Supporting Information

Synthesis of polyaniline nanotubes by self-assembly behavior of vitamin C: A mechanistic study and its application in electrochemical supercapacitor

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1. Reaction mechanism through the effect of solvent and dilution

**Figure S1.** FESEM images of PANI in (a) ethanol, (b) 2-propanol and (c) acetone solvent.
2. Reaction mechanism through the effect of dilution (Figure S2)

Figure S2. FESEM image of PANI in dilute condition.
3. XPS spectra

**Figure S3.** XPS spectra of pure (a) vitamin C (wide scan), (b) PANI$_{0.25}^0$ (wide scan)
4. Surface area measurements and pore size distributions

Nitrogen adsorption–desorption isotherms of pure PANI (synthesized without template), PANI$^{0.1}$ and PANI$^{0.25}$ were shown in Figure S4a. According to the IUPAC classification it exhibited type-IV isotherms and specified the formation of mesoporous (2 – 50 nm) structure. A sharp increase in the adsorbed volume of N$_2$ and a hysteresis loop at a high relative pressure ($\approx P/P^o = 0.95$) are the typical characteristics of mesoporous materials. The specific surface areas calculated by the BET equation for pure PANI, PANI$^{0.1}$ and PANI$^{0.25}$ were 15.39 m$^2$/g, 29.08 m$^2$/g and 39.75 m$^2$/g respectively. Therefore it can be inferred that the specific surface area in PANI$^{0.25}$ was increased significantly compared to pure polyaniline (increased about 3-fold) which was synthesized without any template. Furthermore, pore volume distribution curves as a function of the pore size calculated by the BJH method were presented in Figure S4b which demonstrated the development of nanoporous structure of PANI$^{0.25}$ material. The larger surface area found in PANI$^{0.25}$ is very much desirable for effective ions transportation during electrochemical tests, which produced a larger capacitance value.
Figure S4. (a) N\textsubscript{2} adsorption-desorption isotherms and b) BJH pore size distributions of pure PANI (synthesized without template), PANI\textsuperscript{0.1} and PANI\textsuperscript{0.25}. 
5. Thermogravimetric analysis

In order to study the thermal stability of PANI$^{0.25}$ & PANI$^{0.1}$ samples thermogravimetric analysis (Figure S5) was performed with a TA thermal analysis system at a heating rate of 10°C/min under N$_2$ environment in a temperature range from 100 - 800°C. In the temperatures range of 100 - 170°C, it is apparent from Figure S5 that the percent weight loss for both the polymers was rather negligible indicating the stability of the sample specimens at this temperature range. The percent weight for either polymer started to drop gradually due to the thermal degradation in the temperatures range from 170 - 800°C. Thus, it is clear that the thermal characteristic for either polymer was nearly the same over the entire temperature range.
Figure S5. TGA graphs of a) PANI$^{0.1}$ and b) PANI$^{0.25}$. 

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6. FESEM images after 500 cycles

![FESEM image after 500 cycles](image)

**Figure S6.** FESEM image after 500 cycles
7. Reaction kinetics in presence of vitamin C and APS in aniline polymerization

\[ \text{An} + \text{APS} \xrightarrow{k_1} \text{An}^+ \quad \text{--------- (1)} \]

\[ \text{An}^+ + \text{Vit C} \xrightarrow{k_2} \text{An} \quad \text{--------- (2)} \]

From equation (1) we get, \( r_1 = \frac{d[\text{An}^+]}{dt} = k_1[\text{An}][\text{APS}] \quad \text{--------- (3)} \)

and from equation (2) we get, \( r_2 = \frac{d[\text{An}]}{dt} = -\frac{d[\text{An}^+]}{dt} = k_2[\text{An}^+][\text{Vit C}] \quad \text{--------- (4)} \)

**Case-I:** If \([\text{An}] : [\text{APS}] : [\text{Vit C}] = 1 : 1 : 1\), then

\[ \{\frac{d[\text{An}^+]}{dt}\}_{[[\text{APS}]/[\text{An}]]} = 1 = \{\frac{d[\text{An}]}{dt}\}_{[[\text{Vit C}]/[\text{An}]]} = 1 \]

No polymerization takes place due to the absence of excess \(\text{An}^+\).

**Case-II:** If \([\text{APS}]/[\text{An}] = 1\) and \([\text{Vit C}]/[\text{An}] = x\), where \(x = 0.5, 0.25, 0.1, 0.05 \& 0.01\)

Then, \( \{\frac{d[\text{An}^+]}{dt}\}_{[[\text{APS}]/[\text{An}]]} = 1 > \{\frac{d[\text{An}]}{dt}\}_{[[\text{Vit C}]/[\text{An}]]} < 1 \)

Polymerization takes place due to the availability of \(\text{An}^+\).

i.e. (a) \( \{\frac{d[\text{An}^+]}{dt}\}_{[[\text{APS}]/[\text{An}]]} = 1 > \{\frac{d[\text{An}]}{dt}\}_{[[\text{Vit C}]/[\text{An}]]} = 0.5 \)

(b) \( \{\frac{d[\text{An}^+]}{dt}\}_{[[\text{APS}]/[\text{An}]]} = 1 > \{\frac{d[\text{An}]}{dt}\}_{[[\text{Vit C}]/[\text{An}]]} = 0.25 \)

(c) \( \{\frac{d[\text{An}^+]}{dt}\}_{[[\text{APS}]/[\text{An}]]} = 1 > \{\frac{d[\text{An}]}{dt}\}_{[[\text{Vit C}]/[\text{An}]]} = 0.1 \)

(d) \( \{\frac{d[\text{An}^+]}{dt}\}_{[[\text{APS}]/[\text{An}]]} = 1 > \{\frac{d[\text{An}]}{dt}\}_{[[\text{Vit C}]/[\text{An}]]} = 0.05 \)

(e) \( \{\frac{d[\text{An}^+]}{dt}\}_{[[\text{APS}]/[\text{An}]]} = 1 > \{\frac{d[\text{An}]}{dt}\}_{[[\text{Vit C}]/[\text{An}]]} = 0.01 \)

**Scheme SC1:** Reaction kinetics
8. Electron transfer mechanism in vitamin C

Scheme SC2. Oxidation of vitamin C
References
