Electronic Supplementary Material (ESI) for Biomaterials Science.

Supplementary Information

Para-substituted Sulfonic Acid Doped Protonated Emeraldine Salt Nanobuds: A Potent Neural Interface Targeting on PC12 Cell Interactions and Promotes Neuronal Cell Differentiation

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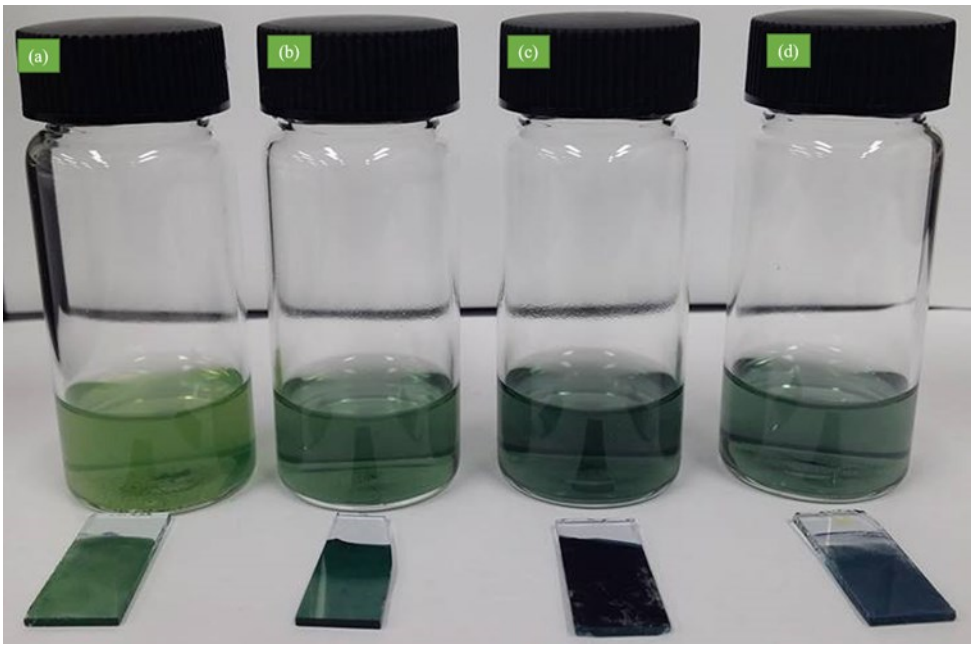


Figure.S1. Digital photos of s-PANINbs at various oxidation potentials (a) protonated emeraldine base (PEB) in light green, (b) protonated emeraldine salt (PES) in deep green, (c) protonated nigraniline (PNA)in (blue), and (d) protonated pernigraniline (PPNA) in violet color at dispersed in phosphate buffer solution(PBS) of pH ~ 7.4 for 24 h.

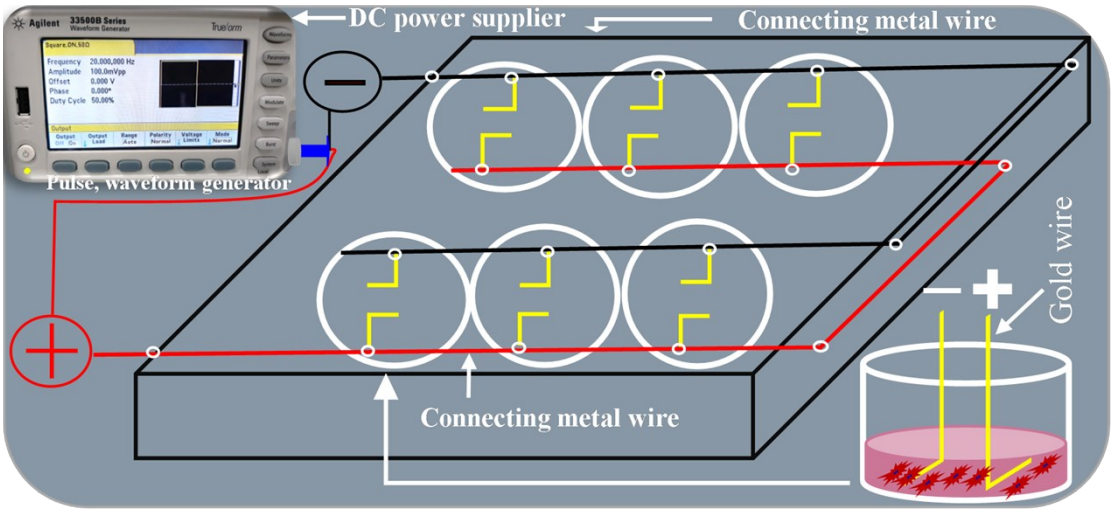


Figure. S2. Schematic representation of in vitro cell culture to promote PC12 cell proliferation and differentiation under electrical stimulation. 12- well plate was used to design of electrical device.

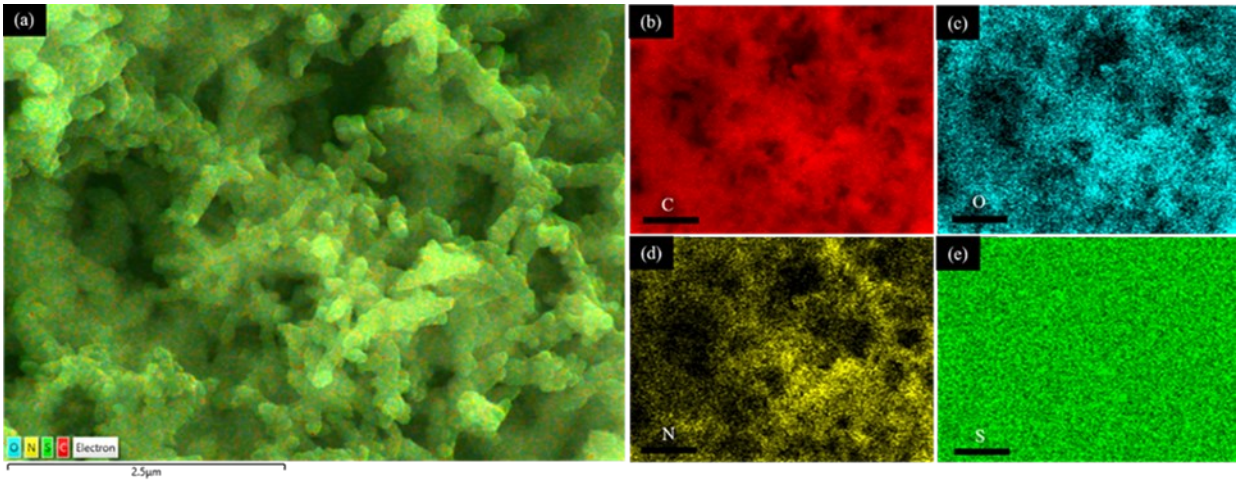
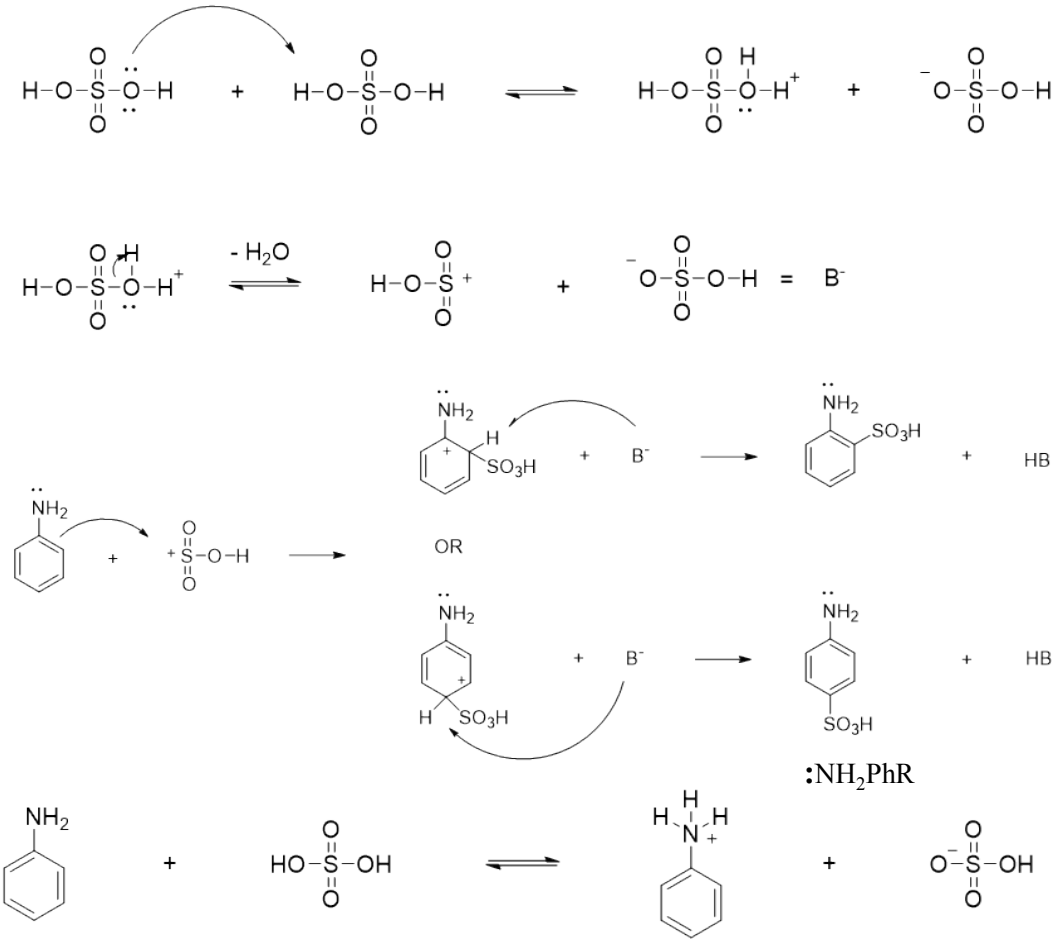


Figure. S3. FE-SEM image of the protonated emeraldine salt of s-PANINbs (a) and the corresponding elemental color mapping of carbon (C-K) (b), oxygen (O-K) (c), nitrogen (N-K) (d), and sulfur (S-K) (e).

Electrochemical polymerization of aniline

Interfacial electrochemical polymerization of sulfonic acid doped aniline (s-aniline) was conducted at low temperature to synthesis of sulfonic group doped polyaniline nanobuds (s-PANI) in uniform shape and size. Basically, s-PANINbs is synthesized in two-step reactions processes and the reaction is proposed by following mechanism;

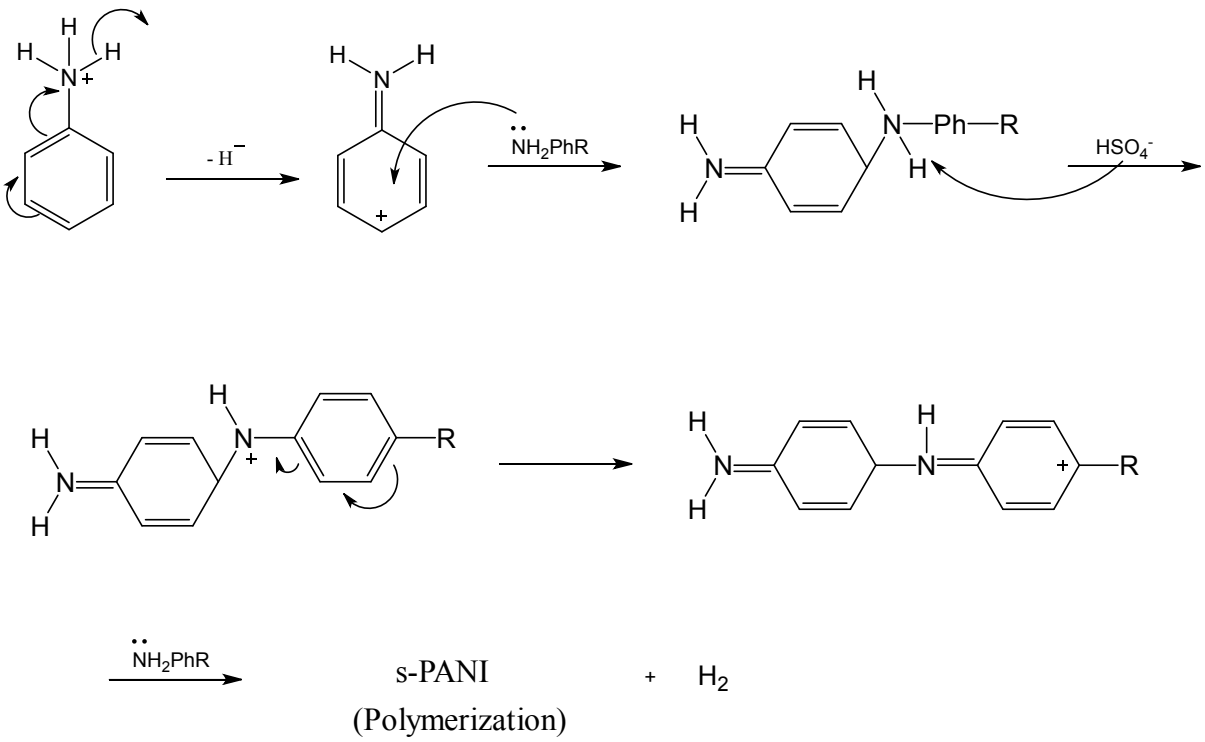


Scheme 1. Equilibrium state of sulfuric acid followed by the electrophilic addition in ortho or para positions of aniline.

In the above reaction mechanism, an ionic equilibrium of sulfuric acid with the formation of sulfonated ions is considered. The release of water molecule from sulfuric acid leads to the formation of conjugated acid (sulfonic cation) and conjugated base along with the reaction equilibrium. Notably, sulfonic cation is obtained through the process of dehydration when the cation is transferred from one sulfuric to another sulfuric acid followed by the formation of sulfonic cation.

The electrophilic substitution reaction of sulfonic cation and aniline was observed at either ortho or para position in aniline monomers. However, the para position is more favorable than meta position due to the crowding effect. Consequently, para position of sulfonic groups is chemically more stable.

The initiation of chain reaction with polymerization of s-aniline monomers containing sulfonic group (-R) can be observed with applied of potential range from -0.2 to 1.0 V. The s-aniline monomers exhibit redox reaction with simultaneously formation of cationic groups. The protonated aryl-amine acts as propagating species at equilibria regarding contact ion pairs ⇌ solvent separated protonated aryl-amine pair ⇌ free protonated -SO_3H doped -aniline. The applied voltage is sufficient to cause redox reactions on s-aniline to the formation of protonated para-substituted sulfonic doped polyaniline at different oxidation states.



$H_2 = H^-$ (from reaction step) + H^+ (from H_2SO_4)

Scheme 2. Reaction mechanism for the formation of sulfonic group doped polyaniline.

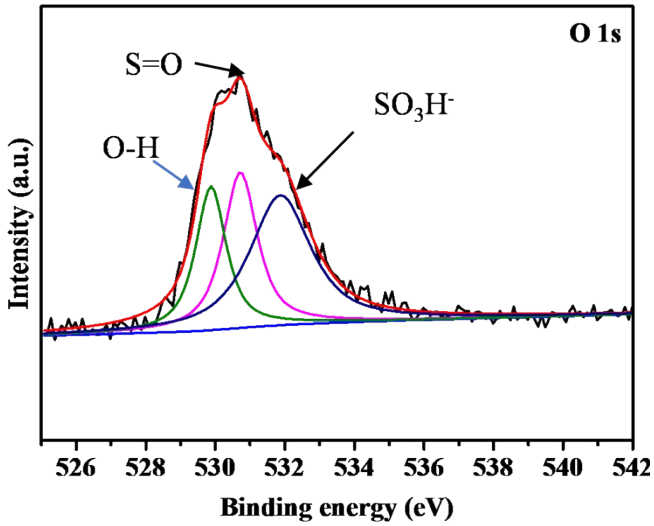


Figure S4. High-resolution, XPS spectrum of O 1s of the protonated emeraldine salt of s-PANINbs.

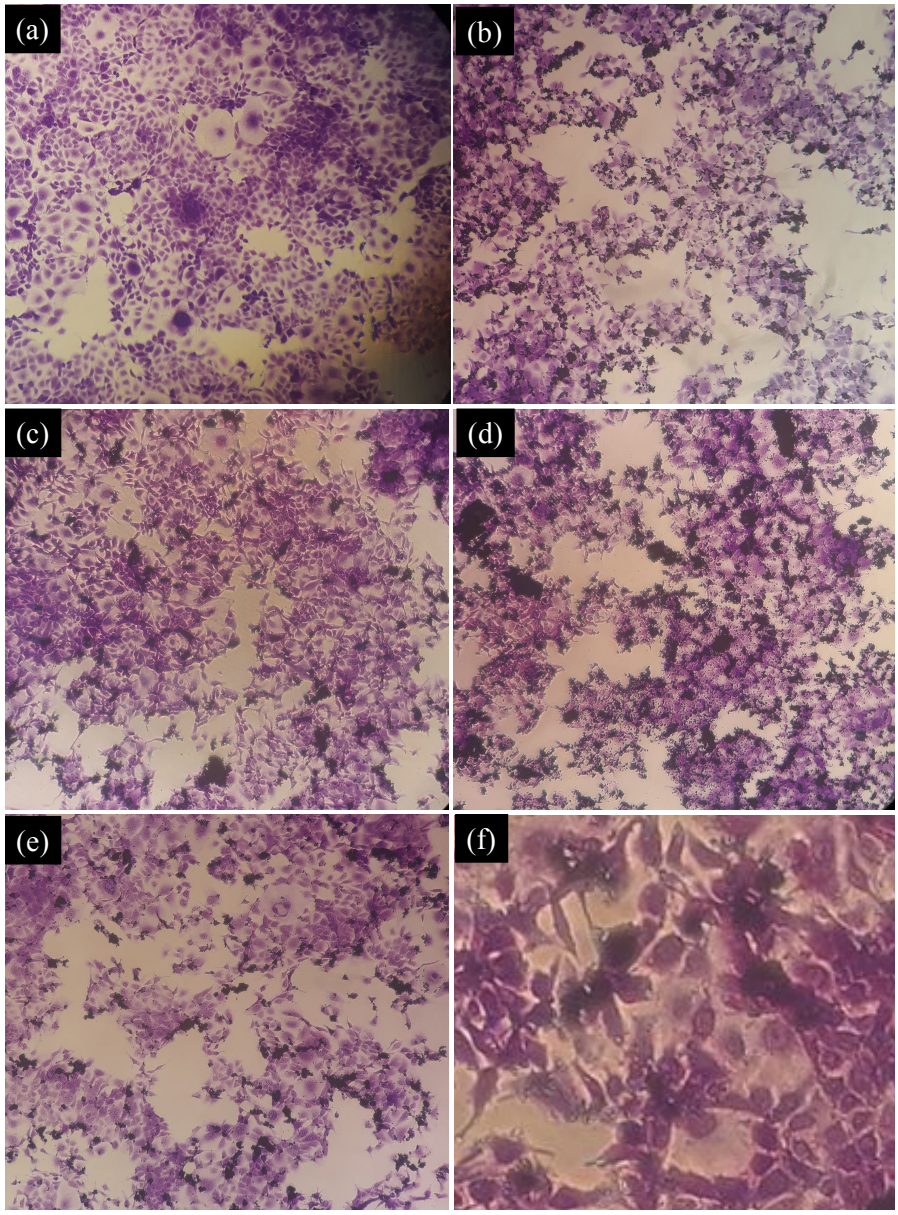


Figure S5. Crystal violet stained for PC12 cells growth on 20µg/ mL of each s-PANINbs (various OSs), dispersed on cell media after 24h. Figure (a) in TCP, (b-e) correspond to protoemeraldine base, protonated emeraldine salt, protonated nigraniline, and protonated pernigeraniline respectively (magnification 10X). (f) high magnification (at 40X) image of (c).

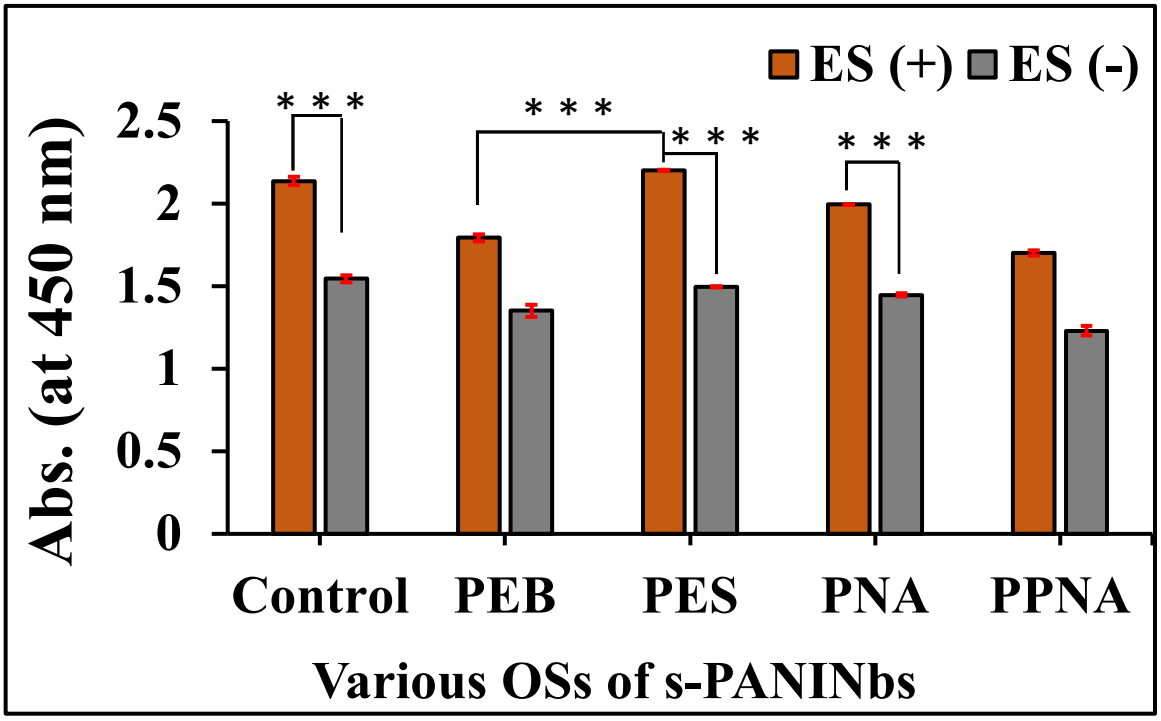


Figure.S6. Quantitative analysis of PC12 cell viability via CCK-8 assay of s-PANINbs (20 μg/mL each) at various OSs in the absence of electrical stimulation (ES (-) or presence of electrical stimulation (ES (+)) of applied DC voltage for 7 days.