(Supplementary data file)

In-Situ Polypyrrole Coating on Copper Foam via Femtosecond laser-Irradiation for supercapacitor applications

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2.1 Materials

Copper (Cu) foam (purity > 99%) of 1 mm thickness was sourced from Tmax Battery Equipment Ltd. (China). Analytical grade potassium hydroxide (KOH) and Pyrrole (C_4H_5N) were acquired from Sigma-Aldrich (USA).

2.2 Preparation of electrode

Detailed descriptions of the Fs laser treatment process can be found in previous work [1, 2]. However, in this study, the laser parameters were set to a power of 2 W, a scanning speed of 20 mm/s, and a pulse duration of 20 femtoseconds, with a 0.04 mm spacing between irradiation points on the Cu foam, producing the final binder free polypyrrole (PPy) coated Cu foam. The entire procedure was conducted using ultrasonicated solution of pyrrole in DI water with the ratio of 500 mg (pyrrole) : 20 ml (DI water) under open-air

conditions. These binder free PPy coated Cu foam will be designated as Femto-Cu PPy, in this work.

2.3 Characterization

X-ray diffraction (XRD) analysis was conducted using an X'Pert3 Powder diffractometer from Panalytical over a 2θ range of 10° to 80° at room temperature, whereas Fourier transform infrared (FTIR) spectra were acquired using a Shimadzu IRTracer-100 spectrometer equipped with a single reflection attenuated total reflection (ATR) accessory. Detailed morphological and elemental characterization was also performed using a TESCAN VEGA 3 LMU scanning electron microscope (SEM), equipped with an INCAx-act energy dispersive spectroscopy (EDS) detector from Oxford Instruments. A CHI 660E electrochemical workstation from CH Instruments Inc. was used for electrochemical measurements. The measurements were carried out in a three-electrode configuration with a 3 M KOH electrolyte, where the Femto-Cu PPy foams served as the working electrode, platinum (Pt) wire as the counter electrode, and Hg/HgO as the reference electrode. Equations S(1) and S(2) were used to calculate the areal (specific capacitance) capacitance (C_{sp}) in F/cm^2.

Electrochemical calculations

Equation (S1) measured the areal-specific capacitance (C_{sp}) in F/cm^2 to investigate the charge storage capability *via* CV analysis.

$$C_{sp} = \frac{\int IdV}{2sA\Delta V} \qquad \text{(S1)}$$

Where, $\int IdV$ = area under the curve (CV curve), s = scan rate (V/s), ΔV = potential window (V) and A = active area of studied electrode (cm^2). From GCD curves the C_{sp} values in F/cm^2 calculated through equation (S2)

$$C_{sp} = \frac{I\,\Delta t}{A\,\Delta V} \qquad \text{(S2)}$$

Where I = applying current (mA), Δt = discharge time (s), ΔV = potential window (V) and A = active area of studied electrode (cm^2).

Power law (Equation S3) or Lindstrom's method [3], which correlates current (i) with scan rate (v) was used to quantify or determine the b-values.

$$i = av^b \qquad (S3)$$

Where, i and v denote measured current and scan rate, respectively. Whereas the parameters 'a' and 'b' correspond to intercept and slope of the plot log (i) vs. log (v).

Further, for a more detailed study, we utilized Trasattis's method [4] (equation S4) to dissect the total stored charge into capacitive and diffusion-controlled contributions from the plots of 1/Qs vs. √(scan rate) and Qs vs. 1/√(scan rate) (Potential window is 0.6 V and Qs = specific capacitance, Csp)

$$Q_t = Q_{cap} + Q_{diff} \quad (S4)$$

Where, Qt is total charge storage capacity (capacitance), Qcap is capacitive mechanisms (surface-controlled capacitance) and Qdiff is diffusion-controlled processes (diffusion-controlled capcitance).

To determine the charge storage contribution, we applied the following modified power law or Dunn's method [5] equation S5.

$$\frac{iV}{v^{0.5}} = K_1 v^{0.5} + K_2 \quad (S5)$$

Where, (iV) is the response current having values at current peak (i) and applied voltage window (V) and v is the scan rate. K_1 and K_2 are the slope and intercepts of the line after plotting graph between $\frac{iV}{v^{0.5}}$ and $v^{0.5}$ [6, 7]

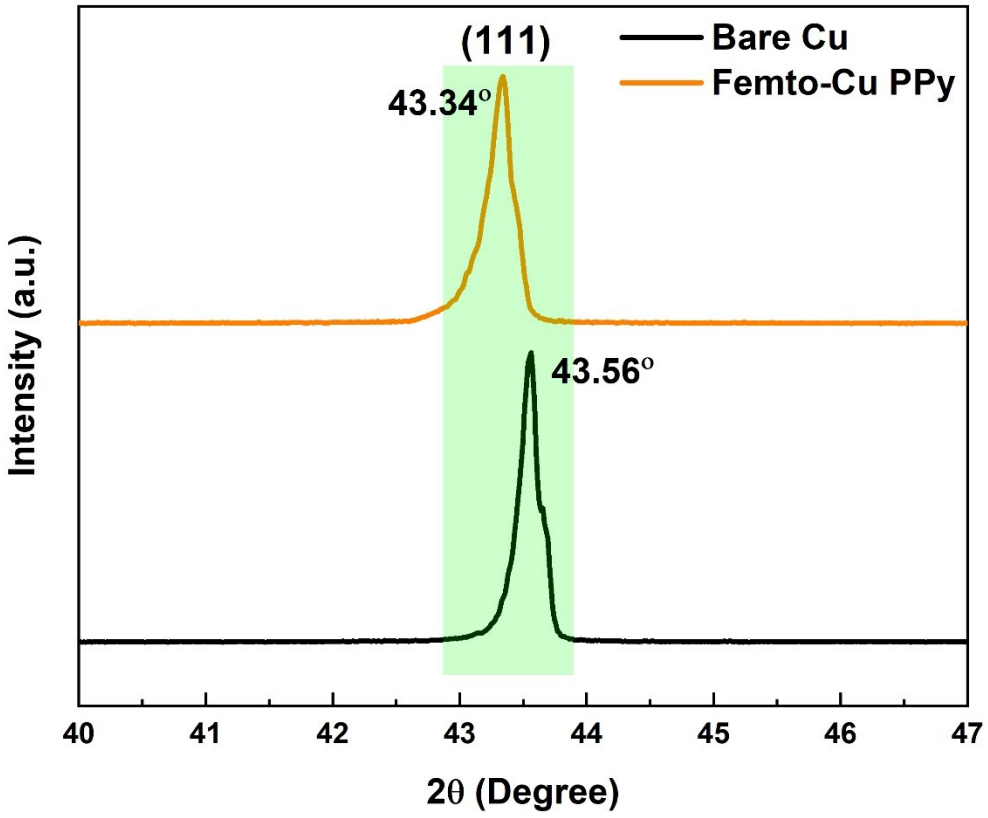

Fig. S1 Enlarged XRD spectra of (111) plane

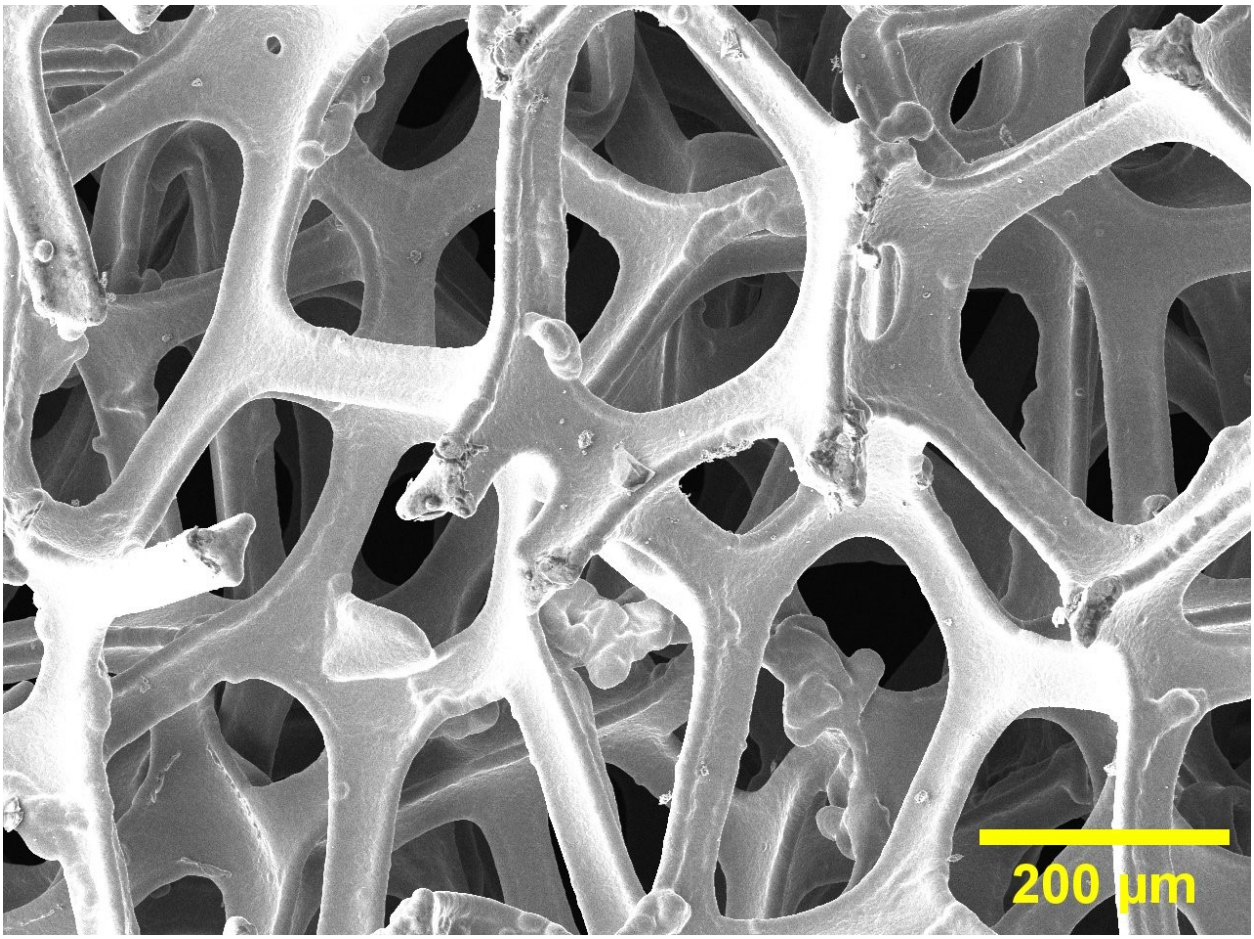

Fig. S2 SEM of bare Cu foam

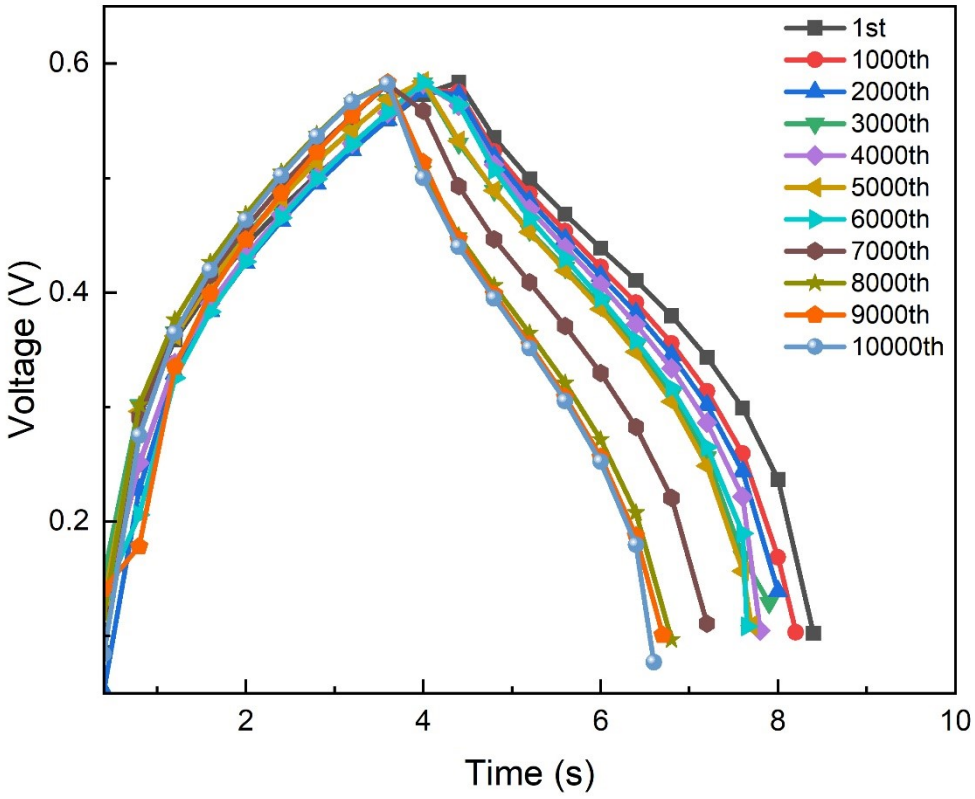

Fig. S3 GCD cyclic stability curves of Femto-Cu PPy at 10 mA/cm^2 current density

Table S1. Trasattis's method utilized to calculate the specific capacitance values from the plots of $1/Q_s$ vs. $\sqrt{scan\ rate}$ and Q_s vs. $1/\sqrt{scan\ rate}$

Q_t (mF/cm^2)	Q_{cap} (mF/cm^2)	Q_{diff} (mF/cm^2)
121.07	58.42	62.65

Table S2. Comparison of electrochemical properties of femtosecond laser-structured materials prepared under different conditions.

Current collector	**Atmosphere**	**Electrolyte**	**Current density ($mA \times cm^{-2}$)**	**C_{sp} ($mF \times cm^{-2}$)**	**Ref.**
Ni plate	Air	2 M KOH	1.0	92.40	[8]
Ni foam	DI Water	3 M KOH	1.0	138.91	[2]
Porous carbon @ Polyimide (PI) sheets	Air	--- H_2SO_4	0.1	22.40	[9]
1T MoS_2 @ PI coated platinum	Air	0.1 M H_2SO_4	1.0	4.20	[10]
rGO/RuO_2 @ polyethylene terephthalate (PET) film	Air	0.1 M H_2SO_4	0.2	7.01	[11]
Graphene @ fallen leaves	Air	--- H_2SO_4	0.03	35.32	[12]
MnO/ Graphene @ wood	Air	1 M Na_2SO_4	1.0	45.00	[13]
MoS2 @ gold coated Si wafer	Air	1 M NaOH	0.022	4.88	[14]
rGO @ glass	Air	1 M H_2SO_4	5.0	2.14	[15]
Polypyrrole @ Cu foam	Pyrrole in DI water	3 M KOH	0.5	148.5	This work

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