

# Upcycled Synthesis and Extraction of Carbon-Encapsulated Iron Carbide Nanoparticles for Gap Plasmon Applications in Perovskite Solar Cells

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## Abstract

An effective method for obtaining large amounts of metal nanoparticles encapsulated by carbon layers through upcycling from floating-catalyst aerosol chemical vapor deposited carbon nanotubes is demonstrated. Nanoparticles with diameters of less than 20  $\mu\text{m}$  are selectively extracted from the synthesized carbon assortments through sonication, centrifugation, and filtration. The particles show an aggregation behavior owing to the  $\pi$ - $\pi$  interaction between the graphitic carbon shells surrounding the iron carbides. By controlling the degree of the aggregation and arrangement, the light scattering by the gap-surface plasmon effect in perovskite solar cells is maximized. Application of the nanoparticles to the devices increased the power conversion efficiency from 19.71% to 21.15%. The short-circuit current density (JSC) trend over the particle aggregation time accounts for the plasmonic effect. The devices show high stability analogue to the control devices, confirming that no metal-ion migration took place thanks to the encapsulation.

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An effective method for obtaining large amounts of metal nanoparticles encapsulated by carbon layers through upcycling from floating-catalyst aerosol chemical vapor deposited carbon nanotubes is demonstrated. Nanoparticles with diameters of less than 20  $\mu\text{m}$  are selectively extracted from the synthesized carbon assortments through sonication, centrifugation, and filtration. The particles show an aggregation behavior owing to the  $\pi$ - $\pi$  interaction between the graphitic carbon shells surrounding the iron carbides. By controlling the degree of the aggregation and arrangement, the light scattering by the gap-surface plasmon effect in perovskite solar cells is maximized. Application of the nanoparticles to the devices increased the power conversion efficiency from 19.71% to 21.15%. The short-circuit current density ( $J_{\text{SC}}$ ) trend over the particle aggregation time accounts for the plasmonic effect. The devices show high stability analogue to the control devices, confirming that no metal-ion migration took place thanks to the encapsulation.

## 1. Introduction

In the context of an environmentally sustainable society, organometallic halide perovskite solar cells (PSCs) have emerged as promising next-generation thin-film solar cells.<sup>1-4</sup> This is owing to the exceptionally high power conversion efficiency (PCE) of PSCs, as the reported certified efficiency is 25.6%.<sup>5-8</sup> To achieve a high PCE, many efforts have been made by researchers globally. Conventionally, a strategy for testing various compositions of perovskites by changing the precursor ratio to adjust the perovskite film bandgap has been reported.<sup>9-13</sup> A more contemporary strategy is to use additives in PSCs. Additive materials, such as polymers,<sup>14,15</sup> small molecules,<sup>16,17</sup> nanocarbons,<sup>18-20</sup> and even biomaterials,<sup>21</sup> have been proven to be effective in increasing the device performance of PSCs by enlarging the perovskite crystals and passivating interfacial defects.<sup>22-24</sup> Such an additive approach is an attractive method because small amounts of materials entailed by a facile process have a tremendous impact on the PSC performance. Another well-established additive approach is the insertion of

metal nanoparticles (NPs) to stimulate light absorption via the plasmonic effect.<sup>25</sup> NPs<sup>26–29</sup> have been utilized in various fields, including biomedicine,<sup>30</sup> batteries,<sup>31</sup> and photovoltaics. The nanoscale size of NPs induces quantum effects, opening up infinite possibilities when employed in devices. Metal NPs are unique among a wide range of NPs, as they can induce optical enhancement via plasmonic effects<sup>32–36</sup> and effective charge extraction by a host–guest electronic interaction.<sup>37–40</sup> A large number of electrons participate in the surface plasmonic resonance, improving the proximity field at the intrinsic frequency of the plasmonic metal NPs.<sup>41,42</sup> Thin-film solar cells such as organic solar cells<sup>43–46</sup> and PSCs<sup>47–50</sup> have exploited the properties of metal NPs to boost their PCE. However, it should be emphasized that applications of metal NP in PSCs are much fewer than those in organic solar cells. This is ascribed to the ion-migration-derived degradation of metal halide perovskite materials.<sup>51–54</sup> Inserting metal NPs within the PSC device system or, even worse, directly next to the perovskite layer, results in degradation of the PSCs. Higgins *et al.* and Yao *et al.* suggested a solution to this, that is, protecting NPs by carbon materials, using which they increased the PCE of PSCs while retaining device stability.<sup>34,38</sup> To date, two types of carbon-encapsulated metal NPs have been reported, namely, metallofullerenes and carbon-encapsulated iron carbide (FeC@C). FeC@C NPs were generated by heating ferrocene particles with carbon allotropes under high pressure.<sup>37,62</sup> In contrast to metallofullerenes, which are produced by inserting metal species into the fullerene cage,<sup>55–58</sup> FeC@C is synthesized by growing carbon from the iron (Fe) core.<sup>59–64</sup> The FeC in FeC@C has an Fe/Fe<sub>1-x</sub>C<sub>x</sub> core/shell structure encapsulated by several carbon layers.<sup>59,63</sup> This is simpler and incurs a much lower production cost and higher yield compared to metallofullerene synthesis.

In this study, we propose a facile and eco-friendly upcycling method of producing FeC@C NPs and demonstrate their applicability in photovoltaic devices as plasmonic NPs. Aerosol-synthesized carbon nanotubes (CNTs) use ferrocene as a catalyst.<sup>65–67</sup> As a result, the produced CNT films inevitably contain FeC@C NPs, which are regarded as impurities by CNT

researchers. Unsuccessful synthesis leaves excess amounts of FeC@C NPs in CNT films, lowering the electrical performance of the CNTs. Instead of treating this as a failed CNT sample, FeC@C NPs can be selectively collected from the CNTs. Accordingly, a method of extracting FeC@C NPs from aerosol-synthesized CNTs is introduced in this work along with their application to PSCs as plasmonic light and charge transport enhancers that do not induce ion migration. FeC@C NPs with a diameter of *ca.* 5–20 nm were extracted via sonication, centrifugation, and filtration. The collected NPs exhibited a fascinating trait of aggregation over time, which was attributed to the  $\pi$ – $\pi$  interaction between the surrounding graphitic carbon layers, as observed from various analyses. By controlling the aggregation time, the gap plasmon coupling between the constituent NPs produced diverse plasmon modes, providing freedom to manipulate the optical properties via different nano-assemblies.<sup>68</sup> This was supported by optical measurements and computational analyses. To exploit this phenomenon, the FeC@C NP solution was drop-cast onto the SnO<sub>2</sub> layer or onto the fluorine-doped tin oxide (FTO) layer, followed by certain periods of waiting time for aggregation to occur before the subsequent PSC fabrication. The FeC@C NP-added PSCs showed a considerably improved device performance compared to the control devices, irrespective of the FeC@C NPs above the SnO<sub>2</sub> layer or FTO layer. The aggregation waiting time of 3 h was optimal, giving the highest PCE of 21.15% and 20.57% from the PSCs with the NPs on SnO<sub>2</sub> and FTO, respectively. This is a substantial increase as the control PSCs without NPs gave a PCE of 19.71%. The increasing trend of short-circuit current density ( $J_{sc}$ ) with the waiting time for NP aggregation revealed that the improved PCE resulted from the gap-surface plasmonic effect of the aggregated NPs. Enhanced electron collection by the inserted FeC@C NPs contributed to the increase in open-circuit voltage ( $V_{oc}$ ) and fill factor (FF), which was corroborated by the investigation carried out herein. We conclude that the addition of FeC@C NPs induced not only the gap-surface plasmon effect but also favorable charge transport. The location of the added FeC@C NPs in the PSCs did not affect the device performance on SnO<sub>2</sub> or FTO. The unencapsulated FeC@C NP-added PSCs

exhibited stable operation for over 40 days under ambient conditions compared to the control devices, confirming that no ion migration occurs and the use of NPs does not damage the perovskite layer. This is the first demonstration of carbon-encapsulated metal nanoparticles used as gap-surface plasmons in device applications. The proposed novel approach is a versatile and cost-effective route which does not promote metal ion migration and will therefore lead to a breakthrough in the field of nanoparticle-based next-generation optoelectronics.

## 2. Results and Discussion

### 2.1. Upcycled Synthesis of Carbon-Encapsulated Iron Nanoparticles

#### 2.1.1. Synthesis of Carbon-Encapsulated Iron Carbide Nanoparticles

Carbon films containing a large proportion of FeC@C NPs were synthesized using the floating-catalyst aerosol chemical vapor deposition under a specific condition described in the experimental section. The produced carbon films were observed using high-resolution transmission electron microscopy (HR-TEM) (**Figure. 1a**). Expectedly, a large amount of FeC@C NPs was attached to the surface of the CNT strands. Energy-dispersive X-ray spectroscopy (EDS) analysis of TEM was used to identify FeC@C NPs by focusing on one of the CNT strands (**Figure. 1b** and **S1**). The presence of Fe along the CNT strand confirmed the existence of FeC@C NPs. The HR-TEM image of the carbon film shows that FeC@C NPs have diameters between 5 nm and 20 nm (**Figure. S2**). NPs with a diameter of ~8 nm were predominant, and they appeared completely wrapped by several layers of carbon sheets (**Figure. S2b**). X-ray photoelectron spectroscopy (XPS) was used to ascertain the identity of the FeC@C NPs by probing the elemental status before and after cleaning the carbon films with acid (**Figure. 1c-g** and **S3**). In this XPS analysis, we introduced conventional CNT films as well for comparison. The intensity of the Fe<sub>2p3</sub>, Fe<sub>3p</sub>, and Fe<sub>2p</sub> peaks from the aerosol-synthesized carbon

film were considerably greater than those from the conventionally synthesized CNT films in which ferrocene was also used as the catalyst (**Figure. 1c** and **S3**). To prove that the produced Fe NPs were thoroughly encapsulated by the carbon sheet, we rinsed the carbon film with triflic acid (TFMS). The intensity of the  $C_{1s}$  peak decreased after the acid treatment, from which we can deduce that any remaining unencapsulated FeO along with carbon impurities were washed away (**Figure. 1d**).<sup>69,70</sup> The fact that the intensity of the Fe peaks is stronger after the acid treatment indicates the reduction of FeO (**Figure. 1e** and **S3b**). The FeC@C NPs were completely encapsulated by the carbon sheet, therefore unaffected by the acid, as evidenced by the conspicuous Fe peaks. The disappearance of the  $O_{1s}$  shoulder at 530 eV indicates the removal of oxygen from FeO, which supports our claim (**Figure. 1f**).<sup>71,72</sup> The overall  $O_{1s}$  peak at 534 eV increased in intensity after the acid treatment, probably due to the hygroscopic TFMS-doped carbon films attracting  $H_2O$  and  $O_2$ .

### 2.1.2. Extraction of Carbon-Encapsulated Iron Carbide Nanoparticles

As the next step, FeC@C NPs were separated from the aerosol-synthesized carbon films by ultrasonication and filtration (**Figure. 2a**). The separation procedure was as follows (**Figure. 2b**): a carbon film containing a large amount of FeC@C-attached CNTs was sonicated intensively for 6 h in chlorobenzene (CB) to separate as many NPs as possible from the CNTs (**Figure. S4**). The FeC@C NPs dispersed in CB showed magnetic properties, confirming the presence of FeC (**Figure. S5** and **Video 1**).<sup>73–75</sup> The solution was centrifuged at 10,000 rpm for 20 min to sink large-size FeC@C NPs and CNTs. The supernatant of the solution was filtered by polytetrafluoroethylene (PTFE) with a 0.20- $\mu$ m pore size to remove further impurities. The effects of sonication and filtration were analyzed using dynamic light scattering (DLS). The DLS data shows that the sonicated solution contains NPs with different sizes as well as some CNTs (**Figure. 2c** and **S6a**); NPs with a size of *ca.* 10 nm were dominant according to the DLS

number graph (**Figure. 2d** and **S6a**). This matches the size of the individual FeC@C NPs observed in the HR-TEM images (Figure. S2). Remeasuring the same solution after a few hours of waiting did not show any peaks, indicating that the NPs and CNTs had sunk down below the detection range (**Figure. S6b**). Interestingly, the measurement of the same solution after giving a gentle swirl showed the NP peaks but with an increased size, revealing that aggregation of NPs might have occurred owing to the  $\pi$ - $\pi$  interaction between the graphitic carbon shells (**Figure. S6c**). Further waiting increased the NP size even greater (**Figure. 2c, 2d, and S6d**). The DLS data of the filtered solution showed that any particles greater than 100 nm, including CNTs, were removed (**Figure. 2d** and **S7**). This means that we can control the size and degree of the FeC@C NP aggregation by waiting before drop-casting a NP solution onto a substrate. To confirm this, we used atomic force microscopy (AFM) and TEM. The FeC@C NPs were uniformly coated on a glass substrate according to the AFM images (**Figure. S8**). However, the resolution of the images were not enough to observe NP aggregation. To verify the aggregation over the waiting time, we prepared FeC@C NPs on an HR-TEM grid according to the waiting time. We observed that some of the FeC@C NPs aggregated (**Figure. 2e**), and the aggregation became stronger with the waiting time (**Figure. 2f**). Despite our attempt to substantiate the  $\pi$ - $\pi$  interaction between the carbon shells of the FeC@C NPs using the XPS technique, the quantity of FeC@C NPs coated on substrates was too low, and the Fe component was not detectable (**Figure. S9**).

## 2.2. Controlled Aggregation of Carbon-Encapsulated Iron Nanoparticles

### 2.2.1. Plasmonic Effect of Aggregated Carbon-Encapsulated Iron Carbide Nanoparticles

The controlled aggregation of the FeC@C NPs with fixed gaps between the NPs indicated that a powerful optical effect could be induced. This can lead to a remarkable improvement in photon absorption when exploited in device applications such as PSCs. To examine this, we conducted ultraviolet–visible (UV–Vis) absorption spectroscopy on the aggregated FeC@C NPs under different waiting time. The data show that the extinction increases with an increase in the waiting time (**Figure. 3a**) and decreases back when the waiting time exceeds 3 h (**Figure. 3b**). This is a typical indication of the plasmonic effect caused by NPs.<sup>76–79</sup> This phenomenon was investigated further using computational analysis. We modelled a spherical Fe core surrounded by a thin layer of C shell with varying diameters of Fe NP ( $D$ ) and varying thickness of the C shell ( $t$ ). The core diameter and the C shell thickness variables were set as 5, 10, and 15 nm, based on the information from the TEM images (Figure. S2), and as 0, 1, 2, and 3 nm based on the reported multilayer graphene thickness (**Table S1**), respectively (**Figure. 3c** and **S10**).<sup>80,81</sup> The absorption and scattering cross-sections were calculated based on the varying core diameter and shell thickness, as well as different NP arrangements simulating NP aggregation (**Figure. 3d** and **S11**). It was postulated that the scattering is favorable for the light absorption of the perovskite active film; however, the absorption of NPs themselves undermines the plasmonic enhancement. Thus, obtaining the conditions where the absorption cross-section is minimal and the scattering cross-section is maximum is important. According to the simulation results, a single FeC@C NP has absolutely no optical effect, regardless of the size (**Figure. S12** and **S13**). However, the aggregated FeC@C NPs showed substantial scattering, despite a relatively small increase in absorption. In fact, the degree of absorption reverses when the number of aggregated NPs exceeds 4–5, whereas the degree of scattering increases continuously (**Figure. 3d**). This indicates that the larger the aggregation, the greater is the plasmonic effect. Therefore, the gap plasmonic effect is a dominant factor in the near-field light absorption enhancement by the FeC@C NPs, and the shell thickness is a key parameter in determining the amount of generated plasmonic polaritons

when electromagnetic fields are coupled with plasmons.<sup>82</sup> With an increase in the shell thickness, the scattering cross-section red-shifts from *ca.* 500 nm to 700 nm, which is within the effective absorption range of the perovskite photoactive films.<sup>83,84</sup> The shell thickness was deduced to be approximately 1 nm with 2–3 graphitic layers in the TEM images (**Figure. S2** and **Table S1**). Hence, we assume the shell thickness,  $t$ , to be 1, which produces a strong scattering cross-section (**Figure. 3e**) and gap-surface plasmon-induced electric field (**Figure. 3f**) for all three core sizes,  $D$ . Raman spectroscopy was also performed on drop-cast FeC@C NPs on glass substrates according to the waiting time to confirm the plasmonic effect. (**Figure. S14**). The Raman peak intensity and band positions depend on the conditions of the carbon nanostructure.<sup>85</sup> The difference in the Raman signal intensity for each excitation wavelength of the laser, namely 532 nm, 633 nm, and 785 nm, serves as indirect evidence for the electromagnetic field enhancement profile.<sup>86</sup> At laser wavelengths of 532 nm and 633 nm, the Raman signal intensity of the D+D' band ( $\sim 3000\text{ cm}^{-1}$ ) was greater than that of the D band ( $\sim 1500\text{ cm}^{-1}$ ). However, at 785 nm, the intensity of the D band intensified as the intensity of the D + D' band decreased in all samples with different waiting times. This evidences the plasmonic effect in which the calculated scattering cross-section value decreases with an increase in the wavelength of the incident light. To our dismay, variation in the Raman intensity over the waiting time was not observed. This means that the surface enhanced Raman scattering (SERS) effect witnessed here is originated perhaps from the charge transfer mechanism of host–guest interaction within the NPs more than the electromagnetic mechanism, the latter of which corresponds to the localized surface plasmonic resonance.<sup>87–89</sup> As the electromagnetic mechanism-driven SERS effect arises from the nanoscale gaps between NPs, aggregation of FeC@C NPs is a key contributing factor.

### 2.3. Perovskite Solar Cell Application of Carbon-Encapsulated Iron Nanoparticles

$\text{Cs}_{0.05}\text{FA}_{0.80}\text{MA}_{0.15}\text{PbI}_{2.75}\text{Br}_{0.25}$ -based PSCs were fabricated in the configurational structure of FTO/SnO<sub>2</sub>/perovskite/spiro-MeOTAD/Au, where the FeC@C NPs were drop-cast onto FTO layers or SnO<sub>2</sub> layers (**Figure. 4a** and **4b**). The top-view SEM images show that the quality of the perovskite films was similar for both cases; however, the perovskite films formed on pristine SnO<sub>2</sub> showed a marginally larger crystal domain size than the perovskite films formed on the FeC@C NP-deposited SnO<sub>2</sub> (**Figure. 4c** and **4d**). We suspect that the presence of FeC@C NPs on SnO<sub>2</sub> may hinder the growth of the perovskite film, even though the FeC@C NPs were not visible in the cross-sectional SEM images (**Figure. 4e** and **4f**). EDS was performed on the same device. However, as the amount of FeC@C NP was too low to be detectable from the cross-sectional images (**Figure. S15**). The devices were fabricated with different waiting times for FeC@C NP aggregations. In both cases, a waiting time of 3 h gave the highest PCEs (**Figure. S16** and **S17**). The statistical analyses show that there is a trend of  $J_{\text{SC}}$  and  $V_{\text{OC}}$  increasing with the waiting time and reducing when the waiting time is longer than 3 h. This verifies the aforementioned plasmonic effect of the aggregated FeC@C NPs, as the increase in  $J_{\text{SC}}$  is related to the number of absorbed photons.<sup>90,91</sup> For the devices with the best performance, the PSCs where FeC@C NPs were coated on FTO gave a PCE of 20.57% with  $J_{\text{SC}}$  of 25.05 mA cm<sup>-2</sup>,  $V_{\text{OC}}$  of 1.10 V, and FF of 0.74 (**Figure. 4g** and **Table 1**). The PSCs with FeC@C NPs on SnO<sub>2</sub> exhibited an even higher PCE of 21.15% with a  $J_{\text{SC}}$  of 25.73 mA cm<sup>-2</sup>,  $V_{\text{OC}}$  of 1.11 V, and FF of 0.74 (**Figure. 4h** and **Table 2**). The difference in device performance was mainly due to the  $J_{\text{SC}}$  values. In general,  $J_{\text{SC}}$  reflects the photon-to-current conversion efficiency not only by the enhanced intensity of sunlight but also by the perovskite crystal domain size.<sup>19–21,92–95</sup> The PSCs with FeC@C NPs on FTO exhibited a larger crystal domain size (**Figure. 4c** and **4d**). Nevertheless, PSCs with FeC@C NPs on SnO<sub>2</sub> produced a much higher  $J_{\text{SC}}$  owing to the FeC@C NPs right under the perovskite film, inducing the plasmonic effect in closer proximity. Steady-state PL and time-resolved (tr-PL) of perovskite films on SnO<sub>2</sub>/FeC@C NPs/FTO samples and FeC@C NPs/SnO<sub>2</sub>/FTO samples were carried out at

different waiting times. The increase in quenching of the PL spectra of both types of samples over the waiting time as well as the blueshifts indicate that the application of FeC@C NPs enhances the charge transfer and reduces the number of trap sites in SnO<sub>2</sub>.<sup>96</sup> This explains the increase in  $V_{OC}$  and FF of the FeC@C NP-applied PSCs in both the cases of FeC@C NPs above/under the SnO<sub>2</sub> layer. We postulate that the high electron affinity of the carbon shell as well as the host–guest electronic interaction<sup>37–40</sup> augmenting exciton extraction. The higher external quantum efficiency (EQE) of the PSC using FeC@C NPs than that of the control device in the short-wavelength region from 300 nm to 600 nm is suspected to originate from the enhanced electron collection by the FeC@C NPs next to SnO<sub>2</sub>.<sup>97</sup> The higher EQE of the PSC using the FeC@C NPs in the long-wavelength region from 650 nm to 800 nm corresponds to the greater light absorption due to the plasmonic effect (**Figure. S18**). The device stability under constant illumination of one sun was checked to examine ion migration. All unencapsulated FeC@C NP-used PSCs showed good operational stability equal to that of the control device in both cases of FeC@C NPs above/under the SnO<sub>2</sub> layer. This indicates that there is no ion migration occurring within the device system owing to the Fe particles being fully encapsulated by the carbon shell.

### 3. Conclusion

The synthesis and extraction of FeC@C NPs from aerosol-synthesized CNT films were demonstrated. Assortments of aerosol-synthesized CNTs containing FeC@C NPs of different sizes were dispersed in CB. FeC@C NPs with a desired size were collected through intensive

sonication and filtration. The presence and size of the FeC@C NPs were verified using various techniques such as SEM, EDS, AFM, and TEM. The FeC@C NPs showed aggregation over time, entailing an increasing intensity of the gap-surface plasmon effect. The self-aggregated FeC@C NPs have great potential for application in optoelectronic devices because tailoring the number and position of the NPs in close-packed clusters can induce diverse plasmon modes exhibiting strong magnetic and Fano resonance. Capitalizing on this point, PSCs were fabricated with aggregated NPs placed on the SnO<sub>2</sub> layer and the FTO layer. The addition of the FeC@C NPs to PSCs improved the PCE, which was attributed to both the enhanced light absorption and charge transfer by the plasmonic effect and by the host-guest electronic interaction, respectively. The excellent device stability shown by the FeC@C NP-added PSCs proves that the metal ions in the NPs did not migrate into the perovskite layer even when FeC@C NPs were next to the perovskite film.

#### 4. Experimental Section

*Preparation of FeC@C:* Aerosol-synthesized CNT films containing a large number of FeC@C NPs were prepared using the floating-catalyst aerosol chemical vapor deposition (CVD) method. Ferrocene (100 cc) was vaporized by passing CO through a cartridge filled with ferrocene powder. To stabilize the synthesis, 1.4% CO<sub>2</sub> was added to CO. The flow containing ferrocene vapor was introduced to the high-temperature zone of a quartz tube reactor through a water-cooled probe and mixed with additional CO. Ferrocene vapor was thermally decomposed in the gas phase of the aerosol CVD reactor at 850 °C. CO gas was supplied at 0.35 L min<sup>-1</sup> and decomposed on the Fe NPs, resulting in the growth of FeC@C NPs. The as-synthesized CNTs and FeC@C NPs were collected by passing the flow through CNTs, and FeC@C NPs were collected by filtering the flow through a nitrocellulose membrane filter (Millipore Corp., USA; HAWP, 0.45- $\mu$ m pore diameter) downstream of the reactor for 93 h. The FeC@C-containing

film was placed in a vial containing CB. To separate the intertwined FeC@C/CNT, sonication was performed at 40k Hz for 6 h. This process separated the FeC@C particles from the CNTs. The supernatant containing FeC@C NPs was separated by centrifugation at 10,000 rpm for 20 min. The supernatant was filtered using PTFE with a pore diameter of 0.20  $\mu\text{m}$ . The presence and size of the FeC@C NPs were determined using various analytical equipment described in the Results and Discussion section.

*Perovskite Precursor:* Formamidinium iodide (FAI), methylammonium bromide (MABr), lead(II) iodide ( $\text{PbI}_2$ , 99.99%), and lead(II) bromide ( $\text{PbBr}_2$ , >98%) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Cesium iodide (CsI, 99.998%) and tin(II) oxide ( $\text{SnO}_2$ , 15% in  $\text{H}_2\text{O}$ ) were purchased from Alfa Aesar Co., Ltd. (Ward Hill, MA, USA). 2,2,7,7-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9-spirobifluorene (spiro-MeOTAD), lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI), tris[2-(1*H*-pyrazol-1-yl)-4-*tert*-butylpyridine]-cobalt(III)-tris[bis-(trifluoromethylsulfonyl)imide] (FK209), 4-*tert*-butylpyridine (*t*BP), isopropyl alcohol (IPA), and chlorobenzene (CB) were purchased from Sigma-Aldrich Co., Ltd. (St. Louis, MO, USA). Dehydrated dimethylsulfoxide (DMSO, super dehydrated) and dimethylformamide (DMF, super dehydrated) were purchased from FUJIFILM Wako Pure Chemical Co., Ltd. (Osaka, Japan).

*Preparation of Perovskite Film:* A  $\text{Cs}_{0.05}\text{FA}_{0.80}\text{MA}_{0.15}\text{PbI}_{2.75}\text{Br}_{0.25}$ -based perovskite precursor solution was prepared by dissolving CsI (44.4 mg, 0.171 mmol),  $\text{PbI}_2$  (1432 mg, 3.11 mmol),  $\text{PbBr}_2$  (61 mg, 0.166 mmol), FAI (450 mg, 0.64 mmol), and MABr (54.3 mg, 0.16 mmol) in DMF (2400  $\mu\text{L}$ ) and DMSO (720  $\mu\text{L}$ ). After stirring for 30 min at 45°C, the solution was filtered through a 0.2- $\mu\text{m}$  PTFE filter. The precursor was spin-coated at 3000 rpm for 30 s on the  $\text{SnO}_2$  layer. This was followed by the application of 300  $\mu\text{L}$  of CB antisolvent. The annealing process was performed at 150°C for 10 min. The spiro-MeOTAD solution was prepared by mixing

108.45 mg spiro-MeOTAD, 13.65 mg of Li-TFSI, 20.25 mg of FK209, and 43.2  $\mu\text{L}$  of *t*-BP in 1.5 mL of anhydrous chlorobenzene. The hole-transporting layer was deposited from the 80- $\mu\text{L}$  spiro-MeOTAD solution at 3000 rpm for 20 s. Finally, a 100-nm-thick Au anode was fabricated by thermal deposition under a pressure of  $10^{-7}$  Torr.

*Fabrication of PSCs:* FTO substrates, pre-patterned FTO/glass substrates ( $7 \Omega \text{ sq}^{-1}$ ,  $25 \times 25 \text{ mm}^2$ ) (Asahi glass) were cleaned using the RCA-2 ( $\text{H}_2\text{O}_2$ - $\text{NCl}$ - $\text{H}_2\text{O}$ ) procedure for 15 min. The substrates were further cleaned by sonication with distilled water, acetone, and isopropanol in an ultrasonic bath for 15 min. Subsequently, tin(IV) oxide ( $\text{SnO}_2$ , 15% in  $\text{H}_2\text{O}$  colloidal dispersion, Alfa Aesar) solution was prepared by adding 5 mL of ethanol to 0.1128 g at room temperature, followed by sonication for approximately 1 min. The  $\text{SnO}_2$  solution was then filtered through a 0.45- $\mu\text{m}$  PTFE filter. Next, the  $\text{SnO}_2$  layer was spin-coated on the FTO glass (or  $\text{SnO}_2$  layer) at 2000 rpm for 30 s, which was later annealed at  $150^\circ\text{C}$  for 30 min. A solution containing FeC@C NPs was drop-casted on either FTO or  $\text{SnO}_2$  after a designated waiting time from sonication to induce  $\pi$ - $\pi$  aggregation. When the FeC@C solvent was dried, 100  $\mu\text{L}$  of the perovskite solution was filtered through a 0.45- $\mu\text{m}$  PTFE filter before being spin-coated on the  $\text{SnO}_2$  layer at 7000 rpm for 40 s. Antisolvent (1 mL of diethyl ether) was applied during the spin-coating of the perovskite solution at 37–38 s after spin-coating, followed by annealing at  $150^\circ\text{C}$  for 10 min. The spiro-MeOTAD solution was prepared by mixing 90.9 mg spiro-MeOTAD, 23  $\mu\text{L}$  of a stock solution of  $516 \text{ mg mL}^{-1}$  Li-TFSI in anhydrous acetonitrile, 10  $\mu\text{L}$  of a stock solution of  $395 \text{ mg mL}^{-1}$  FK209 in anhydrous acetonitrile, and 39  $\mu\text{L}$  of *t*-BP in 1.0 mL of anhydrous chlorobenzene. The hole-transporting layer was deposited from the 100  $\mu\text{L}$  spiro-MeOTAD solution at 4000 rpm for 20 s. Finally, an 80-nm-thick Au anode was fabricated by thermal deposition under a pressure of  $10^{-6}$  Torr.

*Device and Film Characterizations:* The  $J$ - $V$  curves of the PSCs under light were measured using a source meter (Keithley 2400, Tektronix) under simulated sunlight irradiation of 1 sun (AM 1.5G;  $100 \text{ mW cm}^{-2}$ ) using a solar simulator (Oriel® Sol3A™ Class AAA solar simulator, model 94043A). The source meter was calibrated using a standard PV reference cell ( $2 \text{ cm} \times 2 \text{ cm}$  monocrystalline silicon solar cell, calibrated at NREL, Colorado, USA). The incident photon-to-current conversion efficiency also known as external quantum efficiency (EQE) spectrum was measured using an Oriel® IQE-200™ equipped with a 250-W quartz tungsten halogen lamp as the light source and a monochromator, an optical chopper, a lock-in amplifier, and a calibrated silicon photodetector. Prior to the use of light, the spectral response and light intensity were calibrated using a monosilicon detector. The impedance response was measured over the range of 1 Hz to 1 MHz with an oscillation amplitude of 15 mV under dark conditions (Bio-Logic VMP-3). The experimental data were simulated using commercial Z-view software to estimate the values of each component using the corresponding equivalent circuits. The film surface and cross-sectional morphology were characterized via field emission scanning electron microscopy (FE-SEM, HITACHI Regulus8100). Photoluminescence (PL) was measured using a Quantaurus-QY plus (C-13534-12) from Hamamatsu Co., Ltd.

*Computational Analysis:* The finite-difference time-domain (FDTD) simulation of the plasmonic scattering and absorption of NPs was performed using the Lumerical FDTD software. The model comprised a 3D spatial domain of  $80 \times 80 \times 80 \text{ nm}^3$ , which was meshed into 0.1 nm in all xyz coordinates, and its boundary condition was set as a perfectly matched layer that absorbs all outgoing waves. An optical source with a wavelength ranging from 300 nm to 800 nm generates a plane wave propagating toward a target set of scatterers designated with a specific number of NPs with a core diameter ( $D$ ) and shell thickness ( $t$ ). The source type was chosen as a total-field scattered-field, where the model considers only the scattered portion of optical energy from NPs and ignores the rest of the portion that does not interact with any

objects. Two detectors (frequency-domain field and power) surrounded the simulation domain and monitored the absorbed and scattered optical energy by the NPs, resulting in effective scattering/absorption cross-sections. The optical field pattern within the NPs aligned in a plane normal to the incoming plane wave was recorded using a DFT monitor. The time-domain simulation was terminated by either a 100-fs time limit or an early shutoff of  $10^{-5}$ .

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

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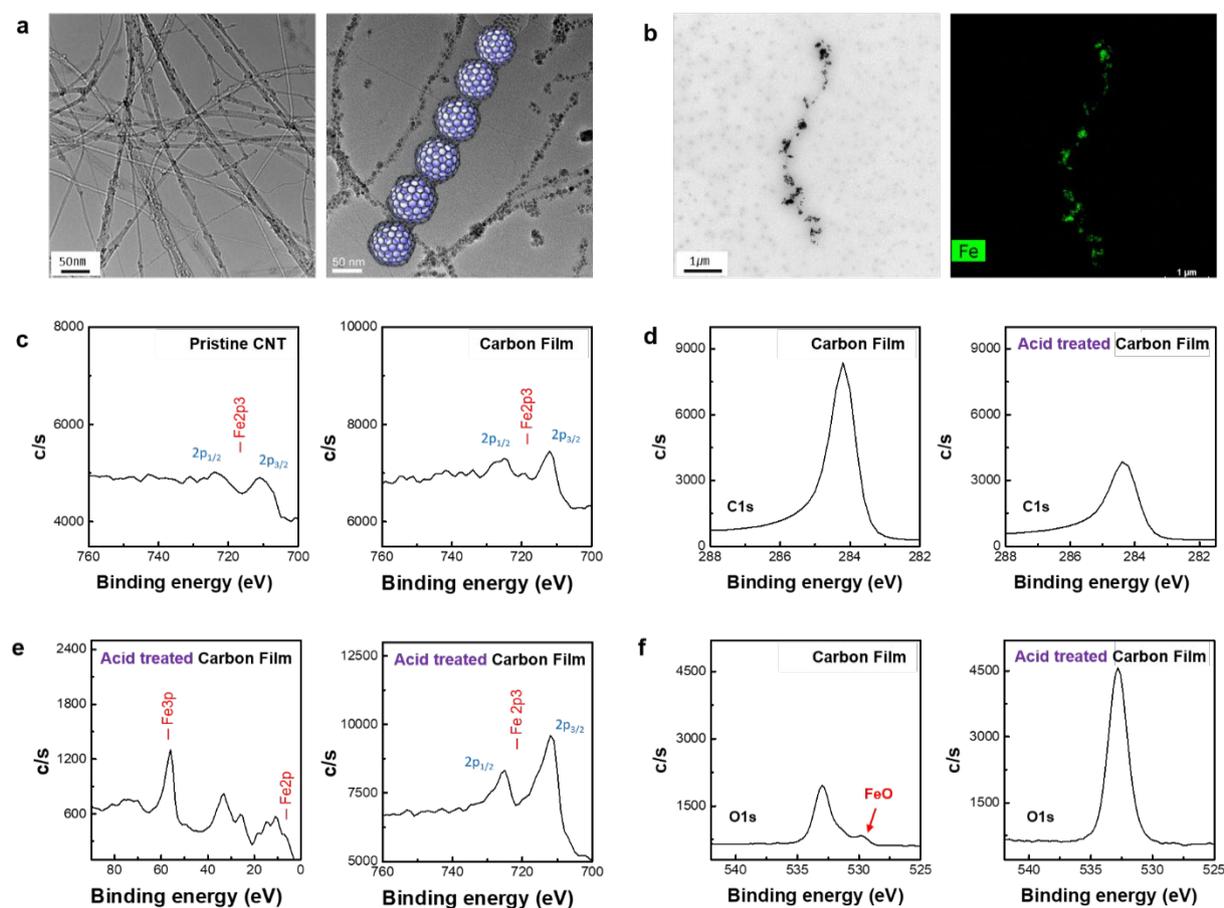
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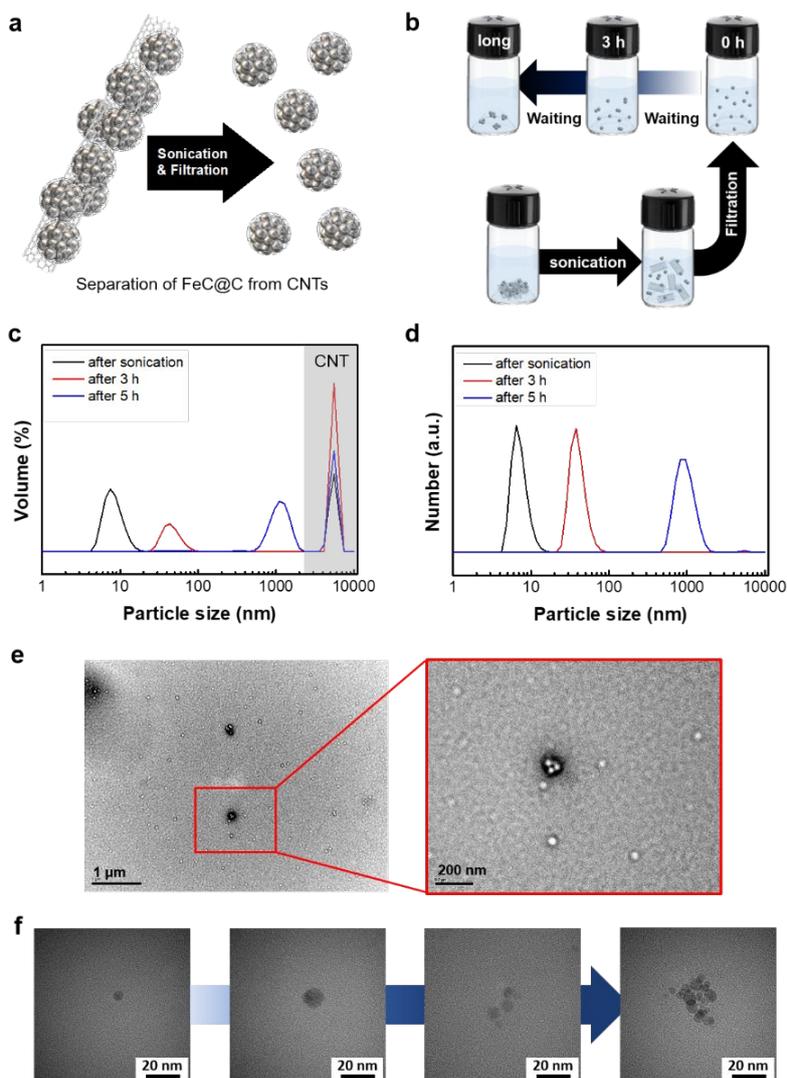
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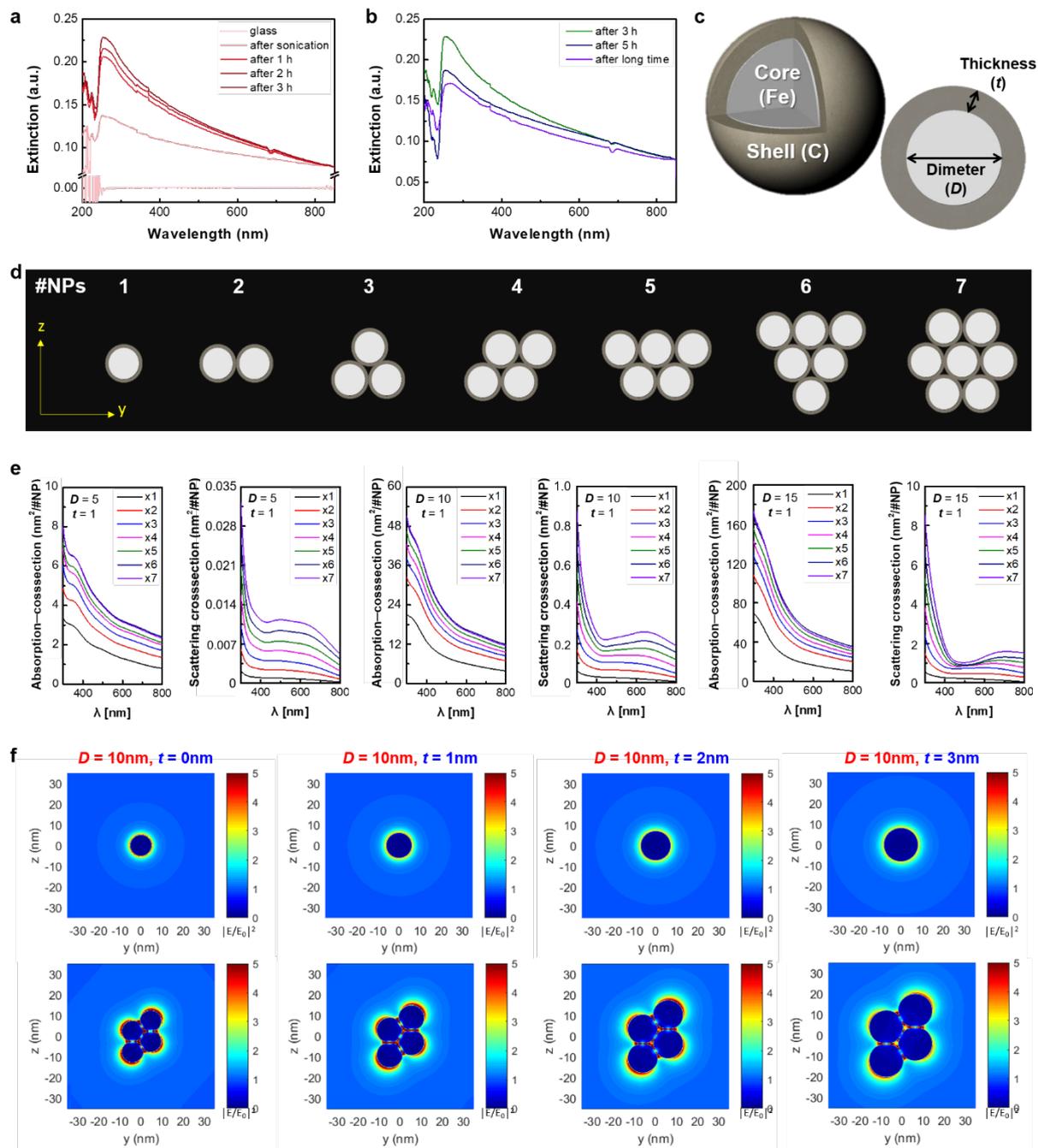
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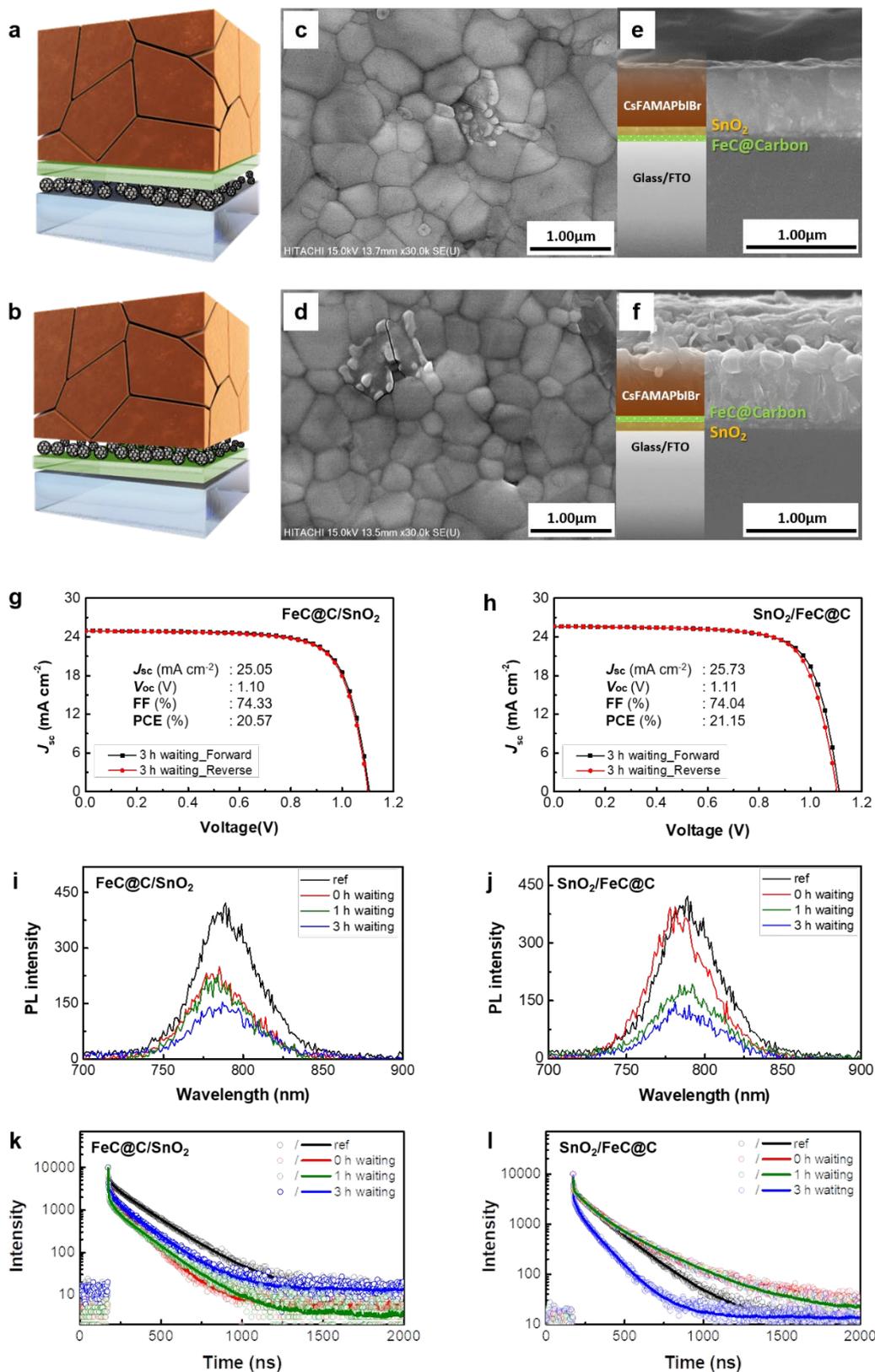
**Figure 1.** (a) TEM image of the aerosol-synthesised carbon film. (b) Result of EDS analysis through TEM to confirm the existence of Fe components. (c) XPS result of iron region (Fe<sub>2p</sub>) in pristine CNT and carbon film. (c-f) XPS result of the C<sub>1s</sub> peak, iron region (Fe<sub>3p</sub>, Fe<sub>2p</sub>) and O<sub>1s</sub> peak before and after acid treatment on the carbon film.



**Figure 2.** (a–b) Illustration of a method of separating FeC@C NPs from CNT. (c–d) DLS analysis of depending on the waiting time. (e) FeC@C NPs and enlarged TEM images. (f) HR-TEM results of FeC@C NPs that are aggregated depending on the waiting time.



**Figure 3.** Optical analysis of FeC@C NPs (a-b) UV–Vis results of FeC@C NPs by waiting time, (c) Schematic illustration of FeC@C NPs, (d) geometry by number of FeC@C NPs, (e) When the  $t$  is 1 nm, graphs of absorption cross-section and scattering cross-section according to the change in the  $D$ , (f) When the  $D$  is 10 nm, the electric field according to the change in the  $t$ .



**Figure 4.** (a–b) Configurational structure and (c–f) SEM image of two type devices. (g–h)  $J$ - $V$  curves of optimized devices based on the photovoltaic performance and the location of FeC@C NPs. (i–l) Steady-state PL and tr-PL of perovskite films on SnO<sub>2</sub>/FeC@C NPs/FTO samples and FeC@C NPs/SnO<sub>2</sub>/FTO samples under different waiting times.

**Table 1.** Photovoltaic parameters of the PSCs with SnO<sub>2</sub> on FeC@C NPs under one sun (AM 1.5 G, 100 mW cm<sup>-2</sup>).

Device structure and NP aggregation time		$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (V)	FF (%)	PCE (%)	$R_s$ ( $\Omega$ ·cm <sup>2</sup> )	$R_{sh}$ ( $\Omega$ ·cm <sup>2</sup> )
Au	ref	24.64 [24.77]	1.10 [1.10]	72.89 [70.77]	<b>19.71 [19.35]</b>	39.34	57089.70
Spiro-MeOTAD							
Perovskite	0 h	23.80 [23.73]	1.14 [1.10]	71.32 [70.15]	<b>19.42 [18.23]</b>	37.38	37274.96
SnO <sub>2</sub>	1 h	24.03 [23.69]	1.11 [1.11]	72.70 [72.37]	<b>19.44 [19.09]</b>	43.46	45399.00
FeC@C NPs							
FTO	3 h	<b>25.05 [24.61]</b>	<b>1.10 [1.10]</b>	<b>74.33 [73.00]</b>	<b>20.57 [19.66]</b>	<b>33.81</b>	<b>27866.66</b>
Glass	long	24.62 [23.87]	1.12 [1.10]	74.79 [72.64]	<b>20.55 [19.08]</b>	20.55	31.38

**Table 2.** Photovoltaic parameters of the PSCs with FeC@C NPs on SnO<sub>2</sub> under one sun (AM 1.5 G, 100 mW cm<sup>-2</sup>).

Device structure and NP aggregation time		$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (V)	FF (%)	PCE (%)	$R_s$ ( $\Omega$ ·cm <sup>2</sup> )	$R_{sh}$ ( $\Omega$ ·cm <sup>2</sup> )
Au	ref	24.64 [24.77]	1.10 [1.10]	72.89 [70.77]	<b>19.71 [19.35]</b>	39.34	57089.70
Spiro-MeOTAD							
Perovskite	0 h	24.59 [24.08]	1.10 [1.09]	72.17 [70.15]	<b>19.59 [18.46]</b>	38.30	30770.20
FeC@C NPs	1 h	25.07 [24.45]	1.14 [1.15]	69.94 [69.20]	<b>19.91 [19.37]</b>	50.81	47750.96
SnO <sub>2</sub>							
FTO	3 h	<b>25.73 [25.70]</b>	<b>1.11 [1.11]</b>	<b>74.04 [73.44]</b>	<b>21.15 [20.78]</b>	<b>34.13</b>	<b>23741.22</b>
Glass	long	24.19 [23.89]	1.07 [1.08]	76.20 [73.06]	<b>19.78 [18.97]</b>	30.17	20324.67

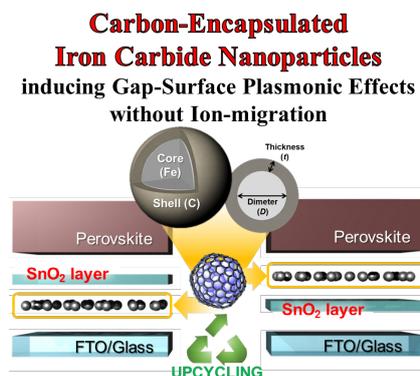
**Carbon-encapsulated iron carbide nanoparticles are upcycled from carbon nanotubes for perovskite solar cell application.** The nanoparticles aggregate owing to the  $\pi$ - $\pi$  interaction of the graphitic shells. A gap-surface plasmon effect is induced depending on the degree of the aggregation and arrangements. When applied to solar cells, the efficiency increases from 19.7% to 21.2%. The added nanoparticles do not instigate ion migration as they are encapsulated by the carbon shells.

**Keywords**

iron nanoparticles, carbon nanoparticles, carbon encapsulation, carbon nanotubes, perovskite solar cells, plasmonic effect

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**Upcycled Synthesis and Extraction of Carbon-Encapsulated Iron Carbide Nanoparticles for Gap Plasmon Applications in Perovskite Solar Cells**

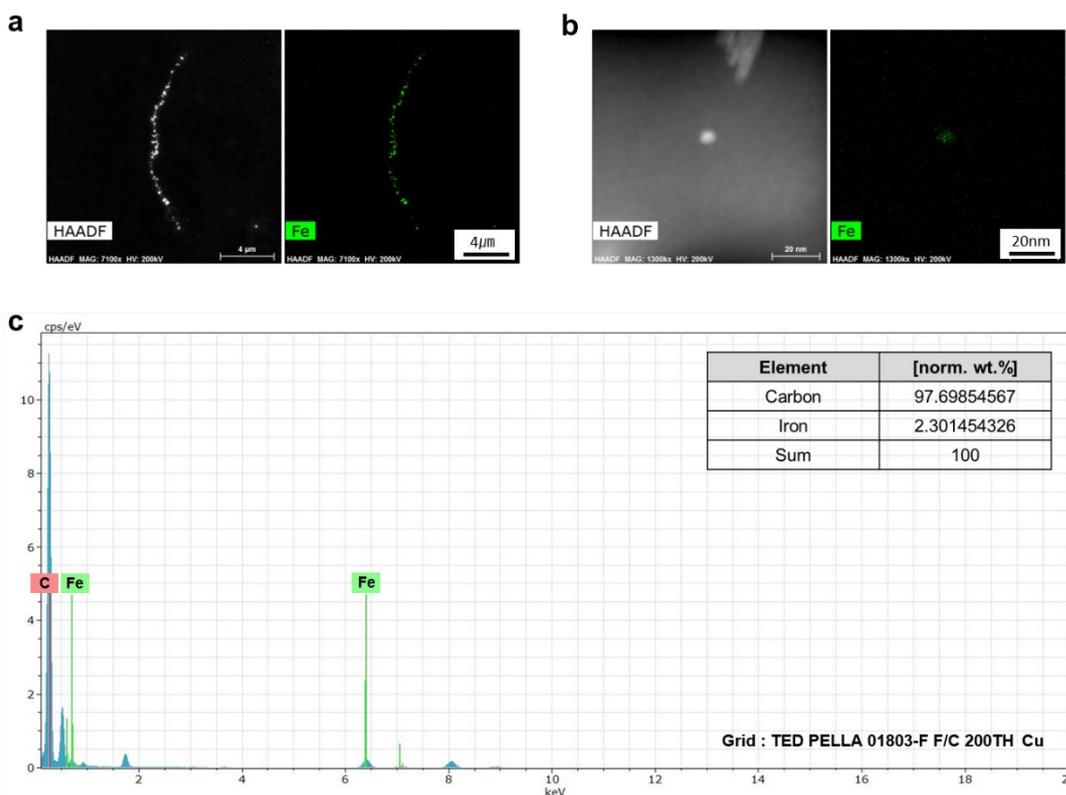


(Supporting Information can be included here using this template)

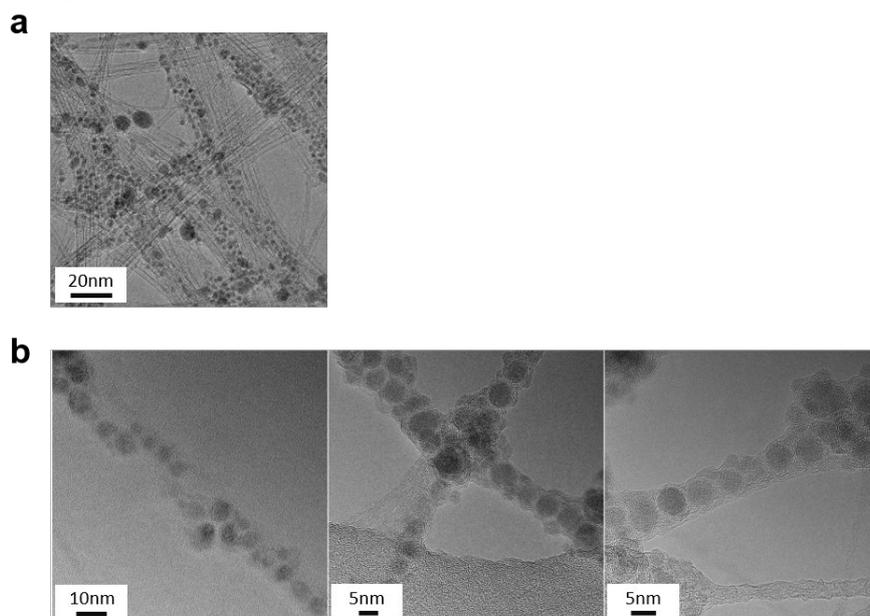
## Supporting Information

### Upcycled Synthesis and Extraction of Carbon-Encapsulated Iron Carbide Nanoparticles for Gap Plasmon Applications in Perovskite Solar Cells

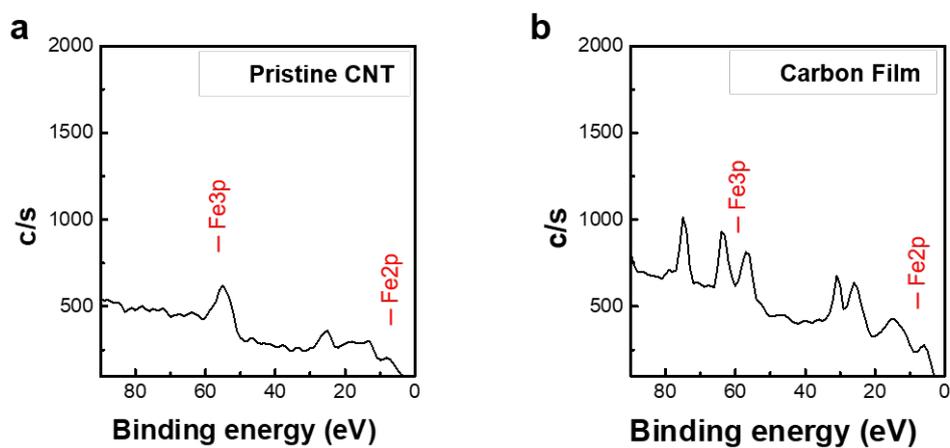
Jiye Han, Kyusun Kim, Mohammad Tavakkoli, Jongmin Lee, Dawoon Kim, In Chung, Aram Lee, Keonwoo Park, Yongping Liao, Jin-Wook Lee, Seung-Ki Lee, Hyokyung Sung\*, Esko Kauppinen\*, Il Jeon\*



**Figure S1.** TEM images of a) FeC@C NP along the CNT strand, b) FeC@C NP, and c) EDS graph.



**Figure S2.** HR-TEM images of the carbon film with a scale bar of a) 20 nm and b) 10 nm and 5 nm.



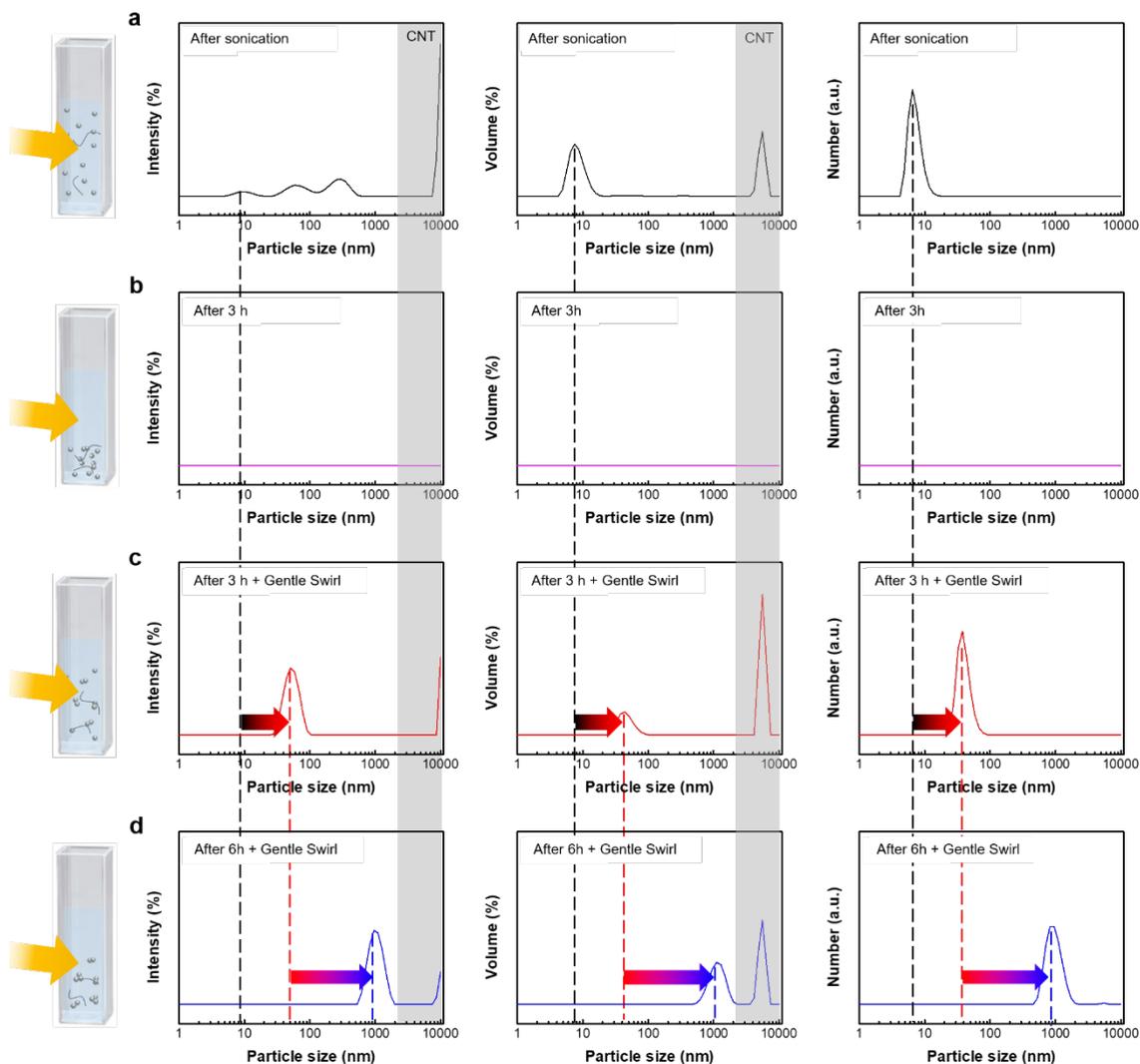
**Figure S3.** XPS results of Fe peak from pristine CNT and carbon film.



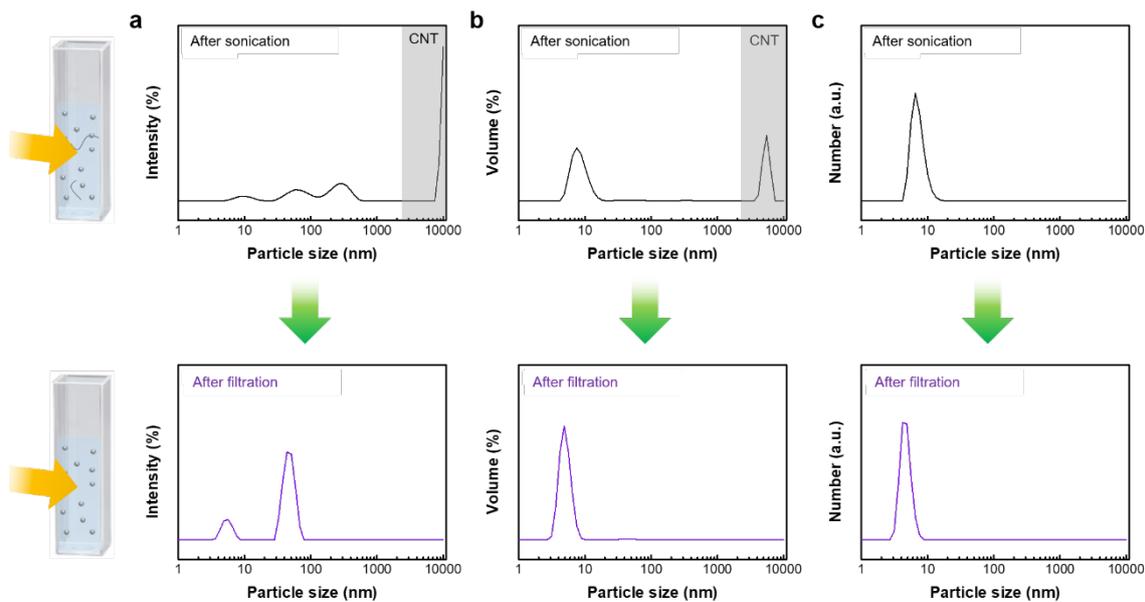
**Figure S4.** Photographic images of the FeC@C NPs-containing carbon film and the centrifuged solution followed by sonication.



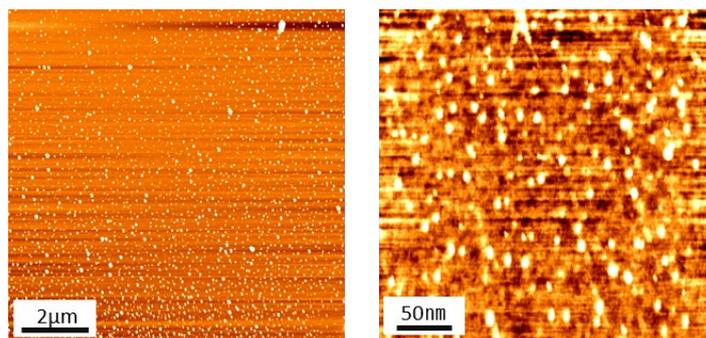
**Figure S5.** Captured images of the video clip attached as separate supporting information revealing the presence of FeC@C NPs in the obtained solution.



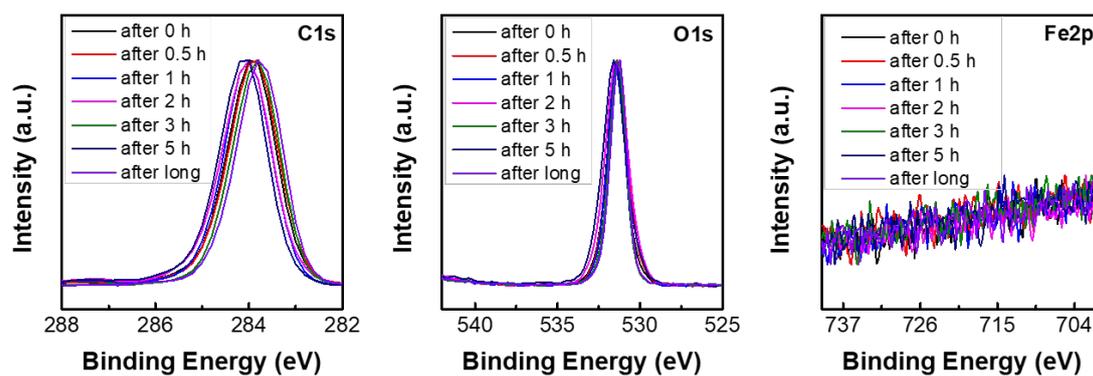
**Figure S6.** DLS results showing a change in size distribution of FeC@C NPs over time: a) after sonication; b) 3 h after sonication; c) 3 h after sonication + gentle swirl; d) 6 h after sonication + gentle swirl.



**Figure S7.** DLS results before and after the filtration: a) intensity, b) volume, and c) number graph.



**Figure S8.** AFM images of FeC@C NPs on a glass substrate.



**Figure S9.** XPS results of C, O, and Fe depending on the waiting time

**Table S1.** Actual graphene thickness according to the stacked-layer and graphene thickness set in the experiment.

Graphene layer	Actual Thickness (nm)	Effective Thickness (nm)
1 layer	0.335	0
2 layer	0.81	1
3 layer	1.285	1
4 layer	1.76	2
7 layer	3.185	3

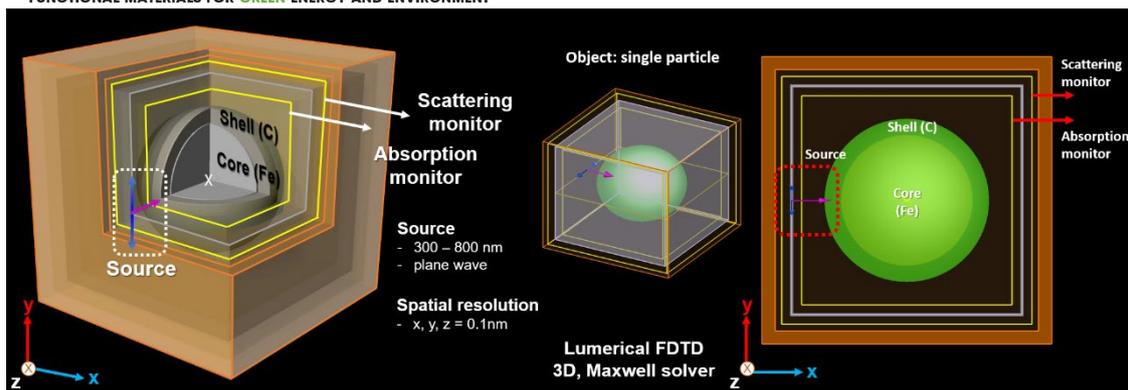
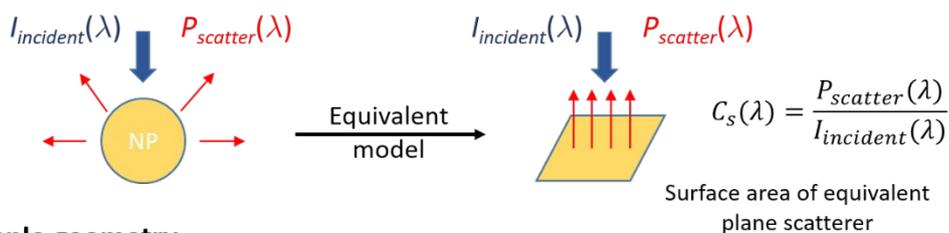


Figure S10. Schematic of the 3D-FDTD calculation.

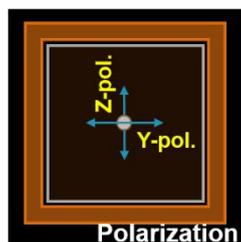
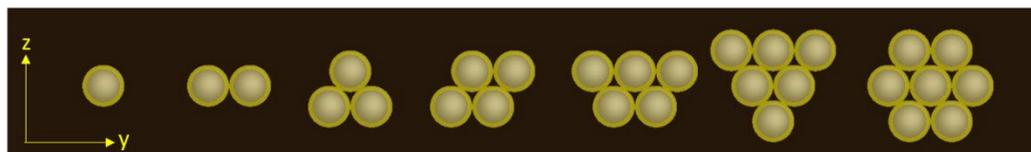
**Output parameters : scattering cross-section, absorption cross-section**

- e.g. scattering cross-section



→ **Sample geometry**

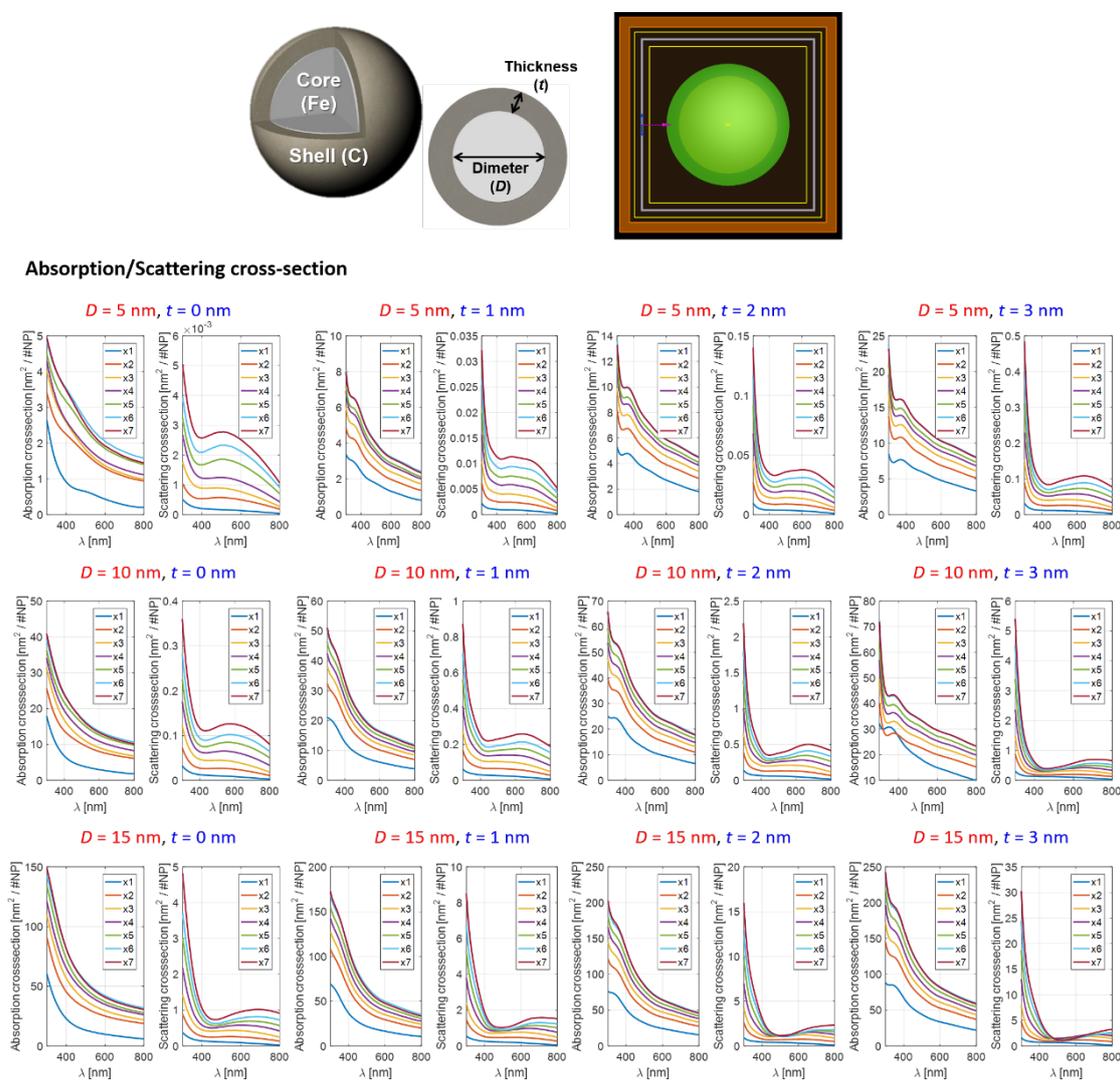
#NPs : 1      2      3      4      5      6      7



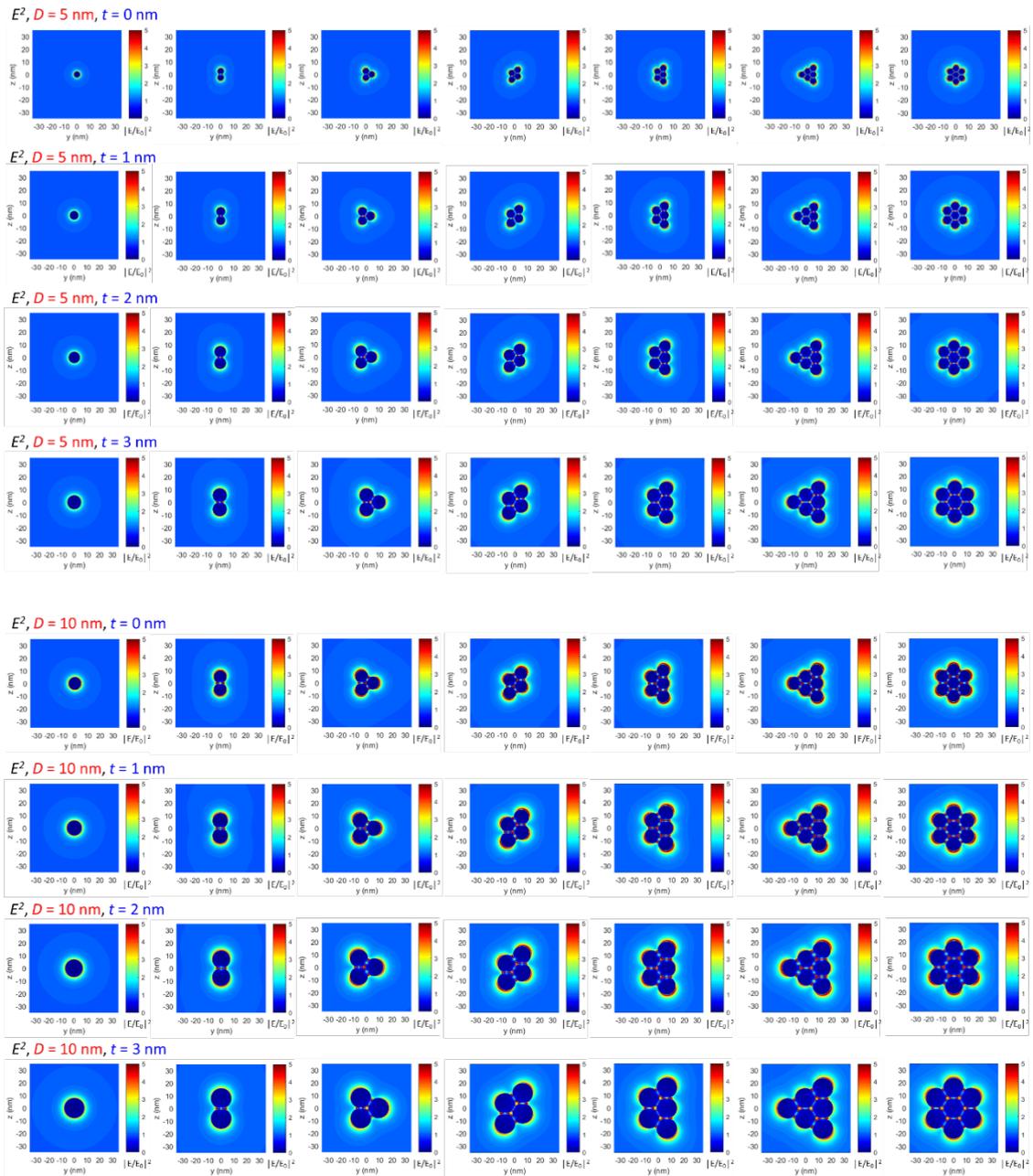
**Random polarization**

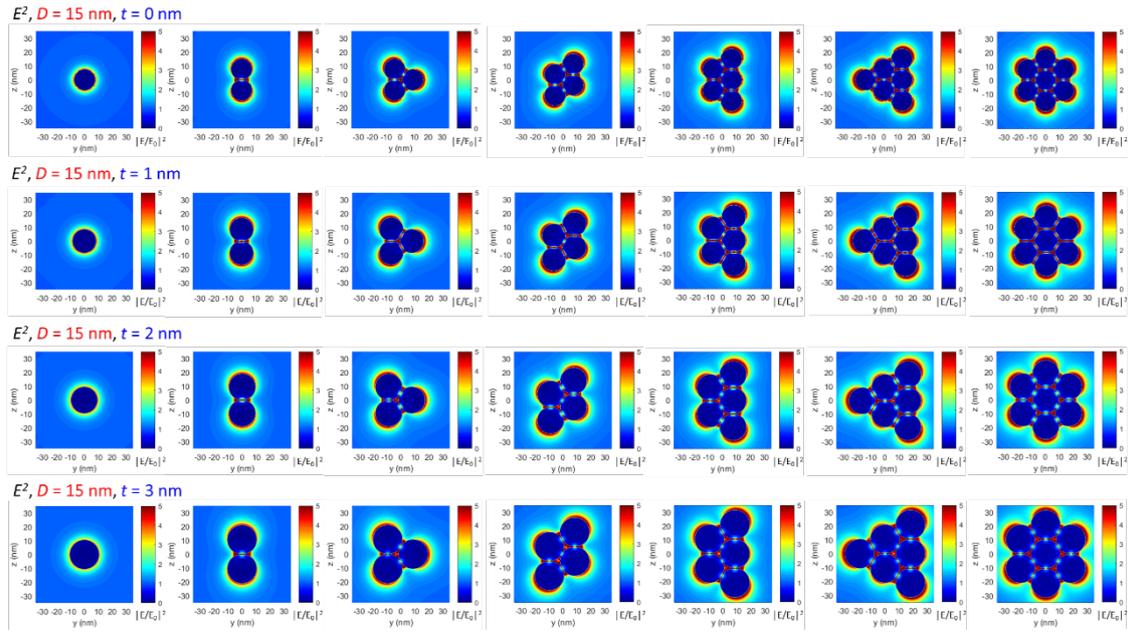
$$= (x\text{-polar result} + y\text{-polar result}) / 2$$

Figure S11. Schematic of output parameters for 3D-FDTD calculation and geometry depending on the number of NPs.

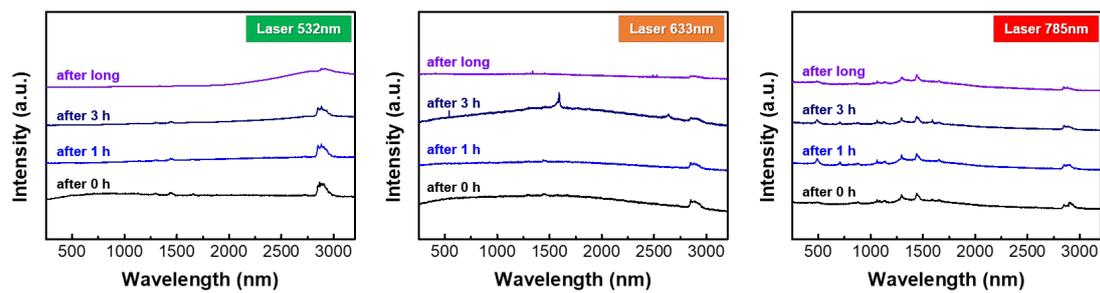


**Figure S12.** Absorption scattering cross-section graph through changes in the core diameter ( $D$ ) of NPs and the thickness ( $t$ ) of shells.

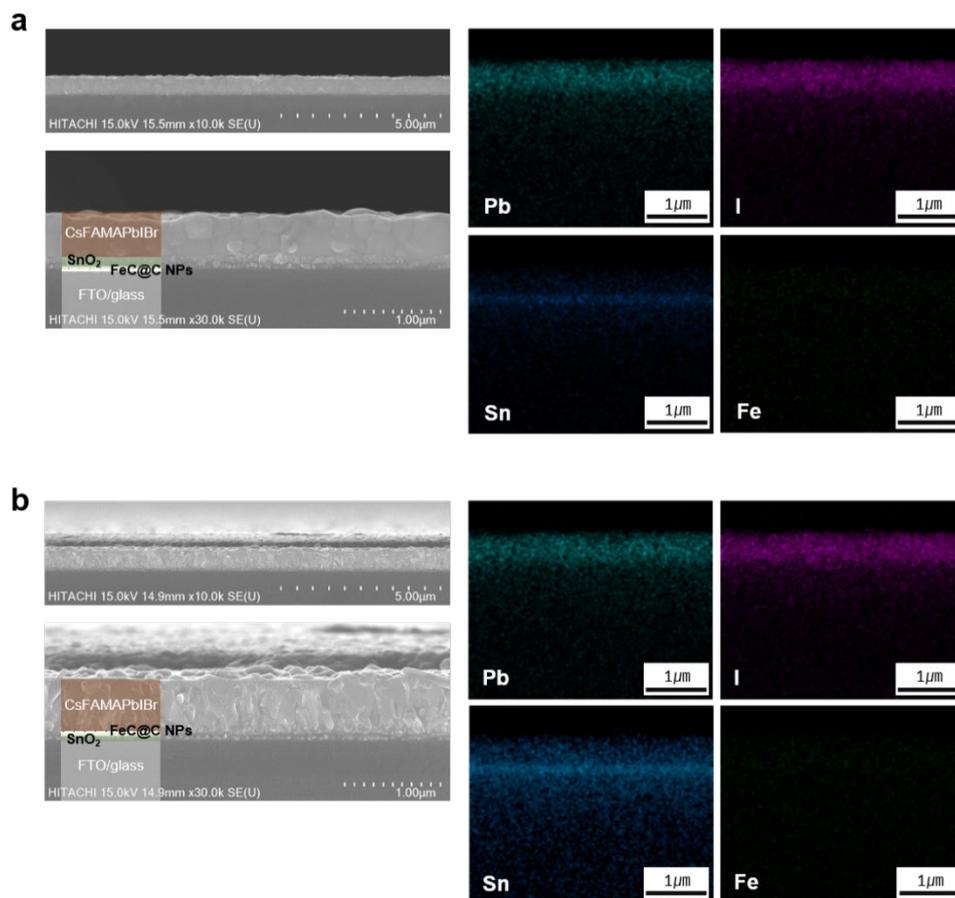




**Figure S13.** 3D-FDTD calculations: Electric field calculated according to the geometry of FeC@C NPs having the core diameter ( $D$ ) and shell thickness ( $t$ ) as variables.



**Figure S14.** Raman spectra according to the waiting time for each laser (532, 633, and 785 nm).



**Figure S15.** Cross-sectional SEM images and EDS of PSCs. a) SnO<sub>2</sub> on FeC@C NPs layer and b) FeC@C NPs on SnO<sub>2</sub> layer

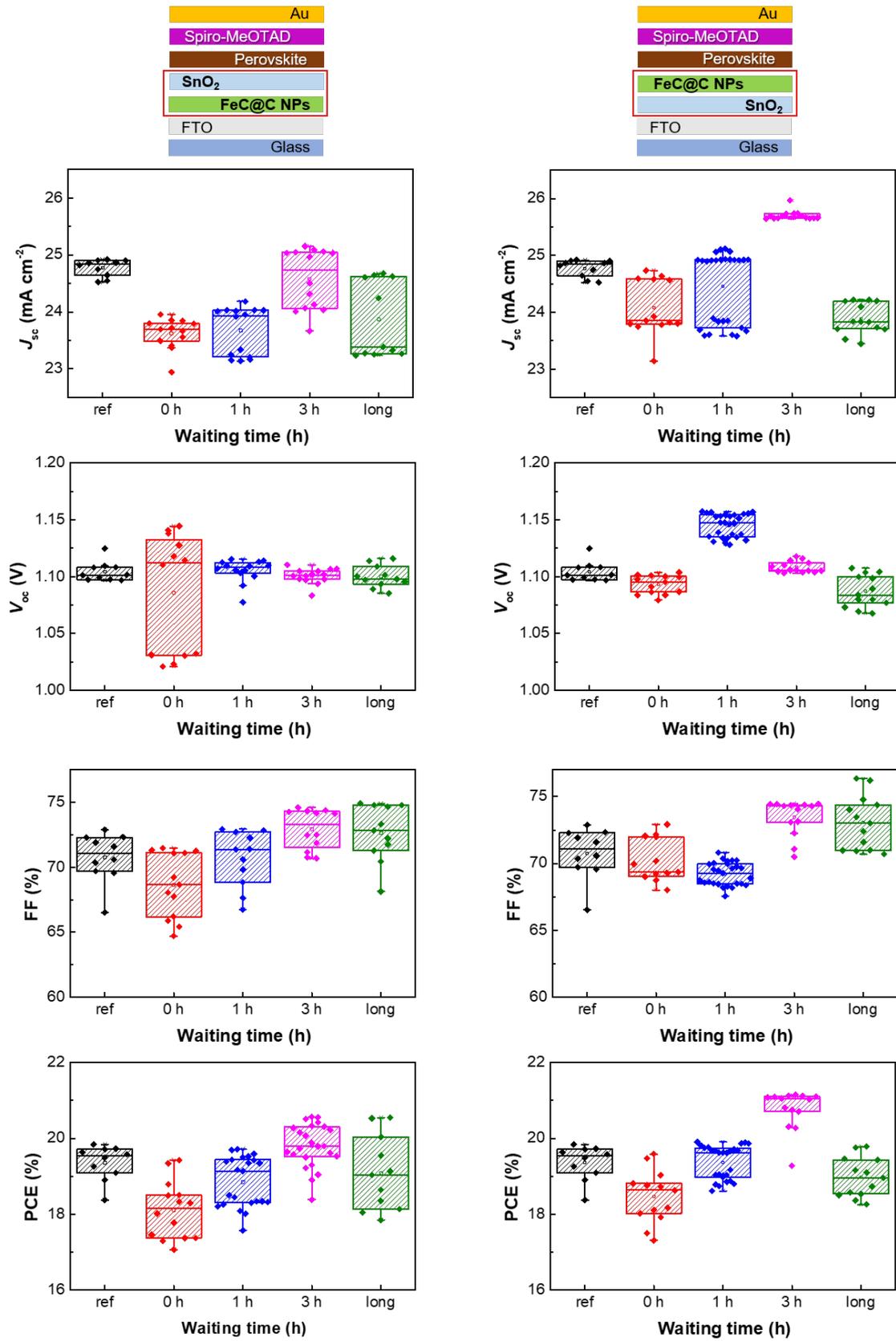


Figure S16. Statistical distribution of photovoltaic parameters for PSC devices.

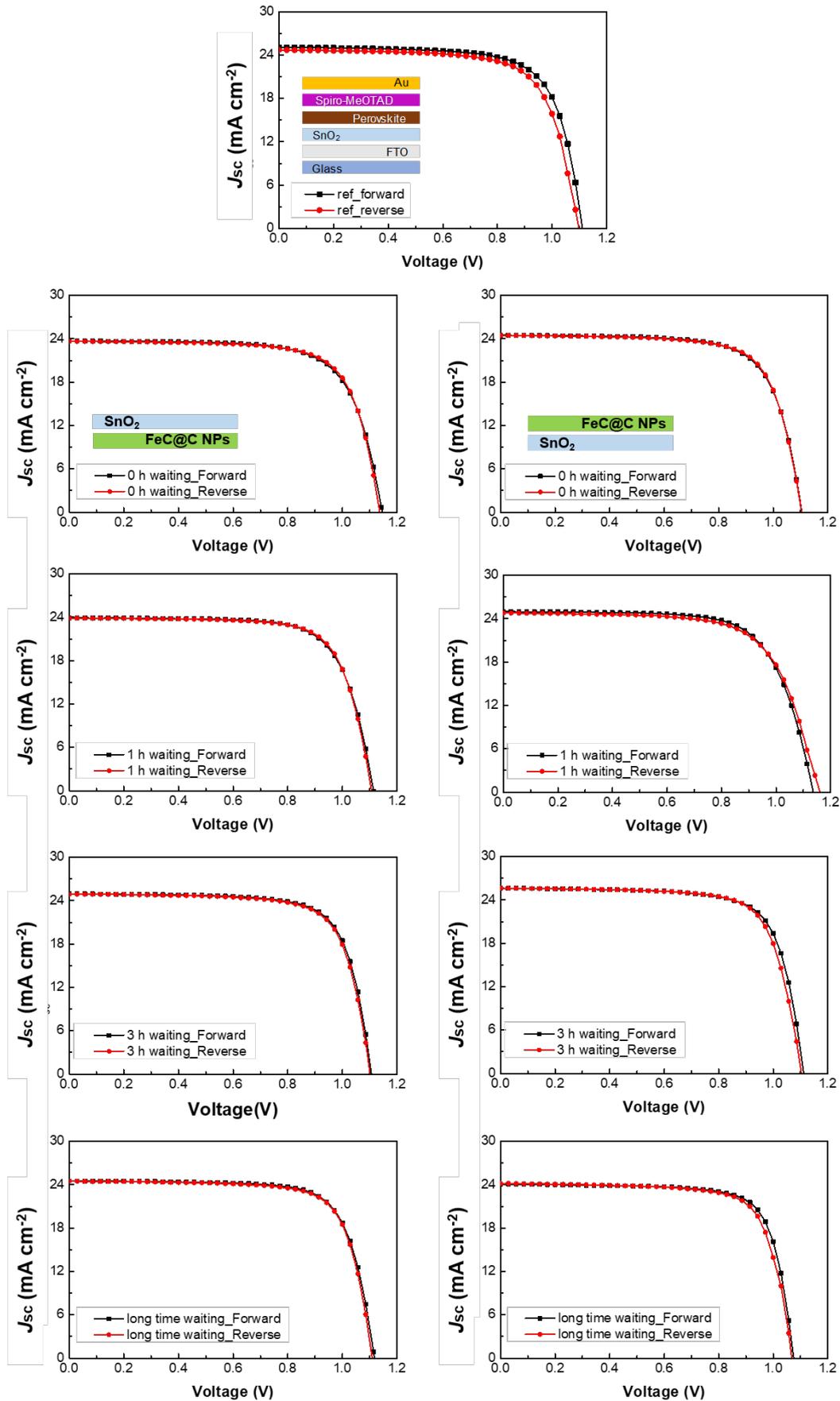
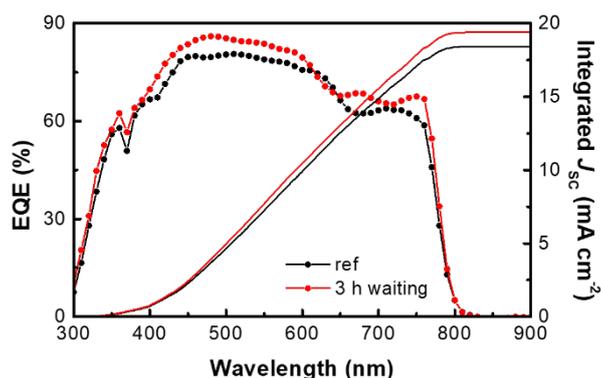
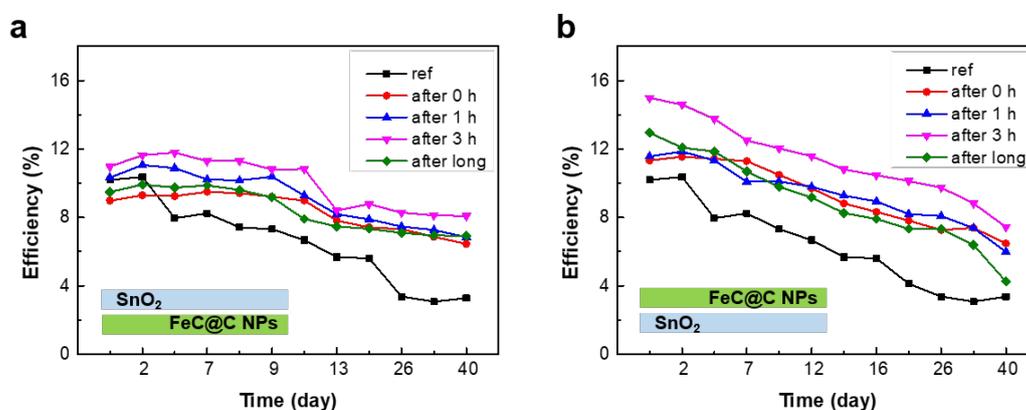


Figure S17.  $J$ - $V$  curves of optimized devices based on photovoltaic performance.



**Figure S18.** EQE spectra and Integrated  $J_{sc}$  of the performing PSCs: ref and after 3 h sample of FeC@C NPs on SnO<sub>2</sub> layer.



**Figure S19.** Long-term operating stability data of the PSCs. a) SnO<sub>2</sub> on FeC@C NPs layer and b) FeC@C NPs on SnO<sub>2</sub> layer.