Electronic Supplementary Material (ESI) for Nanoscale.

Renewable-Emodin-Based Wearable Supercapacitors

Pengfei Hu,[a] Tinghan Chen,[ab] Yun Yang,[a] Hua Wang,*[a] Zihao Luo,[a] Jie Yang,[a] Haoran Fu[a] and Lin Guo*[a]

[a]*School of Chemistry and Environment, Beihang University, Beijing 100191, P. R. China. E-mail: wanghua8651@buaa.edu.cn; guolin@buaa.edu.cn.*
[b]*High School attached to Tsinghua University, Beijing, 100084, P. R. China.*

Experimental part

Preparation of the Emodin/PPy-Based Fiber Electrodes. The hybridized Emodin/PPy @Carbon Fiber was prepared through galvanostatic polymerization with pyrrole and Emodin mixture solution. Briefly, 24 mg Emodin powders and 180 mg p-toluene sulfonic acid were dispersed in 17.7 mL deionized water and then 2.3 mL 0.5 M NaOH aqueous solution was added, followed by sonication to form a homogeneous solution. The stable mixture was maintained in ice bath and 73 μL pyrrole was added. After being purged with N_2, a carbon cloth was immersed into the solution and imposed at a constant current (1mA cm^{-2}) to conduct the electropolymerization process by a CHI660D electrochemical workstation. The obtained product was washed by deionized water and ethanol to remove the residual. The single fiber was taken off the carbon cloth as the final electrode. PPy@Carbon Fiber was prepared through a similar process with Emodin-free solution.

Fabrication of all-solid-state supercapacitor devices. The gel electrolyte was prepared by mixing 5 mL H_2SO_4 and 10 g PVA powders in 50 mL deionized water, heated and stirred at 80 °C with magnetic until the solution became clear. The active parts (1.8 cm) of Emodin/PPy electrodes were immersed into the H_2SO_4/PVA for 2 min and put closed on PET substrate to form a symmetric two-electrode configuration,

Characterizations and Electrochemical Tests. The morphologies were captured by a JEOL JSM-7001F field emission scanning electron microscope

(FESEM). Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed on a JEOL JEM-2100F microscope. Fourier transform infrared (FTIR) spectra were investigated by a Nicolet N10 spectrophotometer in the ATR mode. X-ray photon spectroscopy was carried out by a Thermo Scientific ESCALAB 250 XPS system. The optical photos were obtained by Canon 600D. The electrochemical characterizations were carried out on CHI660D electrochemical workstation. The raw Emodin electrode was made by coating fully mixed slurry of Emodin powders (40%), carbon black (40%), poly(vinylidenedifluoride) (PVDF) (20%) onto carbon cloth and dried in a vacuum oven at 70 °C. Cyclic voltammetry (CV) curves of single electrode were obtained in three-electrode systems in 0.5 M H_2SO_4 aqueous electrolyte with platinum film as counter electrode and Ag/AgCl as reference electrode. The all-solid-state supercapacitor devices were tested in two-electrode configuration. The CV tests were conducted at a scan rate of 100 mV/s and the galvonostatic charge–discharge tests were carried out at a current density of 100 μA cm^{-1}. The Electrochemical Impedance Spectroscopy (EIS) tests were performed at an open circuit voltage in the frequency range of 0.1 to 105 Hz with a 10 mV amplitude.

Calculation Method:

The capacitance of fiber-shaped electrodes or devices was calculated by using the voltammetric charge integrated from CV curves according to the following equations:

$$C = \frac{Q}{2V} = \frac{1}{2Vv}\int_{V_-}^{V_+} i(V)dv$$

where Q is the total voltammetric charge obtained and released during the CV tests, V(=V_+-V_-) is the potential window, v is the scan rate and the i(V) is the current.

The specific capacitance was obtained according to the following equations:

$$C_M = \frac{C}{M} (M = length, weight, area\ or\ volume)$$

where the fiber is considered as a cylinder to calculate its volume.

The volumetric energy density (E_{volume}) and power density (P_{volume}) of the fiber-shaped supercapacitors was calculated by using the following equation:

$$E_{Volume} = C_{volume} \times \frac{V^2}{2 \times 3600}$$

$$P_{volume} = \frac{E_{volume}}{t}$$

where t is the discharge time (divided by 3600 to transfer the unit to h).

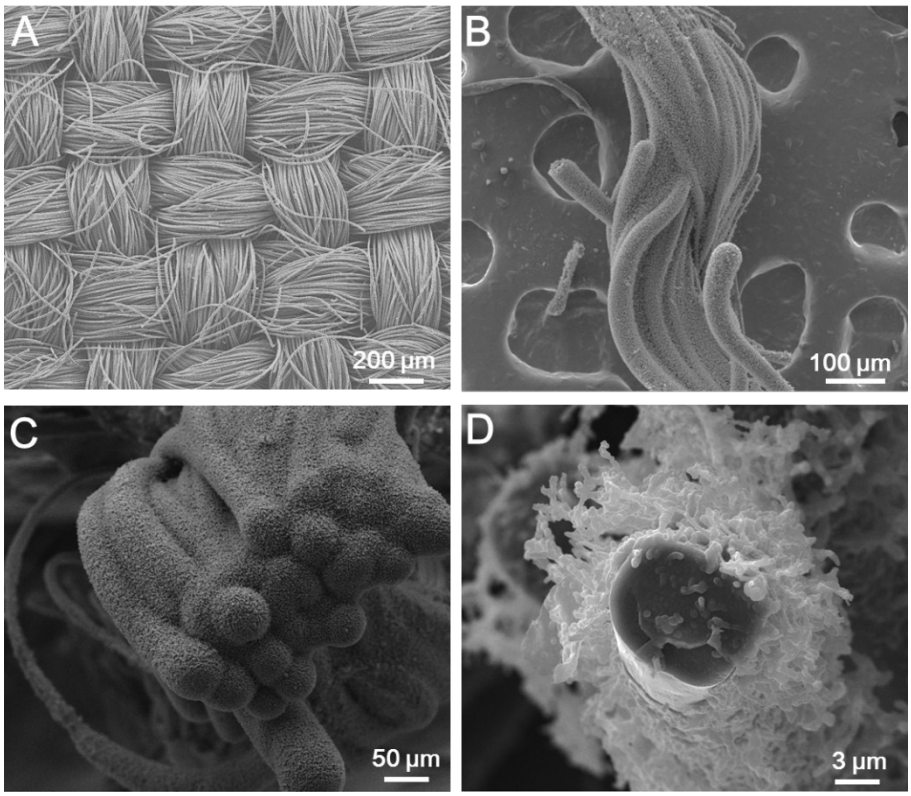


Fig. S1 SEM images of (A) Emodin/PPy@Carbon cloth, (B) fiber electrode, (C) top view of fiber electrode; (D) cross-section of a single fiber.

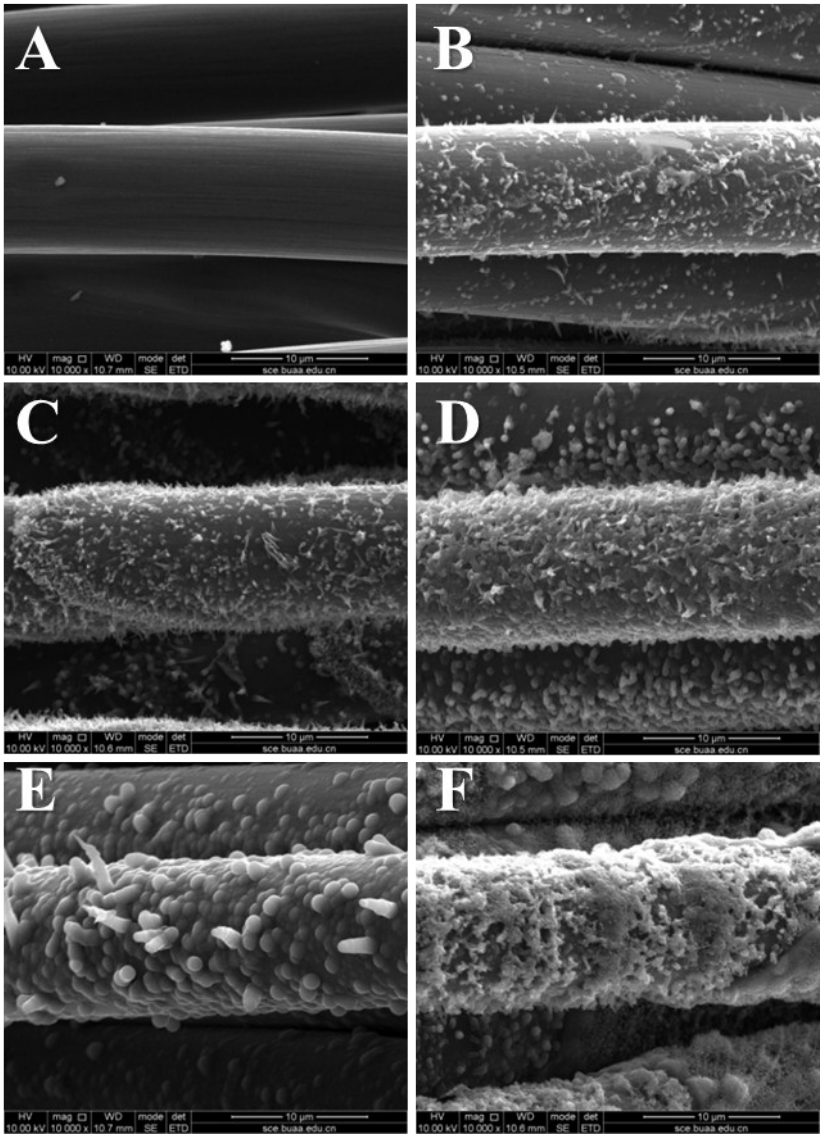


Fig. S2 SEM images of Emodin/PPy hybridized electrode with increasing electropolymerization period: (A) 0 min, (B) 10 min, (C) 30 min, (D) 50 min, (E) 70 min and (F) 90 min.

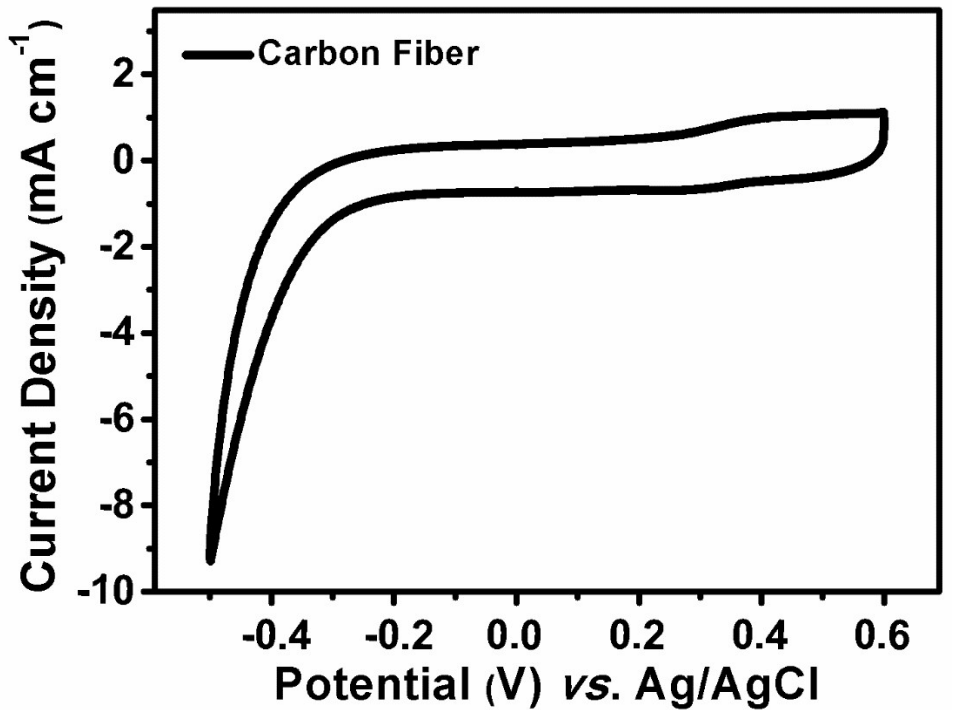


Fig. S3 CV curves of Carbon fiber at a scan rate of 100 mV s^{-1}.

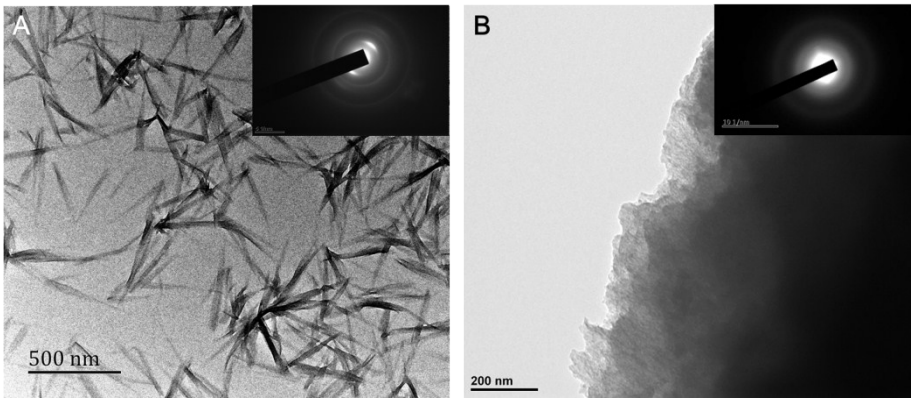


Fig.S4 TEM images and SAED patterns of (A) Emodin and (B) Emodin/PPy.

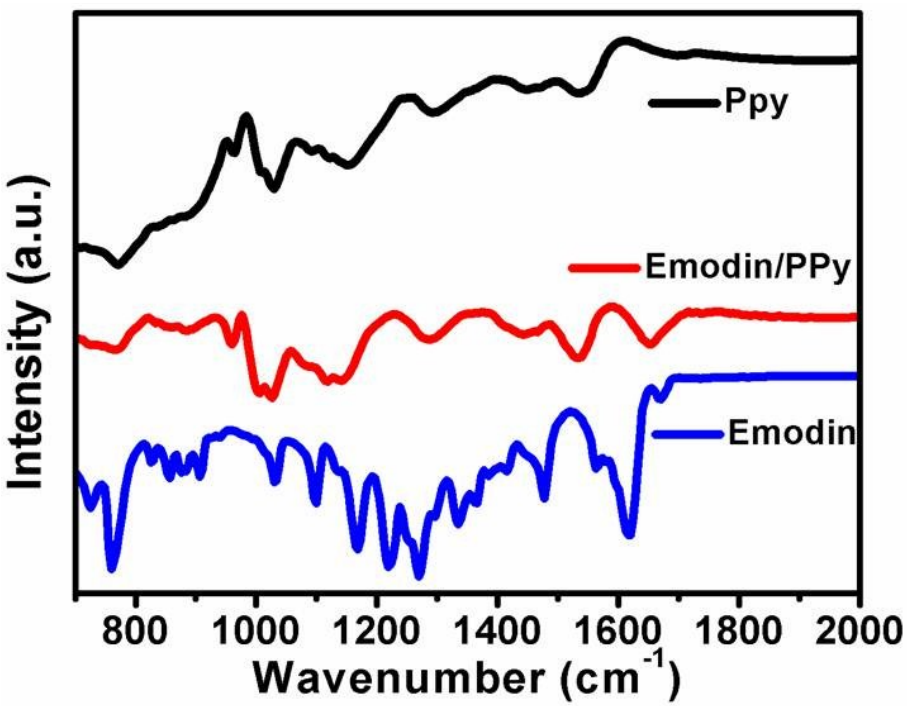


Fig. S5 FTIR spectra of PPy, Emodin/PPy and Emodin powders.

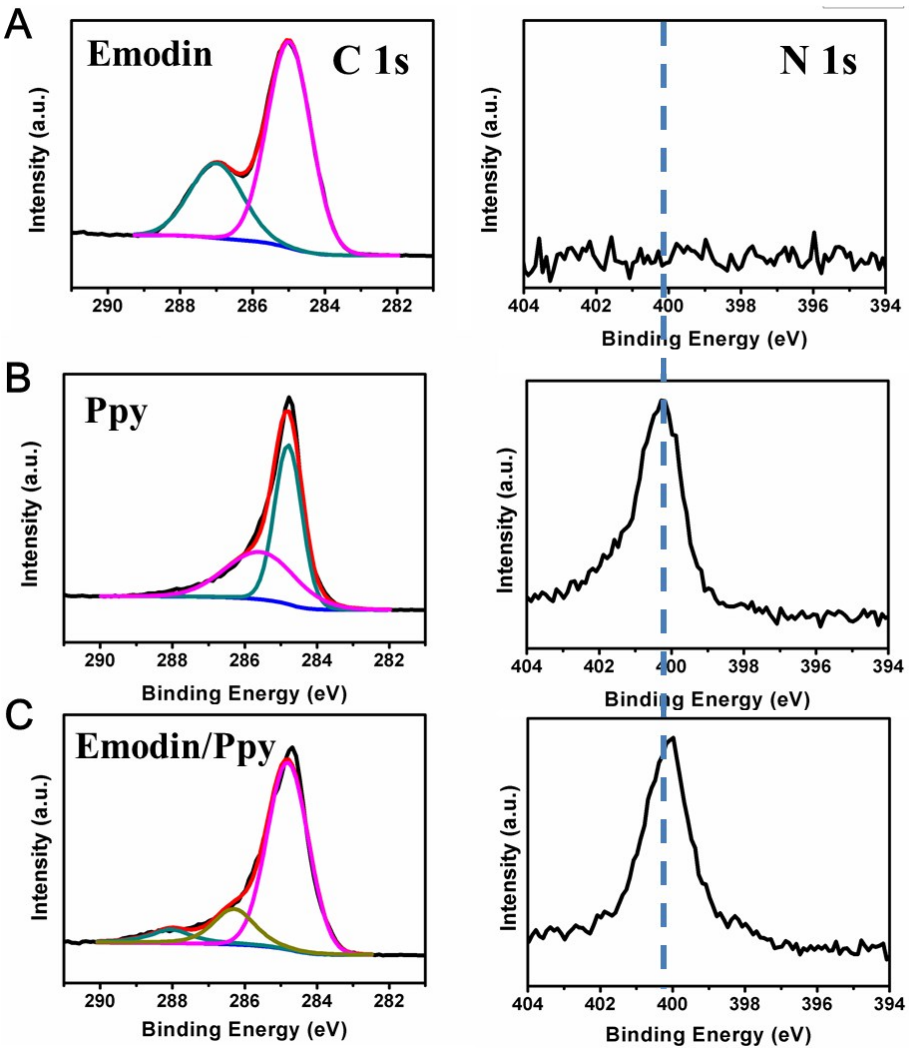


Fig. S6 XPS patterns of (A) Emodin, (B) PPy and (C) Emodin/PPy.

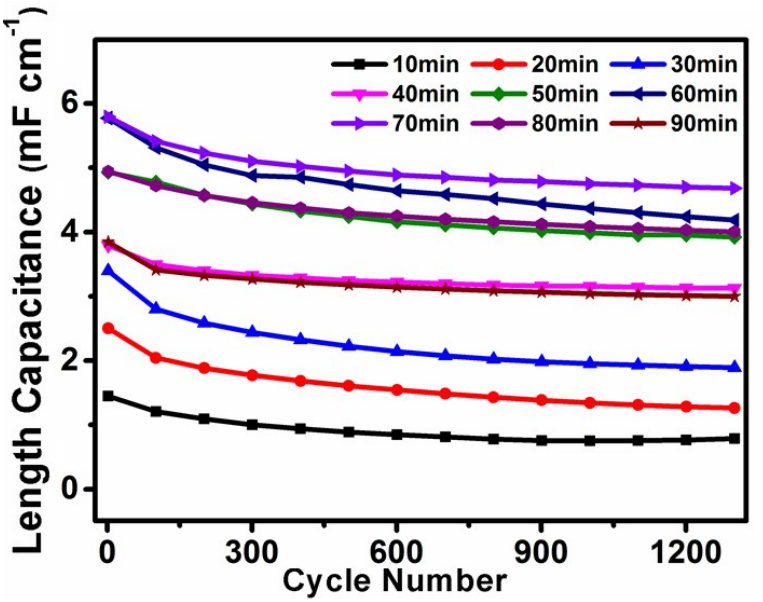


Fig. S7 Capacity retention curves of Emodin/PPy@CF electrodes with increasing electropolymerization period at a scan rate of 200 mV s^{-1}.

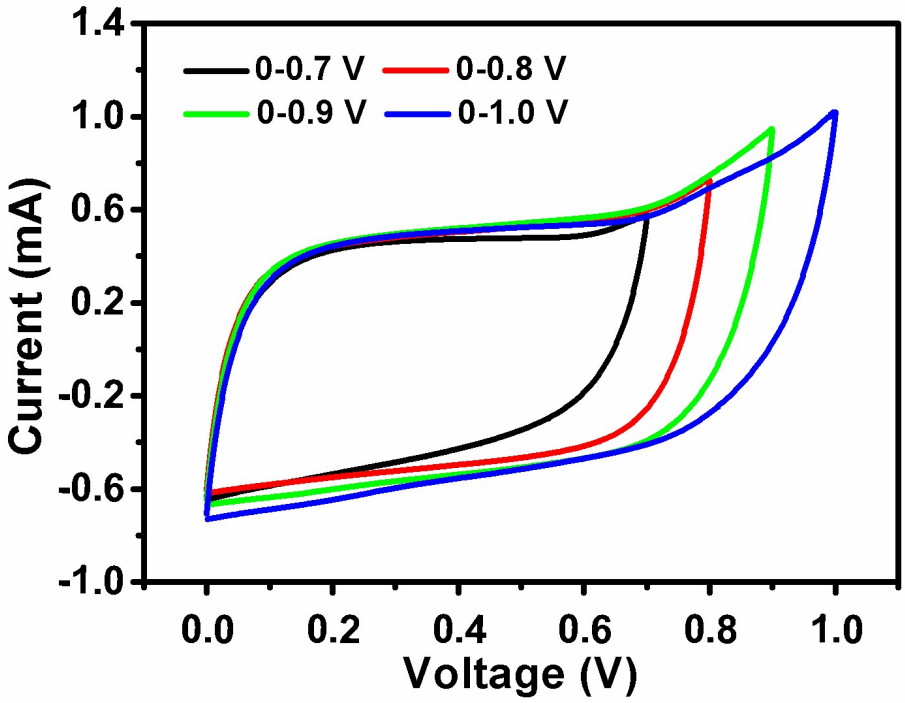
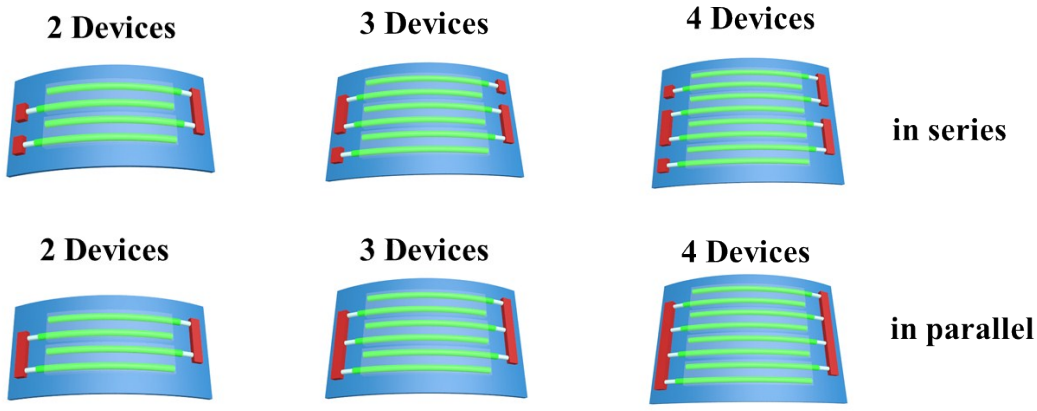


Fig. S8 CV curves of fiber-shaped supercapacitors with increasing voltage window from 0.7 to 1 V at the scan rate of 100 mV/s.



Scheme S1. Schematic configurations of supercapacitors in parallel/series.

Table S1. Electrochemical performances of Emodin/PPy@CF fiber-shaped supercapacitors.

Scan Rate (mV/s)	Length Capacitance (mF/cm)	Areal Capacitance (mF/cm^2)	Mass Capacitance (mF/mg)	Energy density (mWh/cm^3)	Power density (mW/cm^3)
5	5.49	40.88	46.53	1.05	18.92
10	5.38	40.01	45.59	1.03	37.04
20	5.28	39.29	44.75	1.01	72.73
50	5.14	38.26	43.56	0.98	177.04
100	4.83	35.93	40.93	0.92	332.57
200	4.20	31.23	35.59	0.80	578.11