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Supplementary Materials

Biowaste-Derived Heteroatom-Doped Porous Carbon as a Sustainable Electrocatalyst for Hydrogen Evolution Reaction

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Materials

Anacardium occidentale (cashew) nut's skin was collected from Tamil Nadu, India. N-Methyl-2-pyrrolidone (NMP), polyvinylidene fluoride (PVDF), and sulfuric acid (H_2SO_4) were purchased from Sigma-Aldrich, Republic of Korea. The carbon cloth (CC) electrode was purchased from FuelCellStore, College Station, Texas, USA. Nitrogen gas was obtained from Duksan, Republic of Korea. All the chemicals were used as purchased, and deionized (DI) water was used throughout this study.

Instrumentation Methods

Prepared heteroatom-doped porous carbon from cashew nut skin waste was characterized by various physicochemical analytical techniques such as field emission-scanning electron microscopy (FE-SEM) with energy-dispersive X-ray (EDX) spectroscopy, high-resolution transmittance electron microscopy (HRTEM), X-ray diffraction (XRD), Raman spectroscopy, nitrogen adsorption-desorption isotherms, attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS). FESEM with EDX spectroscopy analysis was carried out on a Hitachi S-4800 equipped with EDX at an accelerating voltage of 10/15 kV. TEM/HRTEM images were performed with a JEOL JEM transmission electron microscope with an operating accelerating voltage of 120 kV. XRD measurements were carried out using a PANalytical X'Pert3 MRD diffractometer with monochromatized Cu Kα radiation (λ = 1.54 Å) at 40 kV and 30 mA and were recorded in the range from 10 to 80° (2θ). Raman spectrum was recorded on XploRA Micro-Raman spectrophotometer (Horiba) with a range between 50 and 4000 cm^{-1} at the core research support center for natural products and medical materials of Yeungnam University. Nitrogen physisorption isotherms were measured at −197 °C using Micromeritics ASAP 2000. Before the experiments, the samples were dried at 120 °C and evacuated for 8 h in flowing argon at the flow rate of 60 standard cubic centimeters per minute at 140 °C. Surface area, pore size, and pore volumes were obtained from isotherms using the conventional Brunauer-Emmet-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods. ATR-FTIR spectra were recorded in transmittance mode on a Perkin Elmer Spectrum Two in the wavenumber range from 400 to 4000 cm^{-1} by the addition of 8 scans at a

resolution of 8 cm^{-1}. XPS spectra were achieved using a K-Alpha (Thermo Scientific). CasaXPS software was used for the deconvolution of the high-resolution XPS spectra.

Fabrication of working electrode and electrochemical measurements

The synthesized heteroatom-doped porous carbon material (H-PCM) was used for the fabrication of the working electrodes. H-PCM and polyvinylidene fluoride (PVDF) with the wt. % of 95 and 5 were ground well in an appropriate amount N-Methyl-2-Pyrrolidone (NMP) to make a homogeneous paste for the fabrication of the working electrode, respectively. The resulting homogeneous paste was drop-casting on the carbon cloth (CC) with an area of 1 cm^2, and sequentially the electrode was kept at 100 °C in a hot air oven for 24 h to dry the electrodes. After the fabrication, the obtained modified working electrodes were examined for hydrogen evolution reaction (HER). All electrochemical measurements, including linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) were conducted with a typical three-electrode system and were performed on the CorrTest-CS350 electrochemical workstation in 0.5 M H_2SO_4 aqueous solution. A commercial $Hg/HgSO_4$ (Sat. K_2SO_4) electrode was employed as a reference electrode, a platinum wire was used as the counter electrode, and H-PCM-adorned carbon cloth (H-PCM/CC) was used as working electrodes, respectively. The LSV measurements were performed at a potential window between 0.25 and –1.3 V (vs. Hg/Hg_2SO_4) under the scan rate of 10 mV s^{-1}. EIS measurements were performed in the frequency range of 0.01 Hz–100 kHz with an alternating current amplitude of 5 mV. All the electrochemical tests were conducted at room temperature.

Structural characterizations of the synthesized H-PCM

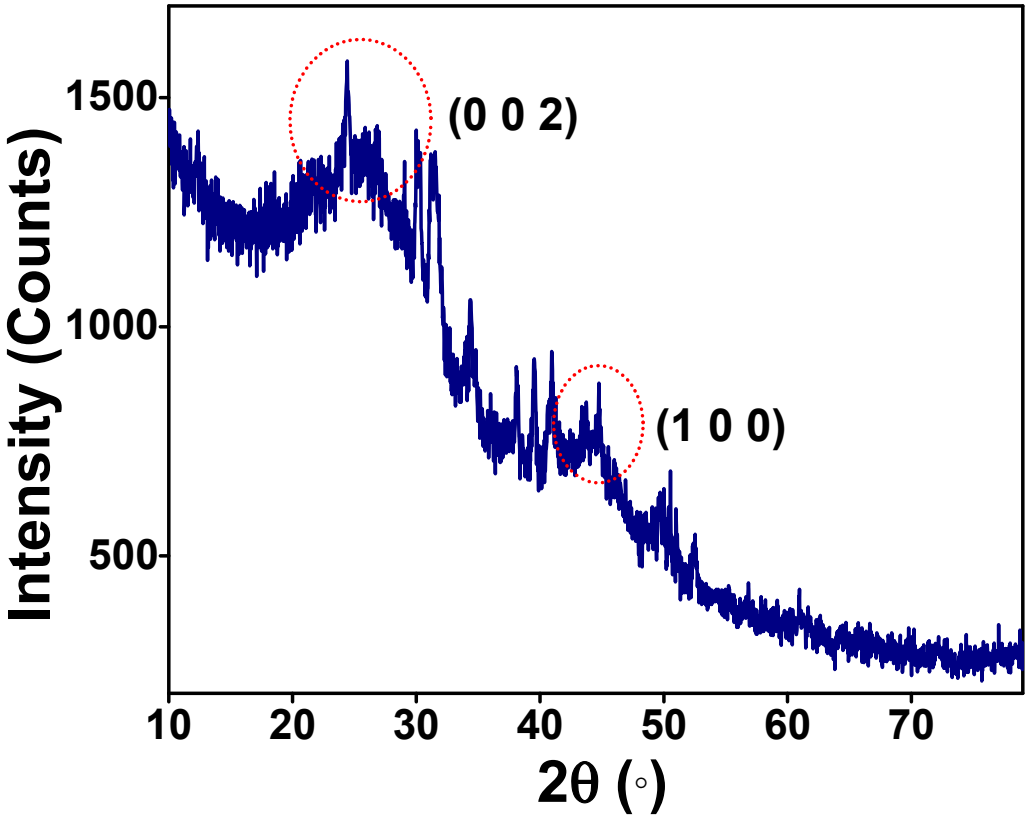

Figure S1. XRD pattern of synthesized H-PCM.

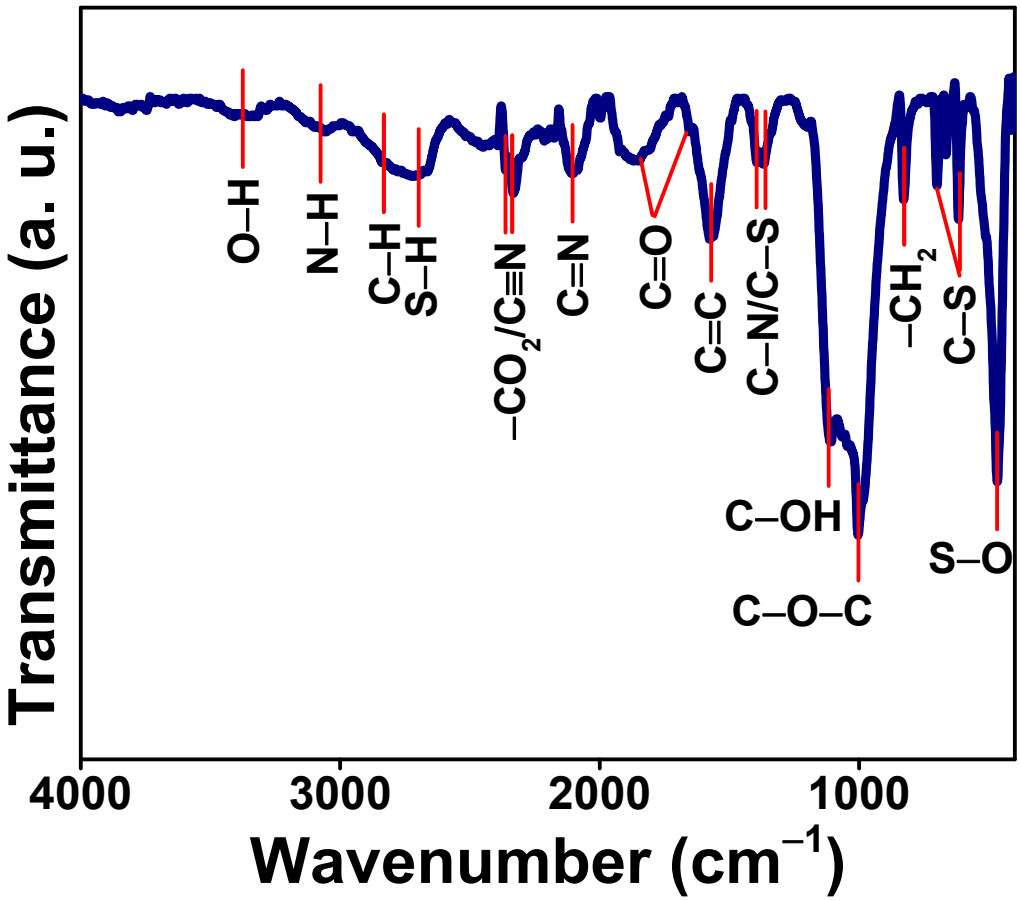

Figure S2. ATR-FTIR spectrum of synthesized H-PCM.

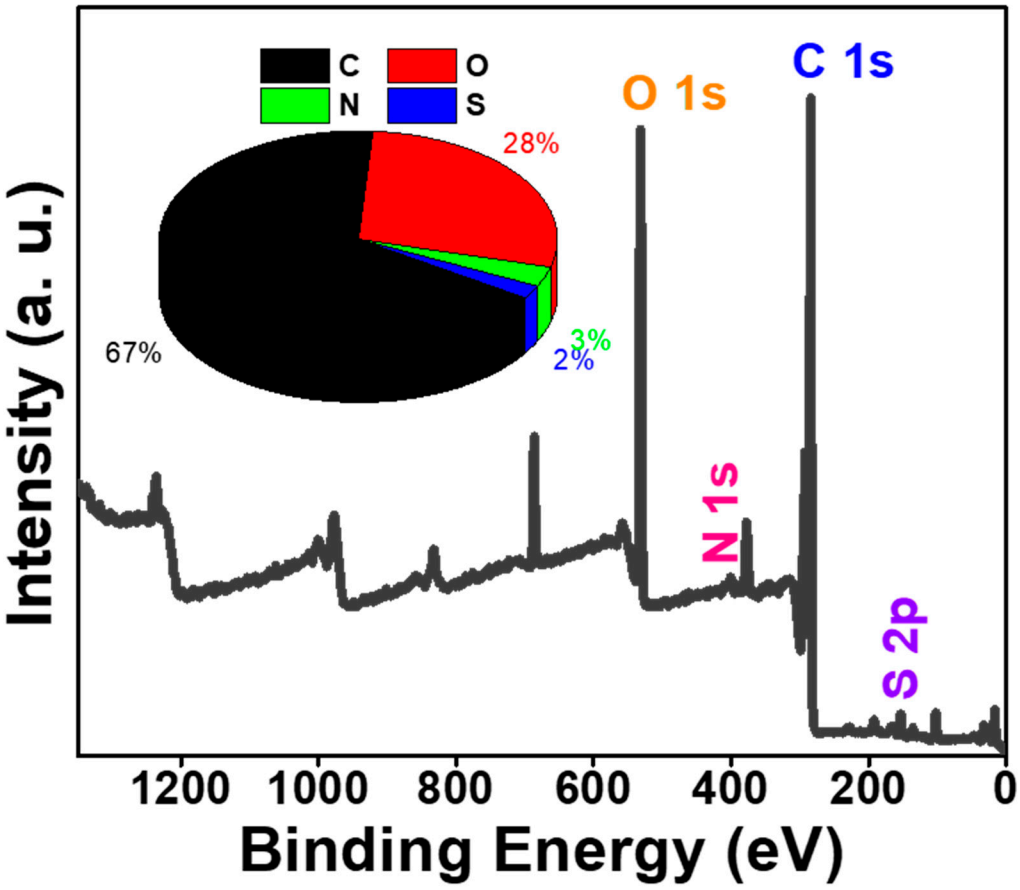

Figure S3. XPS survey scan spectrum (inset of Pie chart: presented elements with atomic %) of synthesized H-PCM.

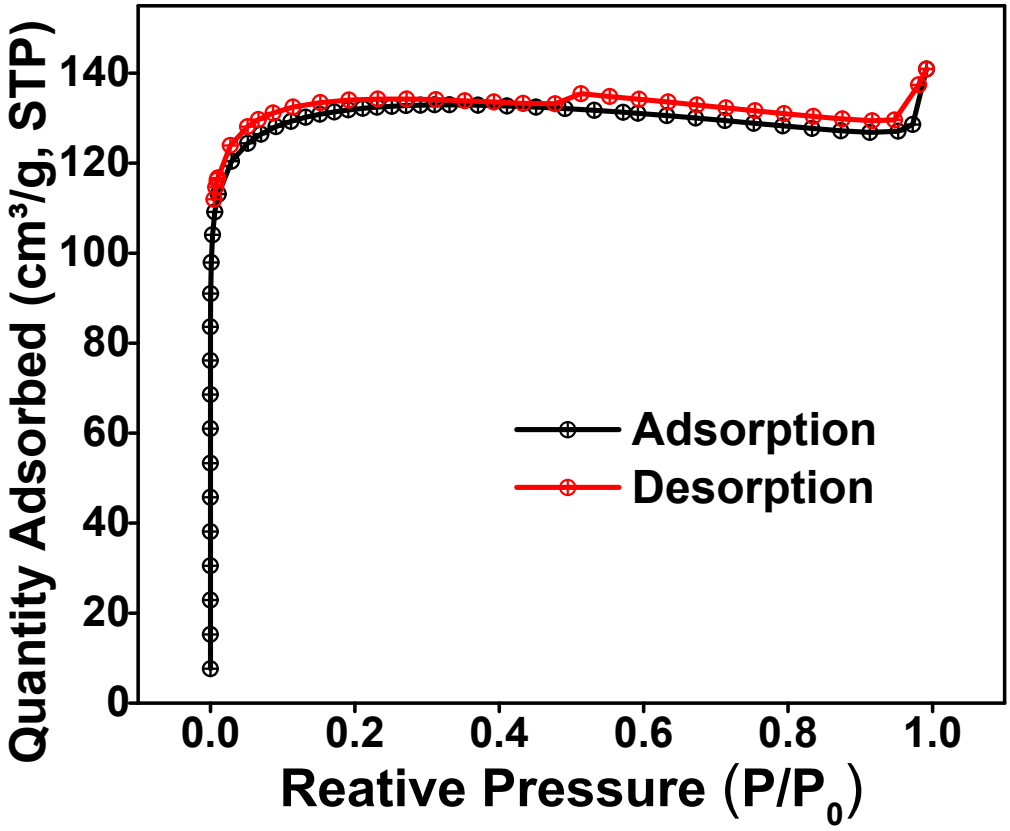

Figure S4. Nitrogen sorption isotherms of synthesized H-PCM under standard temperature and pressure.

Electrochemical characterizations of the synthesized H-PCM

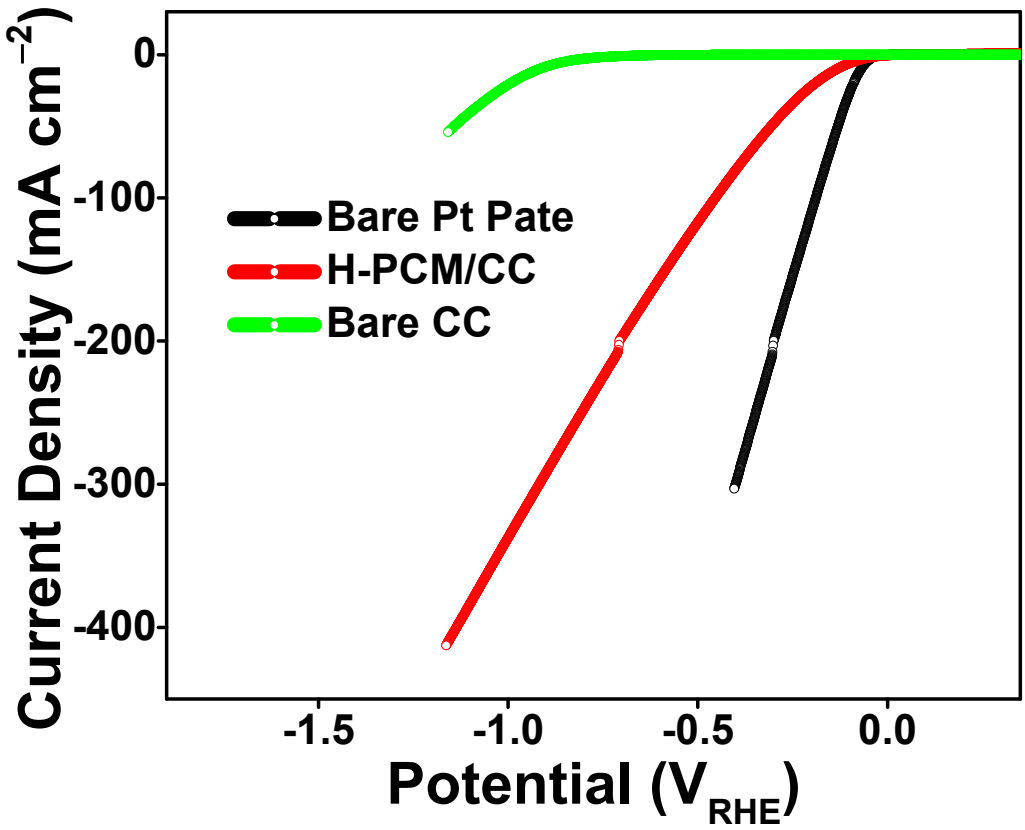

Figure S5. HER polarization (LSV) curves for bare platinum plate, H-PCM/CC, and bare carbon cloth electrodes in 0.5 M H_2SO_4 aqueous solution at a scan rate of 10 mV s^{-1}.

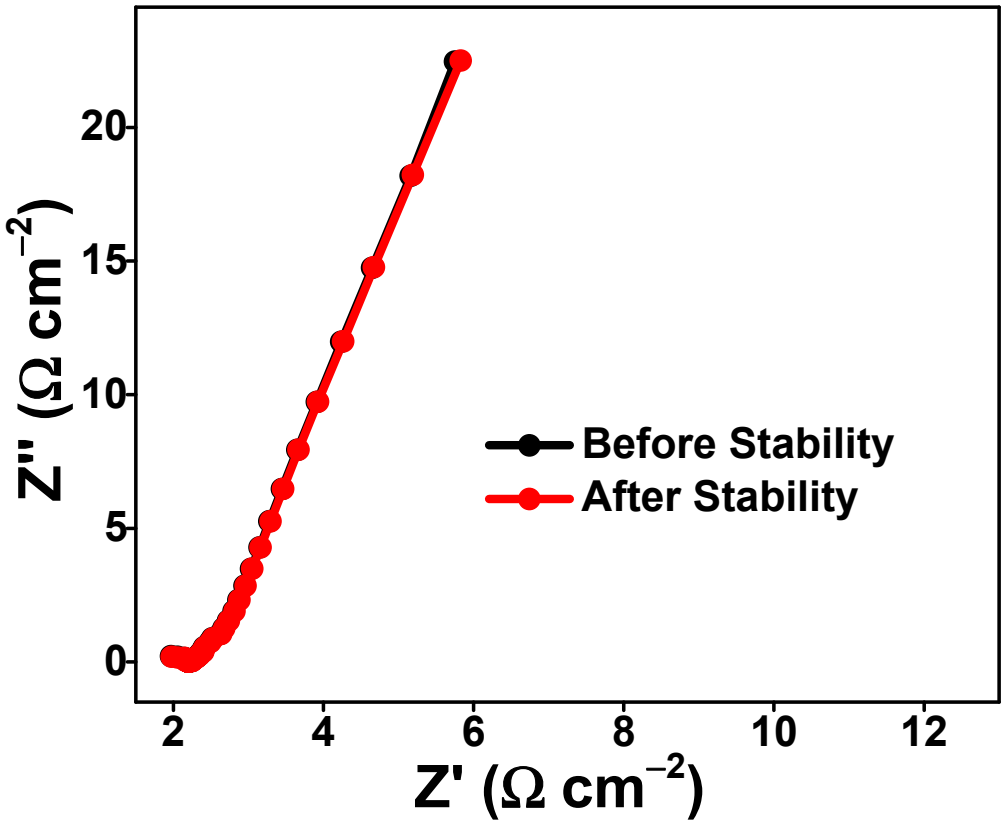

Figure S6. EIS Nyquist plots of synthesized H-PCM electrode obtained before and after prolonged stability.