# Supplementary Information

# Water dispersible Ag@polyaniline-pectin as supercapacitor electrode for physiological environment

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## Contents

## 1. Experimental section

**1A. Materials.** Aniline and $AgNO_3$ were purchased from Sigma-Aldrich, India. Ammonium persulfate, pectin, were purchased from SRL Chemicals, India. Human blood, serum and urine were collected from the healthy volunteers including the authors. L6 mycoblasts cells were purchased from NCCS Pune. Dulbecco's modified eagle medium and 100x Antibiotic – antimycotic solution (Himedia, India), fetal bovine serum (Gibco), 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (SRL India) were used.

**1B. Characterization.** X-ray diffraction (XRD) patterns of the samples were recorded (using Philips Diffractometer PW 1710) from 2• 10° to 90° at the step of 2°/min using monochromatic Cu K• radiation at 40 kV excitation voltage and 30 mA tube current. FTIR spectra of the samples were recorded from 800 to 4000 $cm^{-1}$ using FTIR Bomen Hartman and Braun, MB series. UV-visible spectra of the samples in water medium were recorded from 200 to 900 nm using JASCO V-650 spectrophotometer. Morphology of the samples was studied by field emission scanning electron microscopy (FE-SEM) Auriga, Zeiss, Germany. Elemental analysis was investigated using Energy dispersive X-ray spectroscopy (EDX), JOEL, Japan. Dynamic light scattering (DLS) measurement was performed in Malvern 4800 Autosizer employing 7132 digital correlator. For XPS measurements, PANI-PEC and Ag@PANI-PEC drop cast on silicon substrate was mounted on a specimen holder using silver paste. The conducting path was given from the bottom to the top of the surface of the sample by silver paste, to avoid the surface charging effect. The sample chamber was then evacuated to a vacuum better than $1 \times 10^{-9}$ Torr. The sample was excited by Mg-K**.** radiations (*h*• = 1254.6 eV), photoelectron spectra were analyzed using a VG make CLAIM 2 analyzer system in the energy range of 0–1000 eV. The morphology of the cells during *in vitro* biocompatibility studies were pictured under a scanning electron microscope (SEM) FEI Quanta 200, USA.

**1C. Synthesis of water dispersible polyaniline-pectin (PANI-PEC)** [1]. To 50 ml aqueous solution of pectin (PEC) (1.862 g PEC in 50 ml distilled water), 15 mL of aqueous solution containing 9 mL con. HCl and 0.9313 g of aniline was added (aniline:PEC = 1:2). To the above solution, 2.28 g of ammonium persulfate initiator (in 25ml water) was added drop-wise for the period of 15 min and the reaction was stirred at room temperature for 4 h to yield homogeneous PANI-PEC dispersion. The PANI-PEC was precipitated in 500 mL of 1:1

mixture of ethanol-water, filtered in Whatmann 41 filter paper, washed with 500 mL of 1:1 mixture of ethanol-water to get pure PANI-PEC precipitate. The precipitated PANI-PEC was re-dispersed in water by ultrasonication. Using the similar experimental condition, the amount of PEC was varied (aniline:PEC = 1:1 and 1:3) to understand the effect of PEC on PANI particle size. In all polymerization reactions the molar ratio of monomer, dopant and initiator is kept constant (1:10:1).

**1D. Synthesis of Water Dispersible Silver Decorated PANI-PEC (Ag@PANI-PEC)** [2]. 5 mL of PANI-PEC (4 mg/mL) aqueous dispersion was stirred and heated to 80°C. To the above solution, 5 mL of 0.2 M $AgNO_3$ solution was added drop-wise over a period of 10 min. The reaction was stirred for 4 h at 60 °C. After 2 h, the stirring and heating were stopped and reaction was kept undisturbed for 12 h at room temperature. Then the reaction mixture was centrifuged at 10,000 rpm for 10 min. Thus settled Ag@PANI-PEC was washed with 1% ammonia solution, followed by 1 M HCl and distilled water. Then the Ag@PANI-PEC was separated by centrifuge at 10,000 rpm for 10 min to afford Ag@PANI-PEC precipitate which can be easily re-dispersed in water using ultrasonication. Using similar conditions, the amount of $AgNO_3$ has been varied (0.05 M and 0.2M). When 0.05 M $AgNO_3$ was used, there was no significant formation of Ag@PANI-PEC and when 0.2M $AgNO_3$ was used, the formed Ag@PANI-PEC was not dispersible in water. This could be due to the aggregation of silver and PANI-PEC due the excess amount of $AgNO_3$. Hence 0.1 M $AgNO_3$ was considered as an optimum concentration for the formation of processable Ag@PANI-PEC. Ag@PANI-PEC synthesized using 0.05 M, 0.1 M and 0.2 M was named as Ag1205, Ag121 or Ag@PANI-PEC, and Ag122 respectively.

**1E. Preparation of working electrode and electrochemical measurements.** The working electrode for supercapacitor was prepared by drop casting 1 µL of 2 mg/mL aqueous solution of PANI-PEC or Ag@PANI-PEC which contains 20wt% carbon powder on glassy carbon electrode (GCE) of 2 mm diameter. The electrodes were dried at 50 ºC for 5h. Generally binder is used in the electrode fabrication. In the present work, PEC present in the composite helped PANI to bind well with the GCE electrode. So, additional binder is not used in the present system for electrochemical studies. The electrochemical studies (cyclic voltammetry and charge-discharge) were explored in three electrode cell using a Potentiostat-Galvanostat (PGSTAT20, EcoChemie, The Netherlands). Pt wire and Ag/AgCl were used as counter and

reference electrodes respectively. PANI-PEC or Ag@PANI-PEC coated GCE was used as working electrode. The physiological fluids such as phosphate buffer saline (PBS, pH of 7.3), blood, urine and serum were used as the electrolyte for the electrochemical studies. Cyclic voltammogram was examined in the potential windows ranged from -0.1 to 1.0 V *vs* Ag/AgCl at a different scan rates. The galvanostatic charge-discharge measurement was performed from 0 to 0.9 V *vs* Ag/AgCl at a current density of 1.5A/g.

**1F. Sample preparation and characterization for the biocompatibility/bacterial adhesion studies** [3]. For the biocompatibility studies, the commercial grade stent **(**Tecoflex ®**)** was used as a source of polyurethane (PU) film. 1 g of stent was washed in ethanol, dissolved in 20 ml of tetrahydrofuran (THF), casted in a 10 cm diameter petri dish and kept for room temperature evaporation. After the THF was evaporated, thus formed PU film was kept in oven at 60 °C for 4 h. Dried PU film was cut in to 1.2 cm X 1.2 cm pieces and kept for swelling in 1:1 THF-water mixture for 24 h. Swelled PU films were soaked in aqueous solution contains PEC, aniline, HCl for 24 h and later initiator ammonium persulfate was added in the mixture to initiate the formation of PANI-PEC on the PU films. Homogeneous green color on the PU film indicated the formation of PANI-PEC on the PU films (PU-PANI-PEC) and used for the biocompatibility studies. Few pieces of the PU-PANI-PEC films were treated with 0.1 M $AgNO_3$ solution at 60 °C for 2 h. After 2h, the heating was stopped and reaction was kept undisturbed for 12h at room temperature. Thus formed PU-Ag@PANI-PEC films were washed with 1 % ammonia solution, distilled water and used for biocompatibility/antibacterial studies.

The biocompatibility of polymer films was assessed with L6 rat myoblast cells. L6 cells were cultured in DMEM medium supplemented with 10 % FBS and 1 % antimycotic-antibiotic solution in an incubator humidified with 5 % $CO_2$ at 37 °C. Polymers films were sterilized with 70 % ethanol and equilibrated with phosphate buffered saline (PBS) for 1 h. Approximately $10^4$ L6 cells were counted and added to the polymer films and incubated for 24 h. The cell viability was determined by MTT assay and the percentage cell viability was determined by using the formula,

% cell viability = [Absorbance of cells cultured with polymer/ absorbance of cell cultured alone] x100

Adhesion of Gram negative *Escherichia coli* (NCIM) was tested on polymer films. The films were equilibrated with PBS (pH 7.2) for 24 h and were incubated with 0.5 OD of

*E. coli*. After incubation, the films were washed with ice cold PBS and each film was transferred to a sterile micro-centrifuge tubes containing 0.8 % saline. The adherent bacteria were removed with the help of a low frequency water bath sonicator for 4 min (interval of 1 min on/ off). The number of viable bacteria was calculated as colony-forming units (CFU)/cm$^2$ of the polymer surface.

## 2. Results and discussion

### 2 A. Yield of Polymerization and Amount of PEC in PANI-PEC.

In absence of PEC, the aniline polymerization yields PANI (1.2 g) with macroscopic aggregation and is insoluble in water. Having this value in mind the percentage of PEC in each batch of PANI-PEC was calculated [1] using following equation,

Amount of pectin (%)= {(Yield of PANI-PEC-1.2 g)/(Yield of PANI-PEC)}*100.

**Table S1** shows the yield of the polymerization, amount of PEC present in the PANI-PEC and subsequent particle size when the amount of pectin was increased in the reaction mixture.

**Table S1**. Effect of amount of pectin on the yield and size of the PANI-PEC composite

| aniline:PEC (w/w) used in polymerization | Yield (g) | Amount of PEC present in the PANI-PEC composite (%) | Average particle size of PANI-PEC determined using DLS measurement |
|---|---|---|---|
| 1:1 | 1.4 | 14 | 690±10 nm |
| 1:2 | 1.8 | 33 | 340±10 nm |
| 1:3 | 2.0 | 40 | 730±10 nm |

### 2 B. Energy Dispersive X-ray spectroscopy (EDX) data of Ag@PANI-PEC.

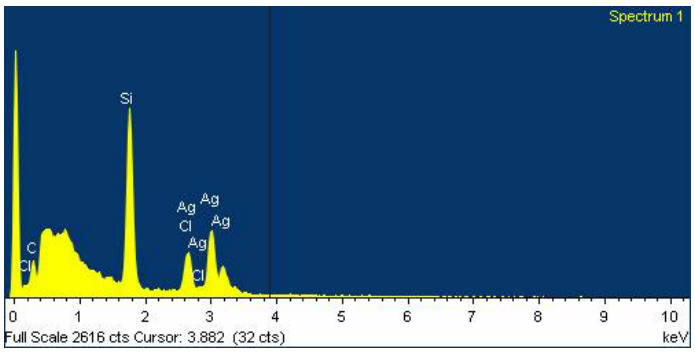


**Fig. S1** EDX of Ag@PANI-PEC

**2 C. UV-Visible spectral data of PANI-PEC.**

The **Table S2** shows the UV-visible spectroscopy data of PANI dispersion which were prepared using 1:1, 1:2, 1:3 aniline:PEC w/w. The **Table S2** shows that increasing the amount of PEC stabilizer does not influence the PANI peak positions. [1].

**Table S2.** Peak positions in the UV-visible spectra of PANI-PEC dispersions in water

| aniline:PEC (w/w) used in polymerization | •1 (nm) •–•* transition | •2 (nm) polaron to •* transition | •3 (nm) • to polaron transition |
|---|---|---|---|
| 1:1 | 330 | 430 | 875 |
| 1:2 | 335 | 435 | 875 |
| 1:3 | 335 | 435 | 870 |

**2 D. Charge-discharge Cyclic Stability of Ag@PANI-PEC**

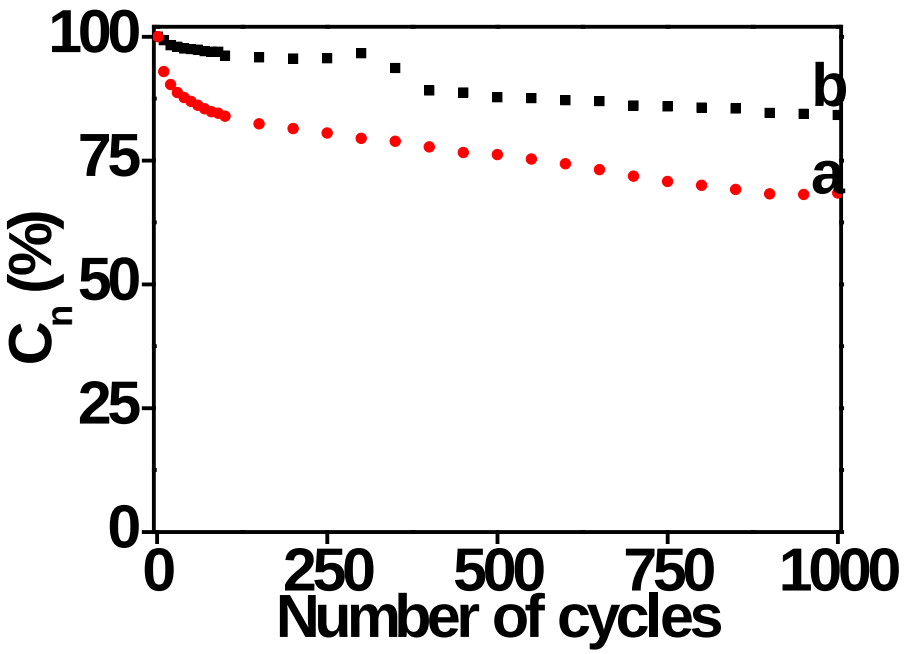


**Fig. S2** Normalized capacitance (%) of Ag@PANI-PEC in PBS over 1000 cycles, in the voltage range of (a) 0 to 0.9 V and (b) 0 to 0.6 V *vs* Ag/AgCl (Current density = 2.5 A/g).

## 2 E. *In vitro* Biocompatibility and bacterial adhesion of Polymer Films

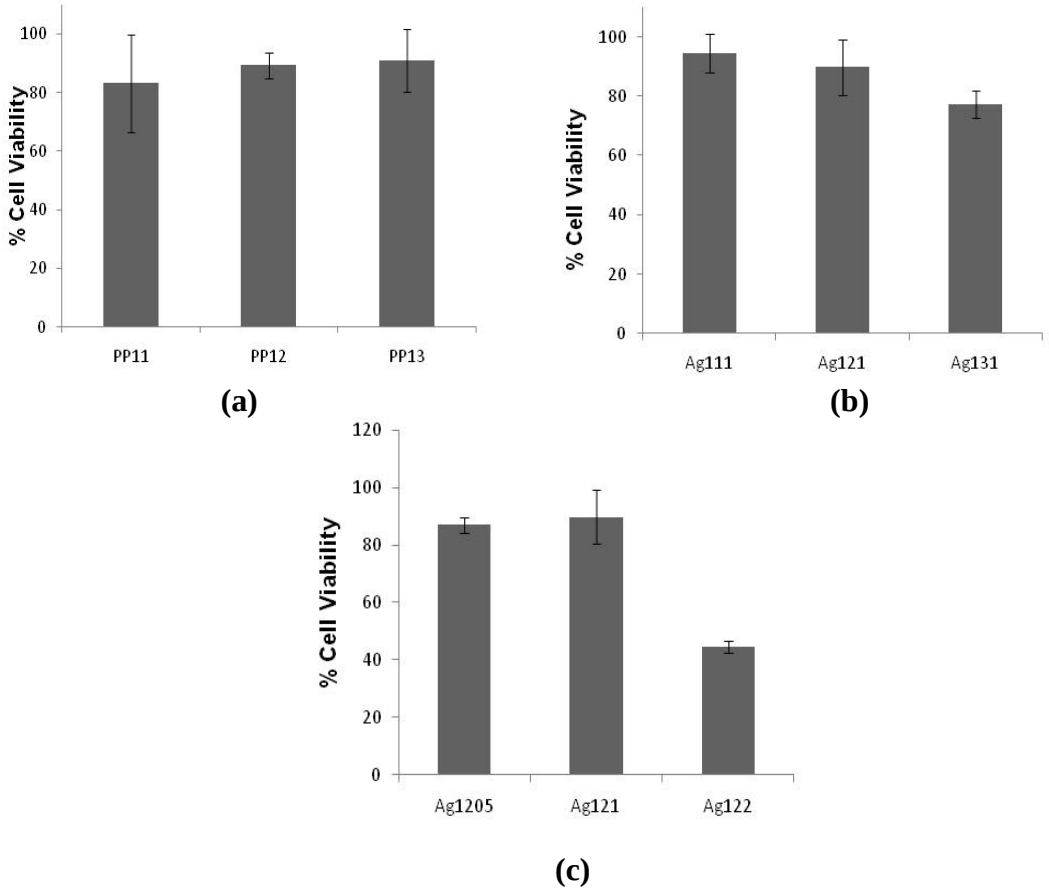


**Fig. S3** Cell viability of **(a)** PANI-PEC which was prepared using different ratio of aniline:PEC w/w, (1:1, 1:2 and 1:3 named as PP11, PP12 and PP13 respectively) (b) Ag@PANI-PEC synthesized from PP11, PP12 and PP13 using 0.1M $AgNO_3$. (c) Ag@PANI-PEC synthesized from PP12 using different concentrations of $AgNO_3$ (0.05M, 0.1M and 0.2M and named as Ag1205, Ag121 and Ag122 respectively).

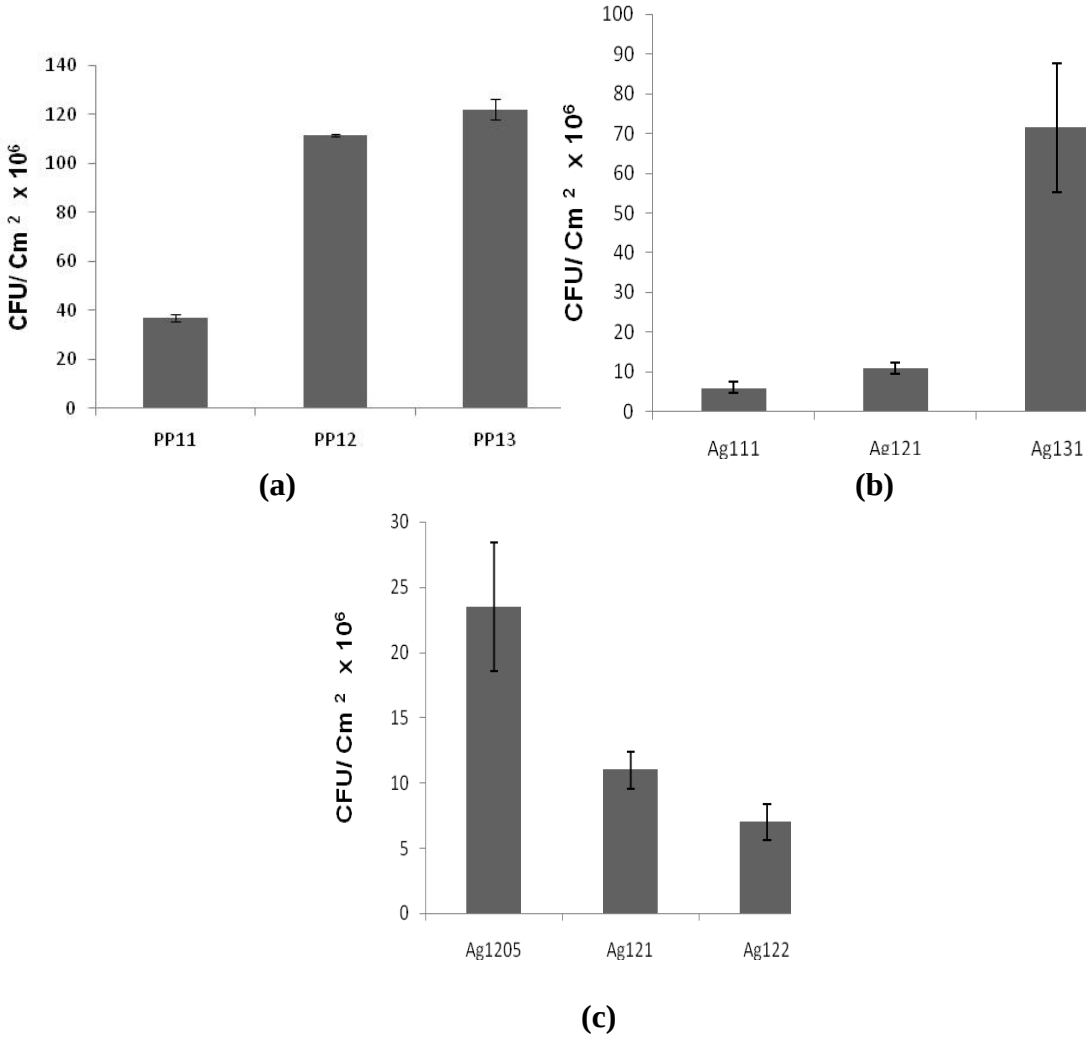


**Fig. S4 (a)** Bacterial adhesion (CFU/cm$^2$) of **(a)** PANI-PEC which was prepared using different ratio of aniline:PEC w/w, (1:1, 1:2 and 1:3 named as PP11, PP12 and PP13 respectively) (b) Ag@PANI-PEC synthesized from PP11, PP12 and PP13 using 0.1M $AgNO_3$. (c) Ag@PANI-PEC synthesized from PP12 using different concentrations of $AgNO_3$ (0.05M, 0.1M and 0.2M and named as Ag1205, Ag121 and Ag122 respectively).

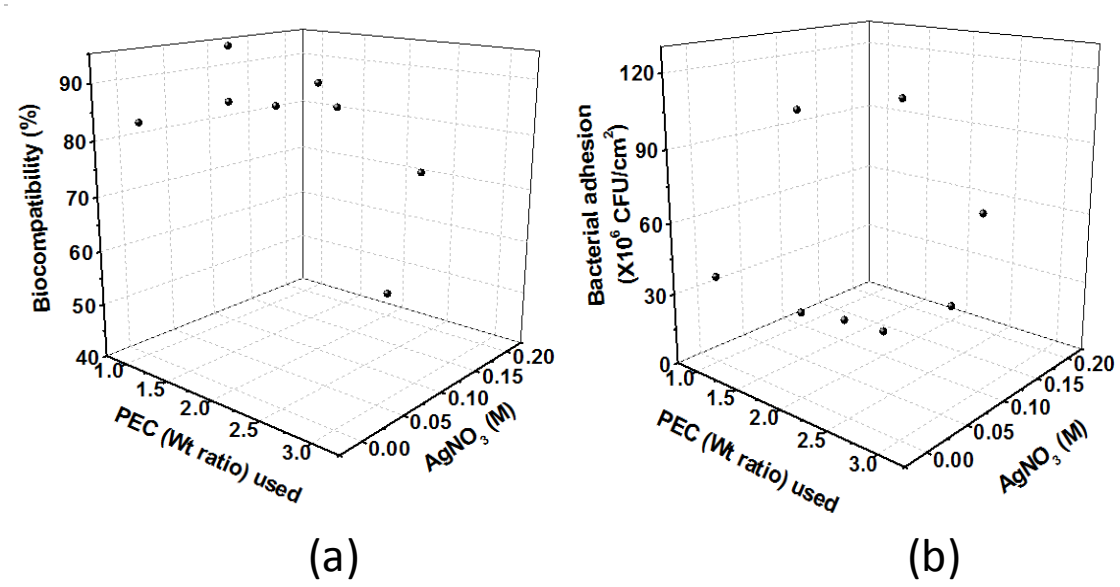


**Fig. S5** The effect of concentration of pectin and $AgNO_3$ on **(a)** Biocompatibility and (**b)** Bacterial adhesion

**Table S3**. Summary of the synthesis details, specific capacitance, biocompatibility and antibacterial activity for various samples of PANI-PEC and Ag@PANI-PEC.

| | Samples | Aniline:PEC w/w ratio | [$AgNO_3$] used (M) | $C_{sp}$ (F/g) | Biocompaibility (% cell viability) | Antibacterial activity (bacterial adhesion $X10^6$ CFU/cm²) |
|---|---|---|---|---|---|---|
| 1 | PANI-PEC (PP11) | 1:1 | --- | 25 | 83.16 | 37 |
| 2 | PANI-PEC (PP12) | 1:2 | --- | 15 | 89.28 | 112 |
| 3 | PANI-PEC (PP13) | 1:3 | --- | 10 | 91.01 | 122 |
| 4 | Ag@PANI-PEC (Ag111) | 1:1 | 0.1 | 40 | 94.41 | 6 |
| 5 | Ag@PANI-PEC (Ag121) | 1:2 | 0.1 | 140 | 89.77 | 11 |
| 6 | Ag@PANI-PEC (Ag131) | 1:3 | 0.1 | 37.5 | 77.35 | 72 |
| 7 | Ag@PANI-PEC (Ag1205) | 1:2 | 0.05 | 25 | 87.18 | 24 |
| 8 | Ag@PANI-PEC (Ag122) | 1:2 | 0.2 | 135 | 44.67 | 7 |

**Notes and references**


1. C. A. Amarnath, S. Palaniappan, P. Rannou and A. Pron, *Thin Solid Films*, 2008, **516**, 2928.
2. M. Rohwerder, S. I. Uppenkamp and C. A. Amarnath, *Electrochimi. Acta*, 2011, **56**, 1889.
3. P. K. Prabhakar, S. Raj, P. R. Anuradha, S. N. Sawant and M. Doble, *Colloids and Surf. B: Biointerf.*, 2011, **86**, 146