4$ was used to decorate the TiO$_2$ nanostructures by centrifuge-based deposition method [41] which yields an eC$_3$N$_4$ thin film of ~700 nm thickness over titania substrates.

2.3. Recovery of spent HF

After the thermochemical etching process was over, the foils were taken out from the polypropylene vials. The residual mixture was further filtered and washed repeatedly. The milky-white filtrate was collected and the red mixture was treated by dropwise adding saturated Ca(OH)$_2$ solution, allowing formation of CaF$_2$. The synthesized CaF$_2$ was filtered, washed repeatedly, and dried at 80 °C overnight. Thereafter, the dried CaF$_2$ powder was vacuum annealed at 500 °C for 2.5 h [42] to allow the dehydration of the crystals.

2.4. Physical and photoelectrochemical characterization

Microstructural information and selected area electron diffraction (SAED) were obtained using FEI Tecnai TF20 high-resolution transmission electron microscope (HRTEM). Field emission scanning electron microscope (FESEM) images were taken by FEI Quanta 200 FESEM instrument, attached with Oxford-EDX
Figure 1. FESEM image of (a) TiO$_2$ nanostructure prepared using 30% H$_2$O$_2$ and (b) TiO$_2$ nanoflower prepared using 100 mM HF in 30% H$_2$O$_2$.

IE 250 X Max 80 system where energy dispersion x-ray (EDX) analysis was carried out. For crystal characterization, x-ray diffraction (XRD) analysis was carried out in Rigaku Ultima Miniflex 600 x-ray diffractometer using Cu K$_\alpha$ ($\lambda = 0.15418$ nm) radiation. Identification of molecular bonds was made using Bruker Vertex 70V Fourier transformed infrared (FTIR) spectrophotometer. The x-ray photoelectron spectroscopy (XPS) analysis was carried out in PHI 500 Versaprobe-II, UlVac-PHI (band pass 23.5 eV, energy band 20 eV). All potentials mentioned in the present work are reported against the reference electrode, Ag/AgCl in saturated KCl ($-0.197$ V vs. RHE at room temperature). A Pt plate-based electrode with exposed geometric area of 250 mm$^2$ was used as the counter electrode. The working electrodes had the geometric area of ~220 mm$^2$. All PEC studies were carried out in 1 M NaOH solution under dark and illuminated conditions (AM 1.5G) using 300 W Xenon lamp (Laser Spectra). EIS studies were done at 0.6 V in the frequency range of 100 mHz to 100 kHz with the AC perturbation amplitude of 10 mV. The faradaic efficiency measurements and chronoamperometry were done at 0.23 V (SI 1.6, 1.7) (available online at stacks.iop.org/JPENERGY/2/035002/mmedia).

For convenience, annealed pristine TiO$_2$ nanoflower are named as NF whereas the annealed pristine TiO$_2$ nanotubular scaffolds are abbreviated as NT. The heterojunctions fabricated for PEC studies are assigned letter H as the suffix to the original sample name. Thus, TiO$_2$ nanotubular based heterojunction with eC$_3$N$_4$ has been abbreviated as NTH while the TiO$_2$ nanoflower based heterojunction with eC$_3$N$_4$ has been abbreviated as NFH. The characterization details of NT and eC$_3$N$_4$ are given in the supplementary information (SI 1.1–1.4).

3. Results and discussion

3.1. Synthesis of the TiO$_2$ nanostructures

3.1.1. Structural characterization

Figure 1 shows the SEM micrographs for the TiO$_2$ nanostructure samples prepared through the thermochemical digestion process. The vertically grown nanowire like TiO$_2$ structure, seen in figure 1(a) evolves, when H$_2$O$_2$ is used for the thermochemical digestion. On the other hand, TiO$_2$ nanoflower array like structure seen in figure 1(b) evolves, when 100 mM HF is used along with H$_2$O$_2$. Additional information on HRTEM is given in supplementary text (SI 1.3).

HRTEM micrographs of the TiO$_2$ nanoflower is shown in figure 2(a). Figure 2(b) shows a single petal and the oxide layer can be seen encasing the inner core. It reveals nearly 2d nature of the nanoflower petals. The opaque core indicates the presence of non-oxidized Ti metal. Figure 2(c) zooms into the oxide layer as marked in figure 2(b) and indicates an inter-planar spacing of ~1.3 Å which pertains to the (1 0 1) crystal plane of TiO$_2$. The SAED diffractogram shown in figure 2(d) points out poly-crystallinity of the evolved TiO$_2$ nanoflower structure which is further corroborated with XRD diffractogram shown in figure 3. The XRD pattern confirms the inference of HRTEM analyses which reveals that the evolved nanoflower structure is comprised of TiO$_2$ layer encompassing the Ti metallic core.

The XRD patterns of the eC$_3$N$_4$/TiO$_2$ heterojunction samples NFH and NTH are shown in figure 3. The SAED pattern (figure 2(d)) has suggested the polycrystallinity of TiO$_2$ nanoflowers, and the same is verified by the XRD data. The XRD pattern reveals the presence of Ti and TiO$_2$ in their respective polycrystalline form in sample NFH. The XRD data match well with JCPDS card numbers #21-1272 (TiO$_2$) and #65-3362.
Figure 2. HRTEM images of NF, (a) a complete nanoflower, (b) flower petal, (c) zoomed view of the flower petal (d) SAED diffractogram.

Figure 3. XRD pattern of the eC$_3$N$_4$/TiO$_2$ heterojunction samples NFH and NTH.
In nanoflower sample, asymmetric crystal facet planes (1 0 1) and (2 0 0) of TiO$_2$ and (0 0 2) of Ti are dominant. Using the XRD data and the Scherrer equation, the crystal size of TiO$_2$ in the nanoflower sample NF is estimated to be within 34–68 nm range. A peak near 2$\theta$ value of 27$^\circ$, for both samples NFH as well as NTH, is also visible and corresponds to eC$_3$N$_4$ sensitizer.

3.1.2. Compositional characterization

The SEM-EDX based elemental mapping of sample NF is shown in figure 4. The elemental mapping points out the homogeneous presence of titanium and oxygen. The atomic percentage ratio of Ti to O is 1:2 which indicates the formation of TiO$_2$. It suggests the consistent presence of Ti and O$_2$ in sample NF.

It is worth mentioning here that sometimes EDX is not deemed a fully reliable technique to determine the oxygen content in compounds. However, it is still a very accessible method to swiftly determine the presence of different constituent elements in the compound. Therefore, to confirm the inferences drawn from HRTEM, XRD and EDX results regarding the TiO$_2$ layer coverage on Ti metallic core, XPS studies with depth-profiling were carried out for sample NF. The core-level elemental scans of Ti 2p and O 1s were done at the as-annealed surface (0 nm) and at the Ar ion-etched depths of 6 nm, 12 nm, and 18 nm from the surface. Figures 5(a) and (b) show the Ti 2p and O 1s spectra, respectively. From HRTEM (figure 2(b)) the estimated thickness of TiO$_2$ layer is ~6 nm. Hence an ion-etching step size of ~6 nm is used. The XPS system was calibrated using Au (4f$^{3/2}$, 84.0 eV), Ag (3d$^{10/2}$, 368.2 eV), and Cu (2p$^{3/2}$, 932.6 eV) standard samples.

From the XPS spectra of figure 5(a), it is seen that at the surface and ~6 nm depth, only Ti$^{4+}$ (fully oxidized Ti, main peak ~458.5 eV and satellite peak ~464.2 eV) [43–45] is present. However, at a depth of ~12 nm, Ti$^0$ (non-oxidized Ti, main peak ~454.8 eV) [43, 46] is also seen along with Ti$^{4+}$. Since the Ti$^0$ peak can be taken to be originating from exposure of Ti metal, the thickness of the oxide layer can be estimated to be between 6 nm and 12 nm, agreeing with the earlier thickness estimation based on the HRTEM. However, neither HRTEM nor XPS can precisely measure the oxide layer thickness.

Further etching and the subsequent XPS elemental scan of Ti 2p at a depth of ~18 nm finds stronger signals of the Ti$^0$ and a bit weaker signal of the Ti$^{4+}$. It can be assumed that such a change in the signal intensities indicates that while going deep, Ti$^0$ availability has increased, and the Ti$^{4+}$ availability has decreased. Hence, further etching and the XPS elemental scans of Ti 2p were carried out at the approximated depths of 24 nm, 30 nm, 60 nm, 90 nm, 120 nm, and 150 nm, to confirm such an assumption. From a concurrent comparison of the peak-fitted XPS spectra of Ti 2p for the NF sample at different etching depths, it is seen that at the surface and near the surface, TiO$_2$ is dominantly present. However, the comparison also
Figure 5. Continue.
Figure 5. (a) Ti 2p XPS spectra of sample NF of TiO$_2$. (b) O 1s XPS spectra of sample NF of TiO$_2$. 
shows that moving deeper from the surface, the availability of the non-Ti$^{4+}$ species, Ti$^{0}$, and Ti$^{3+}$, also increases and can be deemed originating from the exposure of non-oxidized and inadequately oxidized core metal. Further investigation of the matter was reserved for future work. The increasing intensities of the non-lattice and defect oxygen in the O1s spectra [43, 46], along with the increasing depths (figure 5(b)) also confirm the assumption mentioned above. Thus, based on SEM, EDX, XRD, HRTEM, SAED, and XPS, it could be safely accepted that the nanoflower structure of TiO$_2$ contained the titania as the shell on the non-oxidized Ti core.

3.1.3. Photoelectrochemical characterization

The fabricated TiO$_2$–$\text{eC}_3\text{N}_4$ heterojunctions, NFH and NTH, were studied through the linear sweep voltammetry (LSV) and the electrochemical impedance spectroscopy. Figure 6 shows the LSV plots with the current densities and the estimated photocurrent densities of NFH and NTH, under dark and illuminated (AM 1.5G) conditions. For both the heterojunctions current density remains nearly zero under dark conditions and rises sharply under illuminated conditions. The photocurrent density of NFH ($\sim 1.1$ mA cm$^{-2}$ at 0.6 V) is nearly double than that of NTH ($\sim 0.6$ mA cm$^{-2}$ at 0.6 V). The improvement in the photocurrent density of NFH surpasses some of the reported recent works [47–49] (SI 1.5).

Nyquist and Bode plots of EIS data are shown in figures 7(a) and (b) respectively. In the present study, Nyquist, and Bode plots in conjunction reveal that at high to moderate frequencies the impedance has been unchanged under dark as well as illuminated conditions, whereas at lower frequencies they exhibit a significant reduction in impedance, by nearly an order of magnitude for NFH relative to NTH. Near equal impedance values for NFH and NTH at high and moderate frequencies are indicative of near-equal resistances. It points out that the PEC reactions in the studied system are not kinetically limited. The study of the low-frequency EIS data with Bode plot reveals a significant decrease of total impedance in NFH as compared to that in NTH, which means that ion transport is easier in NFH. Bode plot also suggests that at low frequencies, for NFH and NTH, the reactance not only decrease while switching from dark to illuminated conditions but also remain low for NFH relative to NTH under dark as well as illuminated conditions. The reduction in phase lag and shifting of phase angle from more negative value to less negative value for NFH are specific indications to the reduced reactance. It may be inferred that the ion transport has become easier under illumination due to decreased reactance for NFH than for NTH and the interfacial behavior of heterojunction in the electrolyte has become ‘accepting’ rather than ‘reflecting’ the reactant species for NFH [50]. Thus, it is fair to conclude that the replacement of nanotubular array by nanoflower as TiO$_2$–$\text{eC}_3\text{N}_4$ heterojunction substrate is able to reduce ion transport resistance at the electrode-electrolyte
Figure 7. (a) EIS based Nyquist plot for comparison of PEC activities of NTH and NFH. (b) EIS based Bode plot for comparison of PEC activities of NTH and NFH.
3.2. Recovery of spent HF

The presented thermochemical digestion method uses HF, which is a highly active oxidant. In order to recover the spent fluorides and to render the whole process ecofriendly, the HF recovery process has been proposed. The HF recovery process is based on neutralization of the spent acidic solution using \( \text{Ca(OH)}_2 \) and then recovery of HF by treating the dried \( \text{CaF}_2 \) crystals with sulfuric acid. The study of the proposed recovery process was truncated at the recovery of \( \text{CaF}_2 \) crystals, to preserve the scope of the present thermochemical process. The recovery of HF from \( \text{CaF}_2 \) (a constituent of Fluorspar) using \( \text{H}_2\text{SO}_4 \) is a well-known process.

Figure 8(a) shows the SEM micrograph of the recovered \( \text{CaF}_2 \) in its powdered form whereas figure 8(b) shows the SEM-EDX based elemental maps and x-ray diffractogram for the same. It can be seen from the elemental mapping that the recovered material contains Ca and F in stoichiometric proportion confirming \( \text{CaF}_2 \) formation. The XRD suggests the formation of pure and highly crystalline \( \text{CaF}_2 \) as the diffractogram matches with the JCPDS #77-2245. The presented work not only uses a lower concentration of fluoride (0.1 M) but also allows to recover the spent fluorides.

The residual solution was treated through different stages of filtration and separation, and the process has been reported in section 2.3. The supernatant liquid obtained after centrifugation was clean and it indicated
the removal of white-colored TiO$_2$ particles. The TiO$_2$ formation mechanism elaborated later in section 3.3 points out that the supernatant liquid is mainly water, which has been checked by adding it in a dropwise manner to anhydrous CuSO$_4$ powder and dried silica gel granules. Upon addition of the liquid drops, the white anhydrous CuSO$_4$ powder turned blue, whereas the clear silica gel turned sapphire-blue. H$_2$O$_2$ might have also been present but below detection limit.

3.3. The growth of the TiO$_2$ nanostructure

The use of H$_2$O$_2$ for growing clusters of nanorod like morphology of TiO$_2$ on Ti metal surface and use of HF to grow TiO$_2$ nanotubular assembly on Ti metal foils are well known [27, 51]. When used together, fluoride ions act as etchant and peroxide species act as an oxidant. There are primarily two processes involved in the formation of TiO$_2$ nanoflower—the oxidation of the exposed surface and the dissolution of oxides by fluoride species. On clean, fresh surface of Ti foil, a thin passive layer is formed initially under aqueous surroundings [52]. HF etches the oxide layer through the breaking of the passive layer [24] leading to the formation of H$_2$TiF$_6$, which dissolves in hot water. As H$_2$TiF$_6$ dissolves, Ti surface beneath gets oxidized to form a new passive layer, and the process continues till the oxidant or the etchant is exhausted. The reaction mechanism of the process is shown below.

\[
Ti + 2H_2O_2 \rightarrow TiO_2 + 2H_2O, \\
TiO_2 + 6HF \rightarrow H_2TiF_6 + 2H_2O, \\
H_2TiF_6 + 3H_2O \xrightarrow{\Delta} TiO(OH)_{2} + 6HF,
\]
The rate determining step in photoelectrochemical reaction is transfer of ion from electrolyte/electrode interface to the electrode bulk. The semiconductor of photoelectrode heterojunction becomes conductive if it is photoactive and allows transport of photon-generated charge carriers, requiring a smaller biasing overpotential. If the heterojunction is not very photoactive, a larger bias is required for electron transfer through the semiconducting electrode surface. Also, if the semiconductors, used in the fabrication of the heterojunction, are not well contacted with each other, the number of sites allowing the separation of the photon-generated electrons and holes decreases which again results in low photocurrent density. The primary requirement of the perfect fabrication of the heterojunction is the maximization of the contact surface, shared between the two semiconductors which constitute the heterojunction.

Usually, flat sensitizers, e.g. graphene and eC$_3$N$_4$, are dip coated, spin-coated or drop cast to create heterojunctions. All the methods use the dispersion of the sensitizer in an appropriate liquid dispersant. The interfacial tension, between the sensitizer particles and the dispersant, and the substrate surface morphology plays an important role in fabrication of a uniform, thin layered interface. In case of NTH, the sensitizer particles clog the mouth of the nanotubular structure [35] and further restrict sensitizer particles to reach inside the nanotube structure. It results as reduced interfacial surface and decreased PEC activity of the heterojunction, NTH. On the other hand, the open structure of NF allows easy access of sensitizer particles, which produces larger interfacial area between the substrate and the sensitizer. It is the reason why NFH performed better than the NTH. This is further explained through FESEM images and schematics of nanotubular and nanoflower structures of TiO$_2$ coated with eC$_3$N$_4$ sensitizers (figure 9). In NTH, tube openings are coated with eC$_3$N$_4$ but the sensitizer particles block the mouth, which lead to lower interfacial area and high interfacial reactance. On the contrary, NFH offers larger interfacial area with the sensitizer resulting in decreased interfacial reactance. The decrease in charge transport resistance and the interfacial reactance contributes to decreasing the impedance and increasing the photocurrent density.

4. Conclusion

The thermochemical formation of stemmed TiO$_2$ nanoflowers is prepared in a solution of hydrogen peroxide, and hydrofluoric acid. An open-branched nanoflower structure of anatase TiO$_2$, prepared at a low temperature and sensitized with eC$_3$N$_4$, is very effective towards PEC water splitting. It has been found that the nanoflower shape of TiO$_2$ evolves only in the optimum condition when Ti foil is digested for 60 h at 80 °C and in the solution containing 100 mM HF in 30% H$_2$O$_2$. FESEM shows the formation of stemmed nanoflower structure coated with eC$_3$N$_4$ sensitizer. SAED, HRTEM, EDX, XRD and XPS show the presence of polycrystalline anatase TiO$_2$ along with Ti metal core. Linear sweep voltammetry and electrochemical impedance spectroscopy studies show that stemmed TiO$_2$ nanoflower based heterojunction offers a substantial reduction in reactance to allow easier transport of ions which leads to enhanced PEC water splitting. The stemmed nanoflower array based TiO$_2/eC$_3$N$_4$ heterojunction (NFH) gives improved PEC activity towards water splitting by providing better accessibility than nanotubular array based TiO$_2/eC$_3$N$_4$ heterojunction (NTH). The photocurrent density of the heterojunction is nearly doubled from $\sim$0.6 mA cm$^{-2}$ for NTH to $\sim$1.1 mA cm$^{-2}$ for NFH. The impedance of the heterojunctions at the lower frequency domain is decreased from $\sim$3.5 kΩ for NTH to $\sim$0.1 kΩ for NFH. Such significant reduction in impedance is because of decrease of reactance from $\sim$1.2 kΩ for NTH to $\sim$0.1 kΩ for NFH. Furthermore, the present method shows the possibility to recover the spent fluoride from the exhaust thermochemical solution, making the process eco-friendly.

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Conflict of interest

The authors declare no competing financial interest.
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