

Supporting Information

The electric and magnetic responsive nanocomposite of
GdPO₄·H₂O/P3HT/PLGA with electrical stimulation for synergistically
enhancing the proliferation and differentiation of pre-osteoblast

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Materials and methods

Materials

Isopropanol, chloroform, ethanol, nitric acid, ethylene glycol, methanol and tetrahydrofuran (THF) were purchased from Beijing Chemical Reagents Company. The 2-bromo-5-iodo-3-hexylthiophene monomer (97%) was purchased from Sigma-Aldrich. Calcium hydride (CaH_2), stannous octoate and Nickel acetylacetonate ($\text{Ni}(\text{acac})_2$, 95%) were purchased from Aladdin. Lithium chloride (LiCl) and isopropylmagnesium chloride ($i\text{PrMgCl}$, 2.0 M solution in THF) were bought from Acros. The complex $\text{Ni}(\text{dppp})\text{Cl}_2$ (98%) was bought from Pacific ChemSource, Inc. Tetrahydrofuran (THF) and toluene was dried with sodium-benzophenone and distilled. $\text{Bi}(2, 6\text{-diisopropylphenyl})\text{imidazolin-2-ylidene}$ (IPr), $\text{Ni}(\text{IPr})(\text{acac})_2$ was purified by recrystallization from THF at $-35\text{ }^\circ\text{C}$.

Synthesis of PLGA

PLGA was synthesized as follows. Briefly, under dimmed light condition, stannous octoate was evacuated at $80\text{ }^\circ\text{C}$ for 2 h, at the same time, lactide and glycolide were processed under vacuum at $80\text{ }^\circ\text{C}$ for 6 h. After that, lactide, glycolide and stannous octoate were stirred in dry isopropanol for 1h at $80\text{ }^\circ\text{C}$ and 24h at $130\text{ }^\circ\text{C}$ under argon atmosphere. The solution then cooled down to room temperature and precipitated into ethanol, filtered and dried under vacuum overnight to give a white solid. The molecular weight of product was determined at a concentration of 2 mg/mL in chloroform referenced to polystyrene standards via gel permeation chromatography (GPC), $M_w=220\text{kDa}$, $\text{PDI}=1.90$.

Synthesis of $\text{GdPO}_4\cdot\text{H}_2\text{O}$ nanobundles

$\text{GdPO}_4\cdot\text{H}_2\text{O}$ nanobundles were synthesized as follows. Briefly, gadolinium nitrate solution ($\text{Gd}(\text{NO}_3)_3$, 1.0 mol/L) was prepared by dissolving the Gadolinium oxide in nitric acid under agitation and heating. Then, $\text{Gd}(\text{NO}_3)_3$ solution (2 mL) was added to EG (25 mL), and dropwise added a clear mixed solution of $\text{NH}_4\text{H}_2\text{PO}_4$ (0.25 g) and urea (0.5 g) in deionized water (5 mL). Next, glycine (2.0 g) was dispersed into the above-

mentioned compound solution and stirred for 30 minutes. Then, the resulting suspension was heated to 180 °C and kept temperature for 24 h in a Teflon-lined autoclave with heat treatment. Lastly, suspension cooled to room temperature and centrifuged to obtain the products, after that, the products washed with deionized water and ethanol each for three times, and dried at 65 °C overnight. Finally, the white powder was obtained.

Characterizations

Nuclear magnetic resonance (¹H NMR) spectra of P3HT was recorded on a Bruker AV 500 MHz spectrometer in CDCl₃ with tetramethylsilane (Me₄Si) as internal reference. Composites films was characterized by Fourier transform infrared (FT-IR, Bio-Rad Win-IR spectrometer, UK) spectroscopy using KBr slice method. Gel permeation chromatography (GPC) measurements were carried out at 25 °C with a Waters 515 HPLC pump, a OPTILAB DSP differential refractometer detector and a column heater equipped with two Waters Styragel columns (HT3 and HT4). CHCl₃ served as the mobile phase containing 0.01 M LiBr and the flow rate was 1.0 mL/min. The narrow polystyrene standards were used to calibrate the standard curve of molecular weight. The X-ray diffraction (XRD) analysis of the composites from 13° to 35° were carried out on a Bruker D8 Advance X-Ray Diffractometer with a Cu tube anode ($\lambda = 0.154$ nm). Composites magnetic curves were assessed using a Quantum Design-MPMS-XL7 magnetometer at 293 K. The static water contact angle were measured by the standard sessile drop method on a Rame-Hart Goniometer (Model 250 Rame-Hart, New Jersey, USA). The data for water contact angle of one same composite membrane was a mean of five contact angle measurements. The exact contact angle was analyzed with the manufacturer's software.

The morphology and size distribution of the composites were characterized using a field emission scanning electron microscope (FESEM) (Philips XL30 ESEM FEG, Japan). Transmission electron microscopy (TEM) was performed on a FEI Tecnai G2 S-Twin transmission electron microscope.

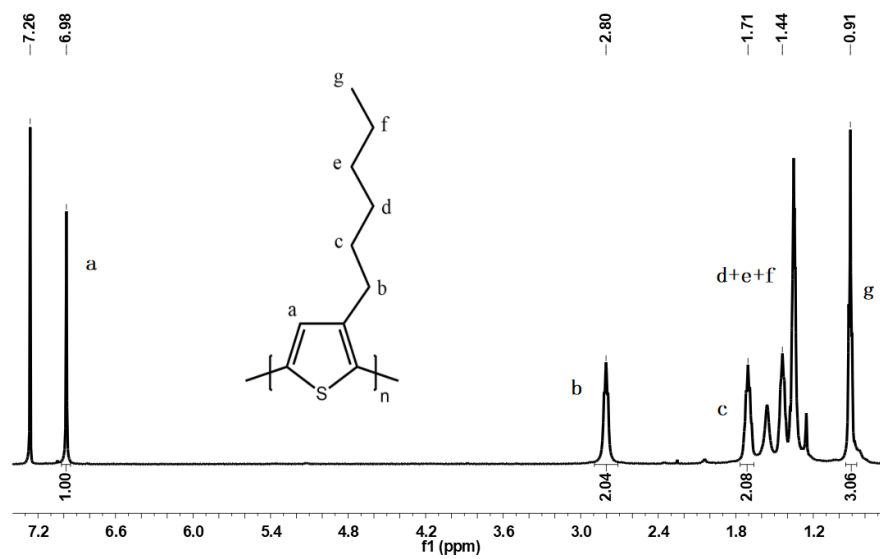


Figure S1. ^1H NMR spectrum of P3HT in CDCl_3 .

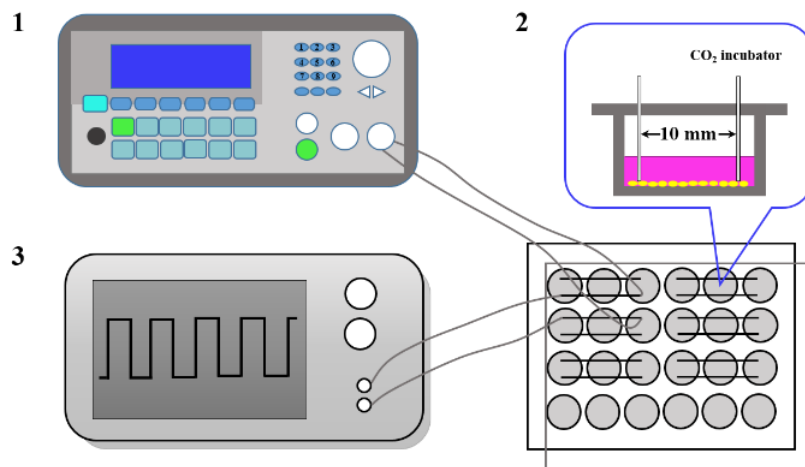
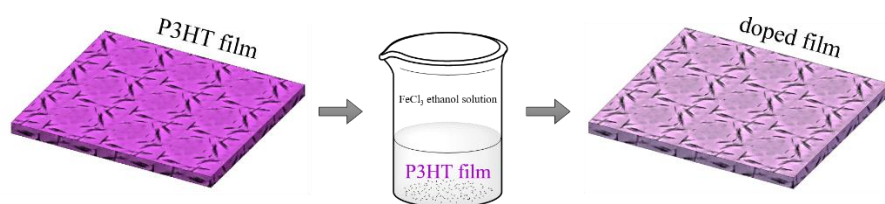


Figure S2. A self-made ES device consisting of ES generator for power supply (1), cell culture unit of platinum electrode chamber design (2) and oscilloscope for ES verification (3).

(a)



(b)

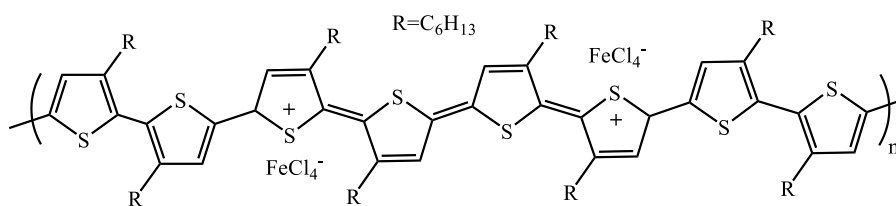


Figure S3. (a) Schematic of FeCl₃ ethanol solution (10 mmol/L) doped film method for 5 min to evaluate conductivity. (b) Chemical structures of P3HT doped with FeCl₃.

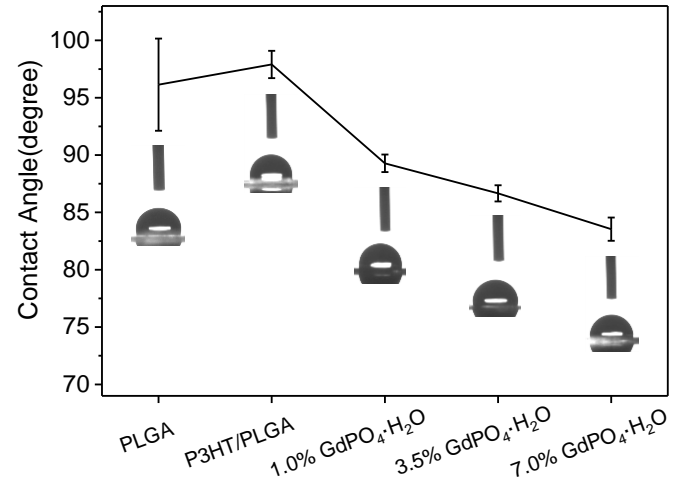


Figure S4. Water contact angle measurement and water droplet for different samples.

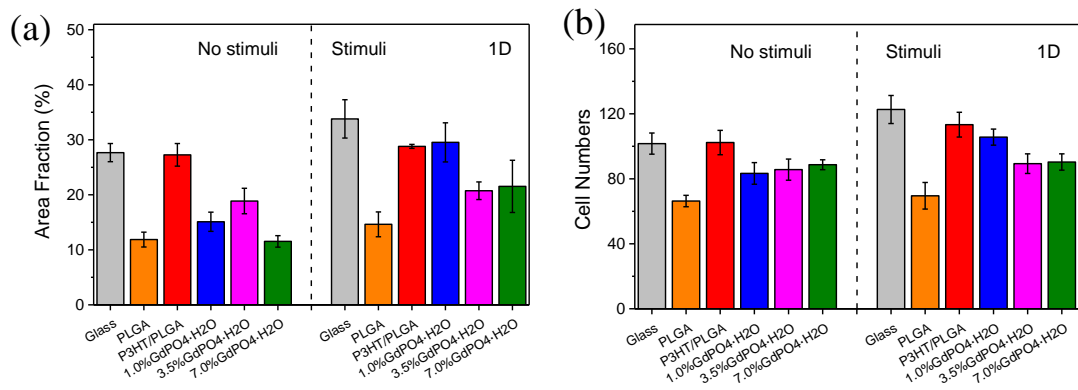


Figure S5. Area fraction (a) and cell numbers (b) of MC3T3-E1 cells on different substrates for 1day with and without ES. The groups are Glass, PLGA, P3HT/PLGA, GdPO₄·H₂O/P3HT/PLGA with different GdPO₄·H₂O contents such as 1.0 wt%, 3.5 wt% and 7.0 wt%.