

Supporting Information for

Converting Carbohydrates to Carbon-based Photocatalysts for Environmental Treatment

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24 pages, 10 sections (text), 18 figures, 3 tables

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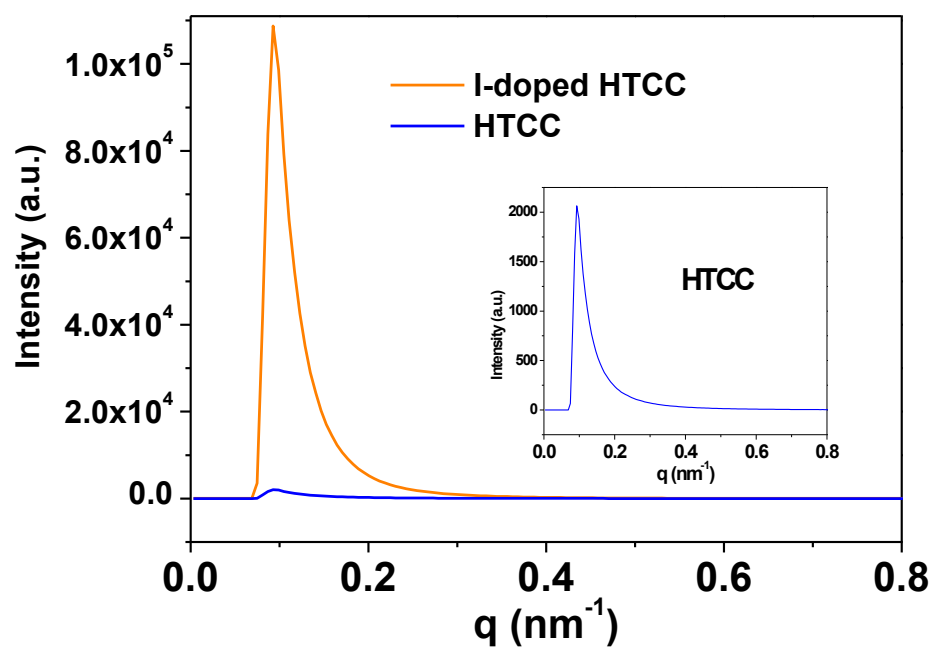


Figure S1. Small angle X-Ray scattering (SAXS) patterns of I-doped HTCC and HTCC.

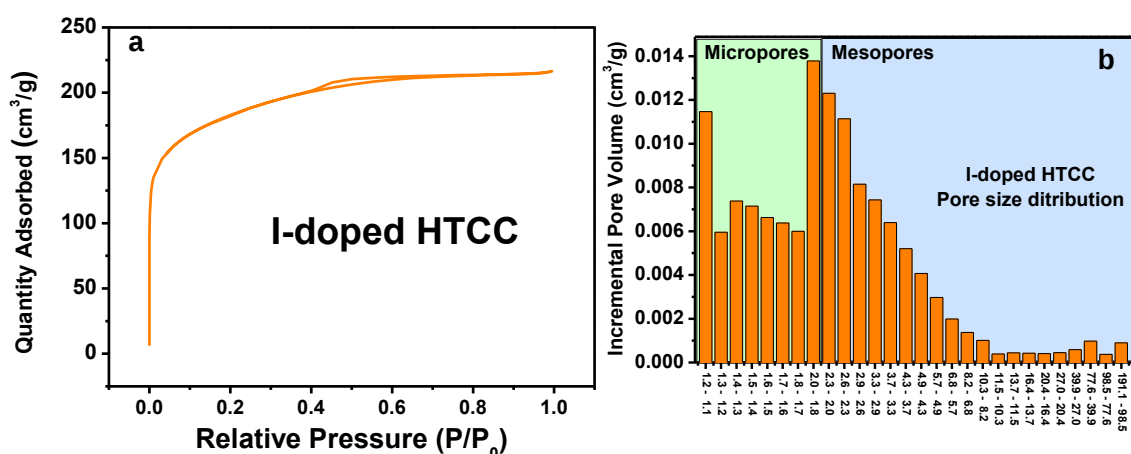


Figure S2. Nitrogen adsorption/desorption isotherms(a) and pore size distribution of I-doped HTCC (b).

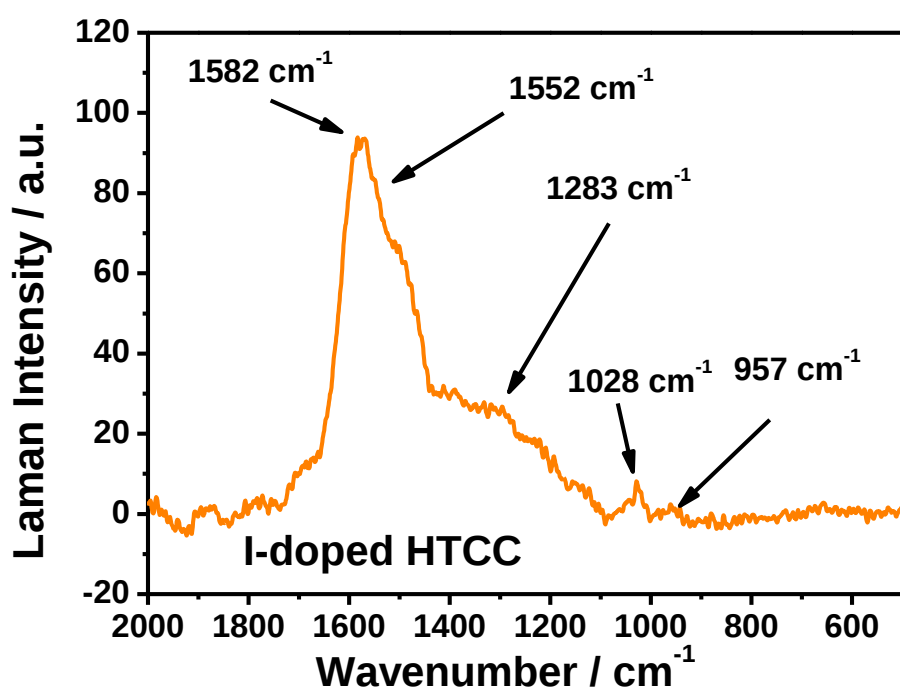


Figure S3. Raman spectrum of I-doped HTCC

Section S1: Analysis of C 1s and O 1s XPS spectra.

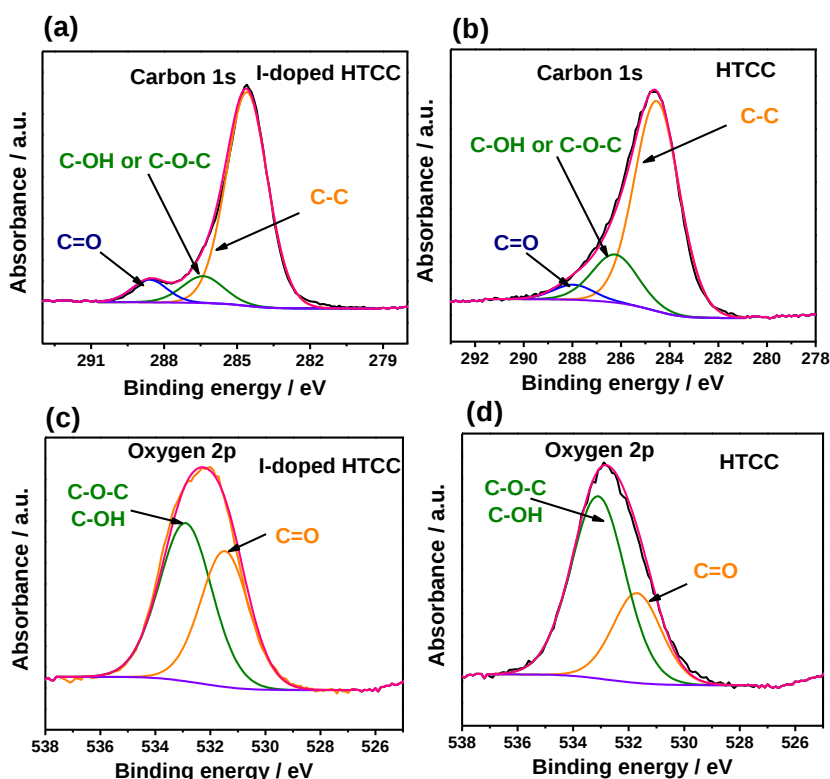


Figure S4. C 1s XPS spectra of the (a) I-doped HTCC and (b) pure HTCC; O 1s XPS spectra of the (c) I-doped HTCC and (d) pure HTCC.

It is shown that the C-O-C peaks are much stronger than the C=O peaks both in C1s and O 1s spectra (Figure S4a-d),¹ indicating that the unsaturated sp^2 -hybridized structures dominate the polyfuran components in HTCC, which is consistent with the results of NMR analysis (Figure 1f). The fine C1s XPS spectra (Figure S4a) of I-doped HTCC can be fitted into three peaks at 284.6 eV (C-C bond), 286.4 eV (C-OH or C-O-C bond) and at 288.6 eV (C=O bond).¹⁻³ The C-O-C and the C=O bonds mainly come from the furanic ring in the sp^2 -hybridized structures.¹ Compared with iodine-free HTCC (Figure S4b), they shift positively by about 0.3 eV and 0.7 eV. This indicates that the C atoms in the sp^2 -hybridized structures are more positive charged in the I-doped HTCC compared with that of HTCC.

Section S2: Depth profile XPS spectra of I from the I-doped HTCC

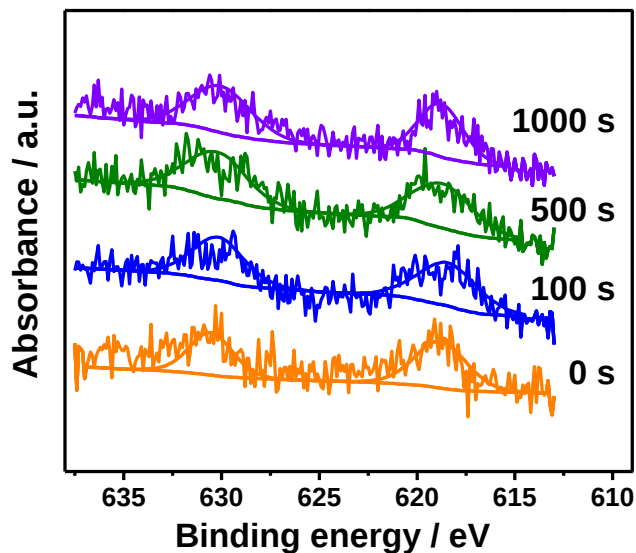


Figure S5. Depth profile XPS spectra of I from the I-doped HTCC by using Argon ion sputtering.

Table S1. Peak area of I 3d 3/2 and 3d 5/2

Argon ion sputtering time	0s	100s	500s	1000s
Peak area of I 3d 3/2	1020.8	1012.5	1065	997.7
Peak area of I 3d 5/2	1034.9	901	1095.8	1104
Peak area of C 1s	123316	127597	133401	136711
Peak area ratio C/I	60	66.7	61.7	65

The peak area and position of iodine hardly change with argon ion sputtered for 100, 500 and 1000s, respectively, as list in Table S1. The peak area of carbon is also presented as reference, which also shows no obvious change with the time proceeding. These suggest that the iodine dopants locate homogeneously in the I-doped HTCC.

Section S3: Calculation of band structure

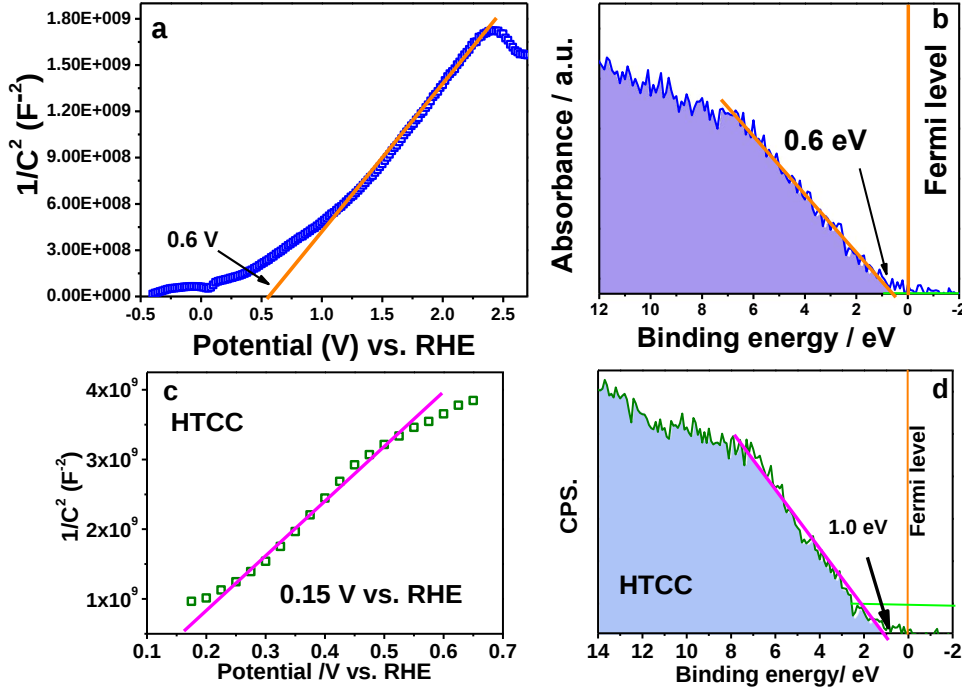


Figure S6. (a) Mott-Schottky plot and (b) valence XPS spectrum of I-doped HTCC; (c) Mott-Schottky plot and (d) valence XPS spectrum of HTCC

According to Mott-Schottky plots based on the following equation⁴⁻⁷:

$$\frac{1}{C^2} = \frac{2}{\varepsilon \cdot \varepsilon_0 \cdot e_0 \cdot N_D} \left(E - E_{FB} - \frac{kT}{e_0} \right) \quad (1)$$

Where C is the space charge capacitance, ε and ε_0 are the permittivity of the electrode and free space, e_0 the elementary charge, E the applied potential, E_{FB} the flatband potential, k the Boltzmann's Constant, and T the temperature.

The flat band potential (E_{FB}) of I-doped HTCC can be calculated to be 0.6 V vs. RHE according to the extrapolation of X intercept in the Mott-Schottky plot (Figure S6a). Furthermore, a positive slope shown in Figure S6a suggests that the material is an n-type semiconductor.⁸ Since the flatband potential is close to the Fermi level,⁹ it is reasonable to consider the Fermi level of I-doped HTCC at 0.6 V vs. RHE. The carrier

density of I-doped HTCC is calculated to be 3.04×10^{18} (Section S4), which is larger than that of iodine-free HTCC (5.2×10^{17}).

The difference in energy between the Fermi level and the conduction band (CB) in a n-type semiconductor can be calculated using the following equation:^{10, 11}

$$E_{CB} - E_F = \frac{kT}{e} \ln\left(\frac{N_C}{N_D}\right) \quad (2)$$

$$N_C = 2\left(\frac{2\pi m_e^* kT}{h^2}\right)^{3/2} \quad (3)$$

Where k the Boltzmann's Constant, T the temperature, N_C the effective density of states in the conduction band, N_D the carrier density calculated by the Mott-Schottky curve, h the Plank's constant, and m_e^* is the effective mass of the electron ($0.166 m_0$, details see Section S7).¹² N_C is calculated to be $1.68 \times 10^{24} \text{ cm}^{-3}$, while N_D is measured to be $3.04 \times 10^{18} \text{ cm}^{-3}$ according to the Mott-Schottky curve (Figure S6c). Combined with its Valence XPS (Figure S6d), these results suggest that the Fermi level is positioned 0.34 V below the CB. Therefore, the CB of the HTCC is at about 0.26 V vs. RHE (0.60 – 0.39 V).

The valence band (VB) position of the I-doped HTCC is estimated to be about 0.6 eV below the Fermi level from the valance XPS spectrum (Figure S6b).¹³⁻¹⁵ Therefore, the band gap of the I-doped HTCC is about 0.94 eV, which is very close to the value measured by the Kubelka–Munk plot of the HTCC (Figure 2b). Therefore, the band structure of the I-doped HTCC is schematically shown in Figure 2e (right part).

Section S4: Calculation of carrier density

The carrier density should be calculated by the following equation:

$$N_D = \frac{2}{\varepsilon \cdot \varepsilon_0 \cdot e_0 \cdot A^2} \cdot \frac{dE}{d \frac{1}{C^2}} = \frac{2}{\varepsilon \cdot \varepsilon_0 \cdot e_0 \cdot A^2} \cdot \frac{1}{slope} \quad (4)$$

Where C is the space charge capacitance, ε and ε_0 are the permittivity of the electrode and free space, e_0 the elementary charge, E the applied potential, E_{FB} the flatband potential, k the Boltzmann's Constant, and T the temperature. By using the ε of carbon material 30, The N_D of the HTCC I-doped HTCC is calculated to be 5.2×10^{17} and 3.04×10^{18} .

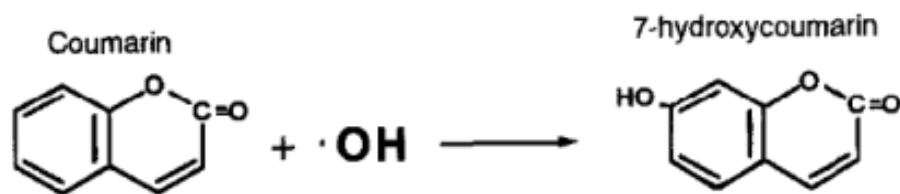


Figure S7. Schematic diagram showing the reaction between OH radical and probe molecules coumarin.

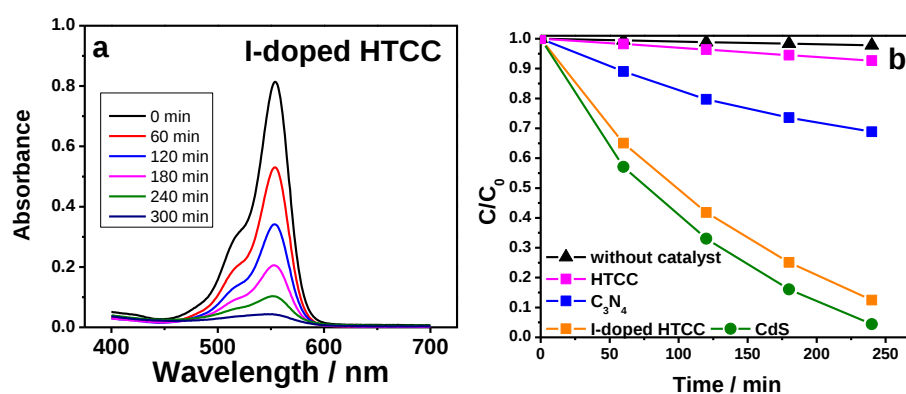


Figure S8. (a) Time-dependent absorption spectra of RhB solution containing 10 mg of iodine-doped HTC carbon under visible light irradiation (b) Temporal course of photodegradation of RhB on different visible-light-driven photocatalysts.

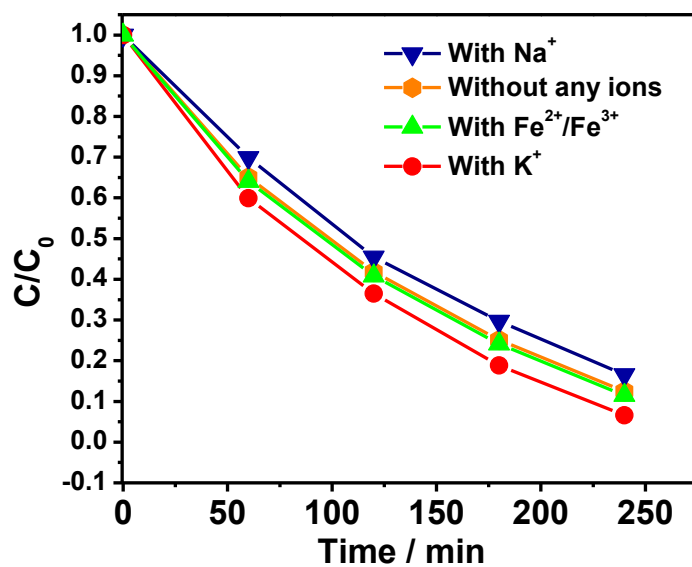


Figure S9. Photocatalytic degradation of RhB under visible light irradiation using I-doped HTCC in the presence of different cations (1 wt%).

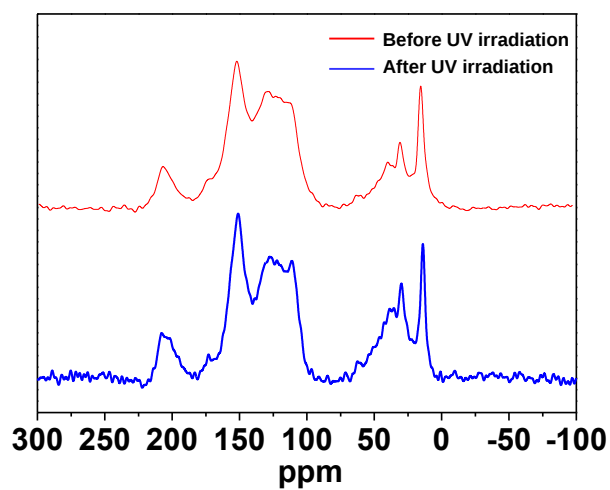


Figure S10. The C^{13} solid NMR spectra of I-doped HTCC before and after UV irradiation for 10 h (20 mg catalyst in 20 mL DI water, 100 W mercury lamp, 360 nm).

Section S5: The adsorption ability of I-doped HTCC

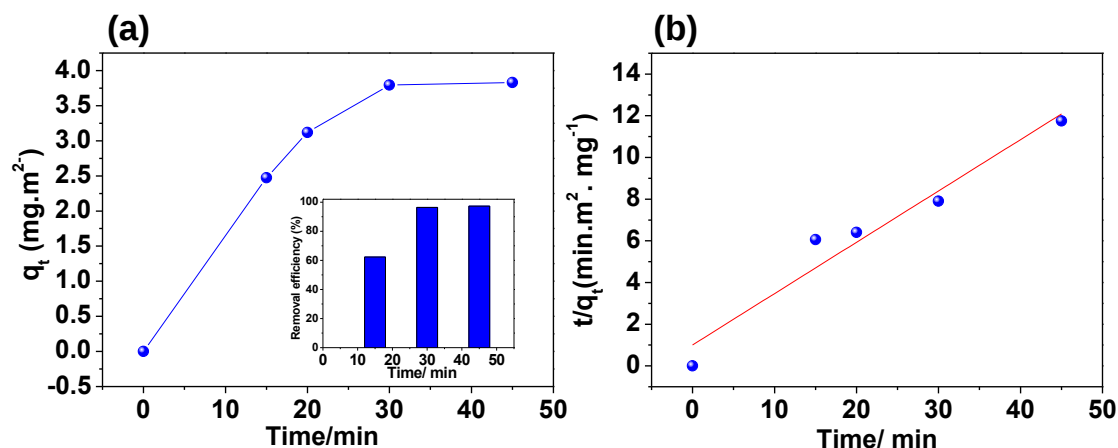


Figure S11. (a) The adsorption efficiency of Cd²⁺ (100 mg.L⁻¹) using I-doped HTCC particles (100 mg dosage in 100 mL solution, 0.1g.L⁻¹) at ambient condition. (b) The corresponding removal kinetics curves of Cd²⁺ on I-doped HTCC.

The Cd²⁺ solution (100 mg.L⁻¹) is selected as the model system to study the adsorption ability of I-doped HTCC. The adsorption solution is 100 mL and the dosage of I-doped HTCC is 100 mg (0.1g.L⁻¹, surface area: 254 m².g⁻¹). The time interval is set to be 10 min or 15 min. The adsorption is proceed to 45 min, and the After agitation, the supernatants were filtered through 0.22 μm syringe filters and the residual Cd²⁺ concentration in the solution was determined by Inductively Coupled Plasma spectrometer (ICP) by diluted 100 times.

Results show that I-doped HTCC can quickly adsorb the Cd²⁺ within 30 min (96.4%) and reached the equilibrium, after extending to 45 min (Figure S11a). The adsorption quantity did not obviously change (97.3%). The adsorption kinetics seems to follow the pseudo-second-order model (Figure S11 a,b).¹⁶

Section S6: Calculation of insertion energy of I doping into HTCC, Density of States (DOS), Project Density of States (PDOS) of HTCC and I-doped HTCC.

The insertion energy of I-doped HTCC can be defined using the following formula:

$$E_{\text{insert}} = E_{\text{tot}}(\text{doped}) - E_{\text{tot}}(\text{pure}) - E_{\text{iodine}} \quad (5)$$

Where E_{insert} is the insertion energy of the iodine; $E_{\text{tot}}(\text{doped})$ the total energy of the I-doped HTCC, which is calculated to be -1217.93eV; $E_{\text{tot}}(\text{pure})$ is the total energy of the undoped HTCC, which is found to be -1215.57eV; E_{iodine} is the energy of the chemical potential of iodine, which is -0.27. Therefore, the E_{insert} is calculated to be -2.09 eV, suggesting the insertion of iodine is energetically favorable.

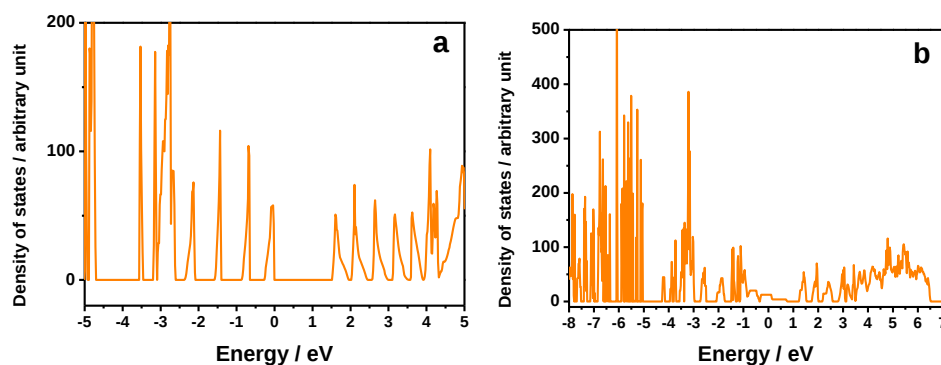


Figure S12. Density of States (DOS) of (a) HTCC and (b) I-doped HTCC.

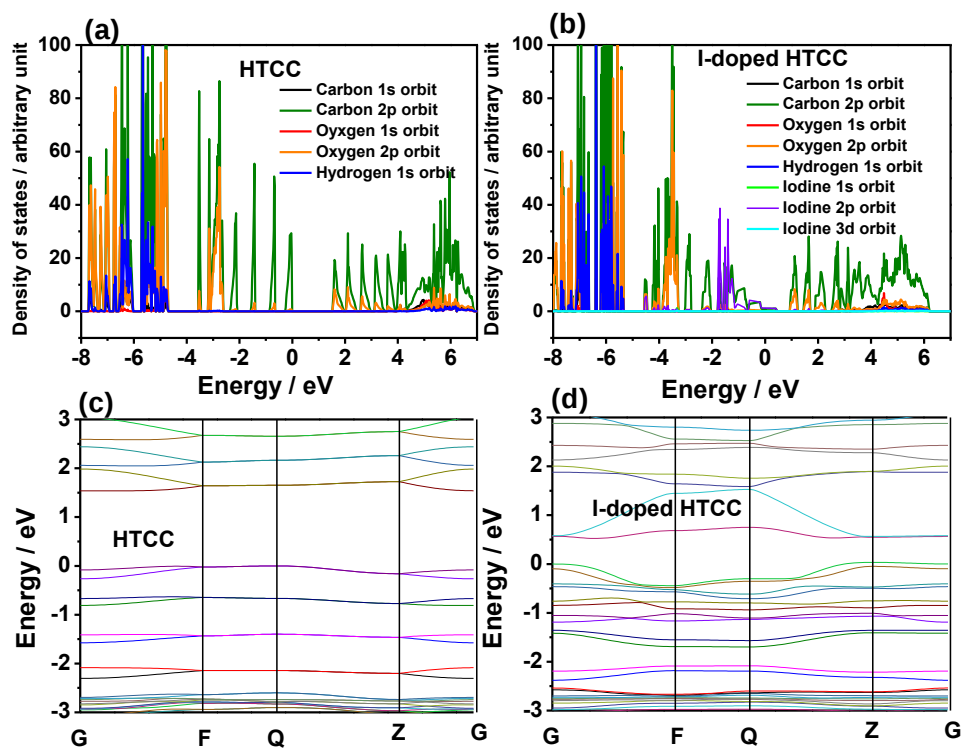


Figure S13. Project Density of States (PDOS) of (a) HTCC and (b) I-doped HTCC; Band structure of (c) HTCC and (d) I-doped HTCC.

Section S7: Calculation of effective electron mass

Since the effective electron mass is calculated according to.^{17,18}

$$m^*(k) = \left(\frac{h}{2\pi} \right)^2 \left[\frac{\partial^2 E(k)}{\partial k^2} \right]^{-1} \quad (6)$$

The $d^2E(k)/dk^2$, which mean the dispersity of the conduction band bottom, is inverse to the effective electron mass.

The band in iodine-free HTCC is very flat, especially at the bottom of conduction band and at the top of the valence band between F and Q points. This suggests charges have very heavy effective mass and low mobility, as supported by the above equation.^{17,18} The effective electron mass is calculated to be 0.353 m_0 at the bottom of the CB. In the presence of iodine, the band become more dispersive, and the effective electron mass is calculated to be 0.166 m_0 . This is greatly beneficial to charge transfer.

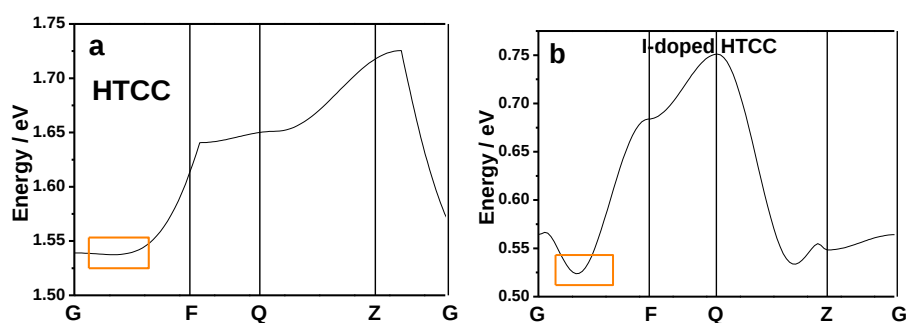


Figure S14. (a) The lowest band of conduction band of HTCC and I-doped HTCC.

Table S2. Charge number of C,O,H and I element in HTCC, I-doped HTCC and isolated state

Element	Charge number in HTCC	Charge number in I-doped HTCC	Charge number in isolated elements
C	3.65	3.64	4.00
O	7.59	7.61	6.00
H	0.92	0.90	1.00
I	0	7.14	7.00

Section S8: band-decomposed charge density isosurface

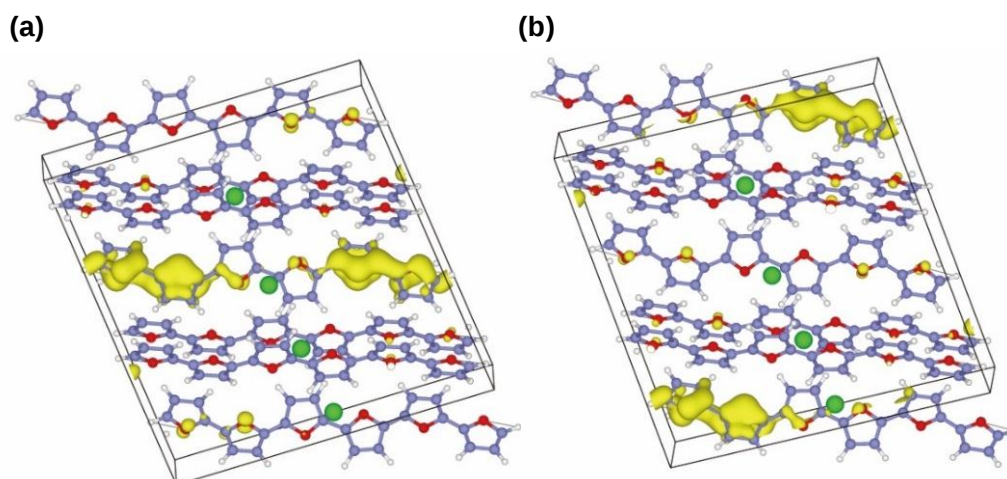


Figure S15. (a) Decomposed charge density isosurface for valence band (VB) edge and (b) conduction band (CB) edge.

The band-decomposed charge density isosurface of the electronic states is performed to study the charge in the spatial charge distribution in the CB and the VB edge. As shown in Figure S15a, the charge of VB edge spatially distributed around a polyfuran chain in the center of the unit cell, while that of CB spread around two other polyfuran chain at the corners, as shown in Figure S15b. This suggests the excitation of charge carriers from the VB to the CB involve charge transfer from one polyfuran chain to another. As discussed above, this inter-chain transfer is difficult for pure HTCC because the “empty” charge region among different polyfuran chain. By contrast, it is easy in the I-doped HTCC due to the presence of the iodine. Therefore, we can conclude that the iodine is favorable for the charge transfer during their excitation.

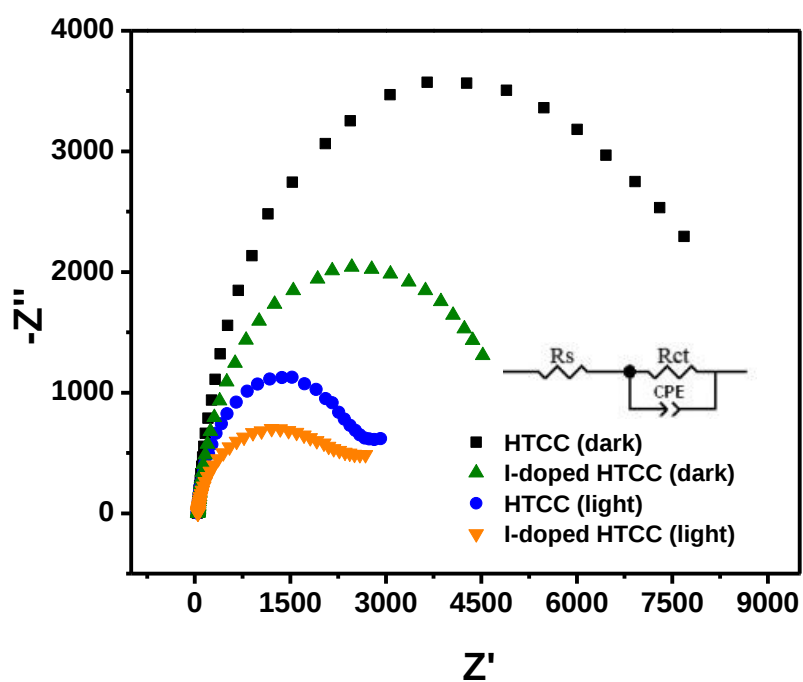


Figure S16. Nyquist plots of HTCC with and without iodine doped in the dark and under visible light illumination in 0.1 M Na_2SO_4 electrolyte, insert shows the equivalent circuit used in the fitting.

Table S3. Values of equivalent circuit elements obtained by fitting the experimental data

	R_s (Ω)		R_{ct} (Ω)		CPE-T (F)		CPE-P (F)	
	dark	light	dark	light	dark	light	dark	light
HTCC	42.22	40.32	8246	2761	5.27E-5	5.31E-5	0.930	0.903
I-doped HTCC	51.36	47.09	4837	2165	6.55E-5	5.83E-5	0.910	0.860

Section S9: The C^{13} solid NMR and FT-IR spectra of I-doped HTCC prepared by different carbon hydrates

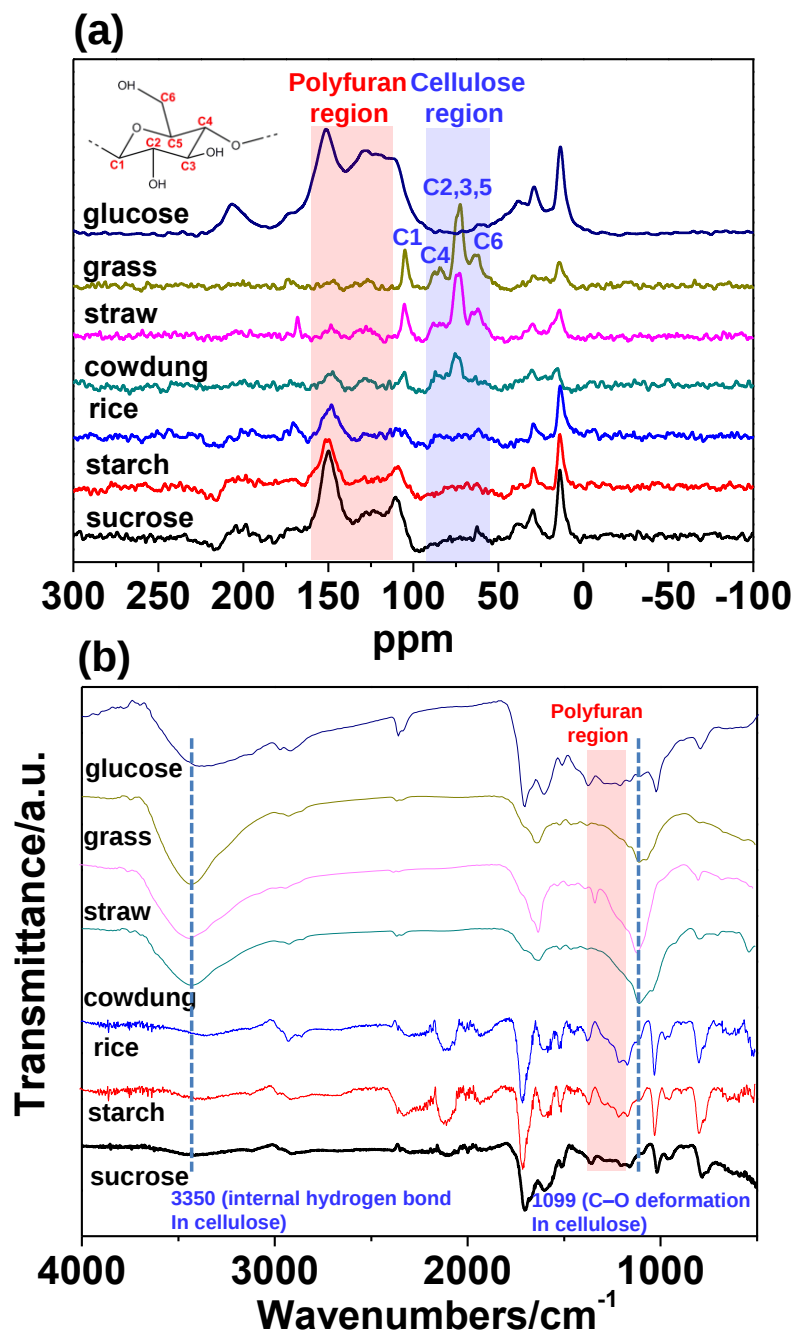


Figure S17. The C^{13} solid NMR (a) and FT-IR spectra (b) of I-doped HTCC prepared by different carbon hydrates. The characteristic regions or bands of cellulose are denoted using blue color, while those of polyfuran are denoted using red color. Inset picture in a is the basic unit of cellulose.

As shown in C^{13} solid NMR spectra (Figure S17 a), the products prepared from carbohydrates with higher polymerization degree such as straw, grass and cowdung

display typical peaks of residue cellulose. The region of 55-95 ppm is composed by several overlapped bands from C2 to C6 in the basic unit of cellulose, and the single band at c.a. 105 ppm can be ascribed to the C1 signal of cellulose basic unit (inset picture in Figure S17 a).^{19, 20} However, they show weak peaks of polyfuran at the region of 110-160 ppm. On the contrary, products obtained from carbohydrates with lower polymerization including sucrose, starch and rice, show very weak peaks cellulose, but display strong peak of polyfuran. Similar phenomena can be found in the FT-IR spectra (Figure S17b). Products from straw, grass and cowdung, show a strong band at c.a. 1099 cm^{-1} , which can be ascribed to the C-O deformation in secondary alcohols and aliphatic ethers of cellulose.^{21, 22} Products from sucrose, starch and rice show no obvious band at that position. In the region of 3300-3500 cm^{-1} , the products from straw, grass and cowdung show a strong band centered at 3350 cm^{-1} , which is assigned to the internal hydrogen bond in cellulose.^{21, 22} While for products from sucrose, starch and rice, they show much weaker band at that place, which is due to their no or less composition of cellulose with higher polymerization.

According to the results of C^{13} solid NMR and FT-IR spectra, the products from straw, grass and cowdung have less polyfuran and more cellulose residue compared with those from sucrose, starch and rice, which might be the reason for their lower photocatalytic activity.

Section S10: Cytotoxic effect of samples

The cytotoxic effects of the I-doped HTCC were evaluated by using Human Umbilical Vein Endothelial Cells (HUVEC) and T84 cell via WST-1 assay. The sample was dissolved in PBS in 10mg/0.5ml, sonicated for 10min and UV for 20 min. Subsequently, the sample suspension was added into 500ul Endothelial cell growth medium (EGM) to reach a concentration of $5\mu\text{g}\cdot\text{ml}^{-1}$. The tetrazolium salt 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-(2,4-disulfophenyl)-2H-tetrazolium, (WST-1 from Roche, Mannheim), was used to detect the viability. After treatment of the sample with the cells for 48 hours, the supernatant medium was replaced added by WST-1 for 1 hour incubation. The colored supernatants were moved into a clean Quartz developed into a 48 wells plate and their absorption was measured at 450 nm.

HUVEC Cell culture: Passage normal HUVEC cells when culture has reached approximately 80% confluence. Warm both the Trypsin-EDTA for HUVEC cells to room temperature prior to dissociation. Warm EGM medium to 37 °C prior to use with the cells. For each flask, carefully discard the remaining culture medium without disturbing the monolayer of cells. Rinse the cell layer two times with 5ml sterile PBS to remove residual traces of serum. Add pre-warmed trypsin-EDTA solution (1 to 2 mL for every 25 cm²) to each flask. Gently rock each flask to ensure complete coverage of the trypsin-EDTA solution over the cells. Observe the cells under the microscope. When the cells pull away from each other and round up (typically within 1 to 2 min), remove the flask from the microscope and gently tap it from several sides to promote detachment of the cells from the flask surface. When the majority of cells appear to have detached, quickly add EGM medium to each flask. Gently pipette or swirl the culture to ensure all reaction of Trypsin can be stopped by EGM medium. Transfer the dissociated cells to a sterile 15ml centrifuge tube and centrifuge the cells at 800 x g for 5 min. Discard the solution from the cell pellet and resuspend the cells in 10 mL fresh, pre-warmed, EGM medium. Count the cells and seed new flasks at a density of 2,500 to 5,000 cells per cm². Place newly seeded flasks in a 37 °C, 5% CO₂, incubator for at least 24 to 48 h before processing the cells further.

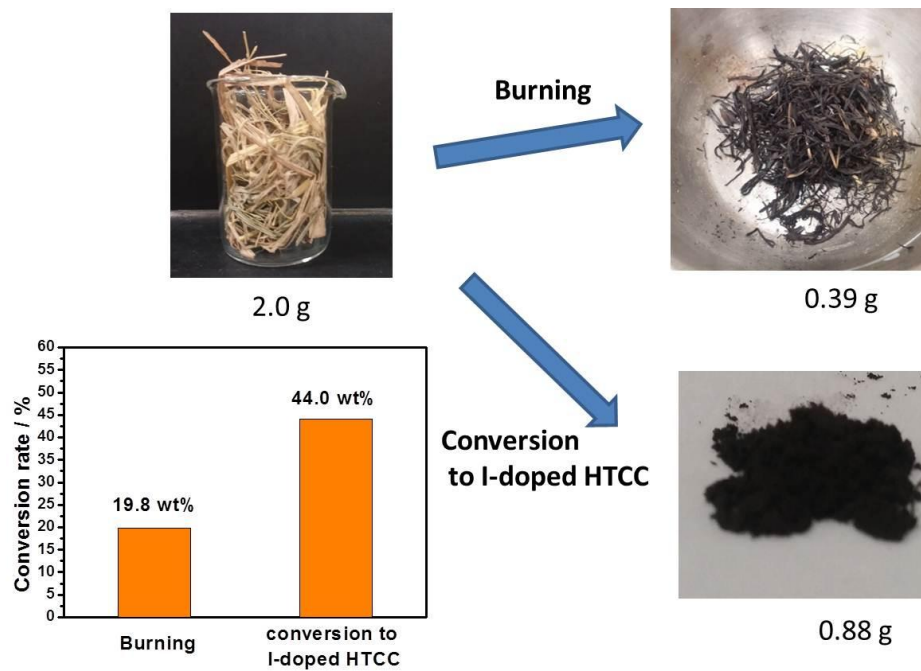


Figure S18. Comparison between conversion of straw into I-doped HTCC and burning.

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