†Electronic Supplementary Information (ESI)

SM. 1. Synthesis of CS-Ag NCs and CS-Ag-PE NCs.

Chitosan-silver nanocomposites (CS-Ag NCs) were prepared according to the process developed by Calvo et al.,1997 & Sanpui et al., 2011, based on the ionotropic gelation of chitosan by sodium tripolyphosphate (TPP) by cross linking of TPP and AgNPs with amino groups of chitosan polymer (Sigma-Aldrich, average molecular weight, MW, 672 kDa). Briefly, the aqueous TPP solution (0.8 mg/mL) was added to chitosan and AgNPs solution (2.5 mg/mL) and stirred for 1 h at room temperature. The resulted whitish yellow solution was further precipitated and the unbound Ag ions, if any, present in the solution were removed by washing with Milli Q water.

CS-Ag NPs were used to conjugate (PE), which was isolated and purified from the red algae *Solieria robusta* (Greville) Kylin according to the method reported by Senthikumar et al., 2013. The stability properties of PE in different organic solvents were performed (Senthilkumar et al., 2013). CS-Ag-PE NCs was synthesized by adding equimolar volume of aqueous CS-Ag NCs solution (10 mM) to PE solution (50 mg/mL) at 37ºC under vigorous stirring in different pH (3.5, 4.5, 5.5, 6.5, 7.5 and 8.5). After 2 min, 0.5 mL of NaOH solution (1 M) was added to the mixture, and the reaction was allowed to proceed at the same temperature for 12 h to obtain pale pink solution. 1.5 g of mPEG (Mw=2000) solution (0.75 mM) was added to was added to the solution containing mixture of methoxyPEG (mPEG) and CS-Ag-PE NCs to form amide bond between the amine group of mPEG and the carboxylic group of PE of CS-Ag-PE NCs. The mixture was stirred for one day at room temperature till the yellowish pink solution was obtained. This mixture was further dissolved in DMSO to carry out spectral characterizations. Ionic interaction between negatively charged PE and positively charged CS-Ag NPs stabilized the CS-Ag-PE NPs in acidic pH (pH 5.5).

Step 1. Green Synthesis of Ag nanoparticles:

The silver nanoparticles (Ag NPs) were synthesized by the reduction of Ag^{+} ions to Ag^{0} from silver nitrate solution using polysaccharide fraction of (1→4) linked b-D-Xylofuranose as a reducing agent. During the reaction, (1→4) linked b-D-Xylofuranose-Ag complex are formed as an intermediate complex, which is then converted to reduced silver ions with lose of hydrogen in (1→4) linked b-D-Xylofuranose (Sukumaran Prabhu and Eldho K Poulose, 2012).

Step 2. Synthesis of CS-TPP complex:

Chitosan is used for drug delivery application in medical sciences. The abundance of free amino groups in chitosan makes it to bind easily with drug, peptide and/or protein. Chitosan film or membranes are formed with TPP as a cross-linking agent. Both H+ and multivalent tripolyphosphate ions are present in the acidic TPP solution and free amine groups on chitosan molecule will be protonated followed by cross-linking with negative charged multivalent TPP ions (Falguni Pati et al., 2011).

Step 3. Synthesis of CS -TPP-Ag NC complex:

Bio-synthesized Ag^{0} NPs have negative charge when cross-linked with amino groups of chitosan-TPP complex (Abdel-Mohsen et al., 2011).

Step:4. Synthesis of CS-TPP-Ag NC- mPEG complex:

mPEG has free amino group and is used as a porogen. The electrostatic interaction between the OH^{-} group of CS-TPP-Ag NP complex and amino group of mPEG leads to the formation of CS-TPP-Ag-mPEG complex with the removal of proton (Abdel-Mohsen et al., 2011).

Step 5. Synthesis of CS -TPP-Ag NP- mPEG complex:

Phycoerythrin consist of free negatively charged carboxylic group that interact with amino group of mPEG-chitosan-TPP-Ag complex while removing H^{+} ions from carboxylic group of Phycoerythrin. The synthesis of Phycoerythrin-mPEG-chitosan-TPP-AgNPs is favored by the

formation of amide bond between the primary amine groups of mPEG and the free carboxylic end group of Phycoerythrin.

References

1. Calvo, P., Remunan-Lopez, C., Vila-Jato, J. L., & Alonso, M. J. (1997). Novel hydrophilic chitosan-polyethylene oxide nanoparticles as protein carriers. *Journal of Applied Polymer Science*, *63*(1), 125-132.
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7. A.M. Abdel-Mohsen, R. Hrdina1 and A.S. Aly (2011). Novel method for the preparation of silver/chitosan-o-methoxy Polyethylene glycol coreshell nanoparticles. Advances in Chitin Sciences, Vol. XIII, pp 1-7.

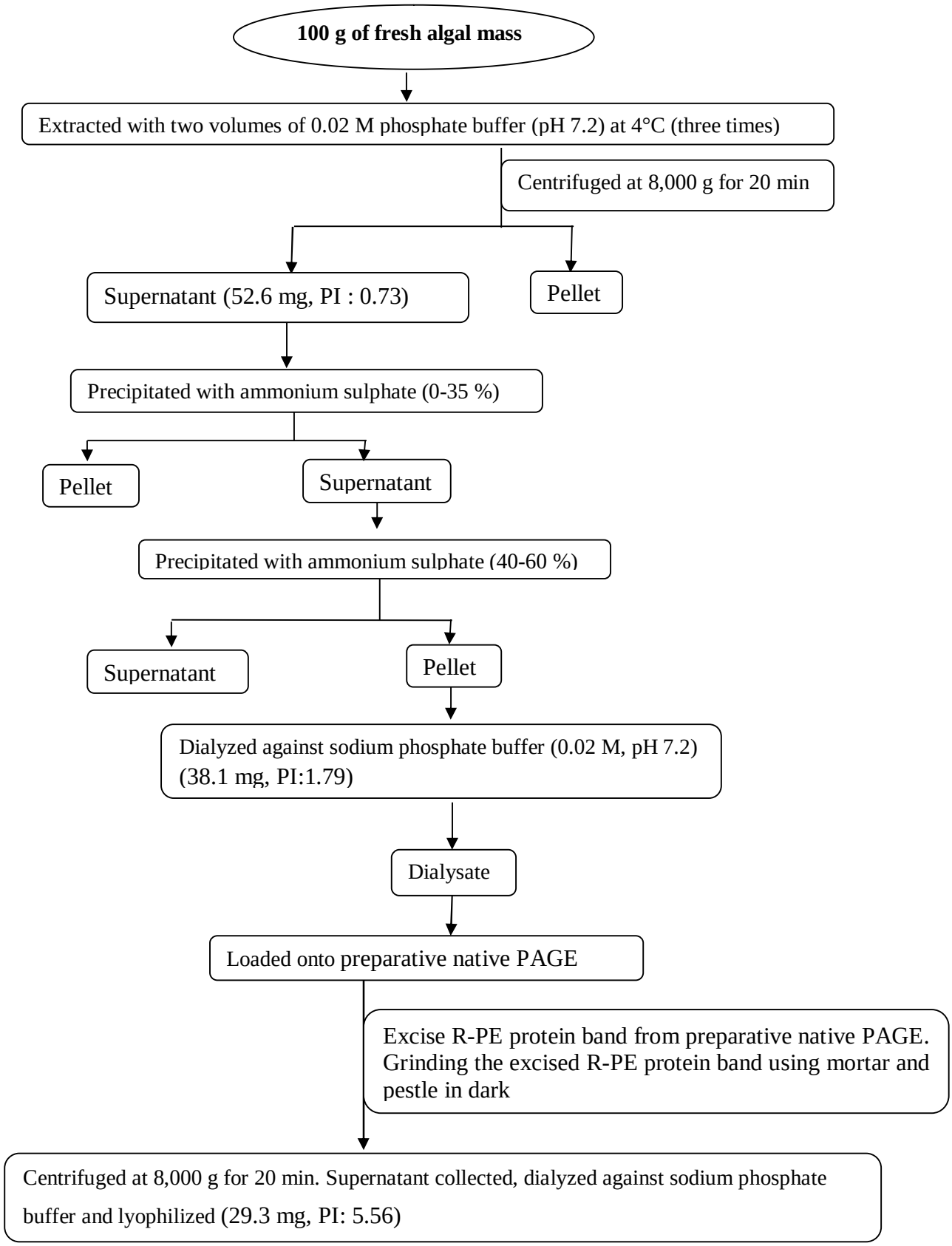


Figure S1. Steps involved in the extraction and purification of R-Phycoerythrin from *Solieria robusta*

PI: Purity index

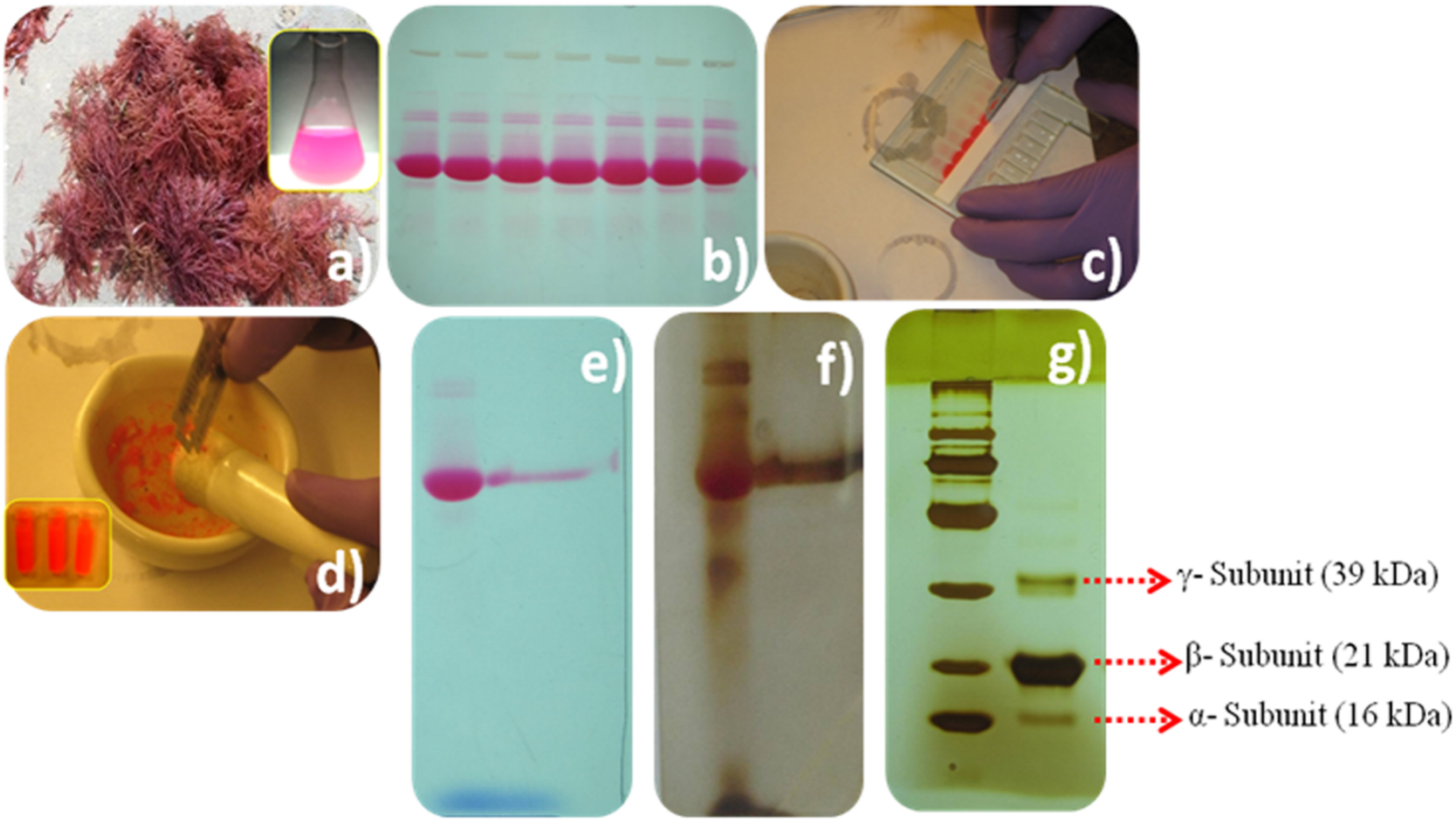


Figure S2. a) Fresh thallus of the red algae, *Solieria robusta* (**Inset figure-**crude Phycoerythrin solution)

b) Native PAGE showing R-Phycoerythrin (R-PE)

c) Excise R-PE protein band from preparative native PAGE.

d) Grinding the excised R-PE protein band using mortar and pestle in dark.

e) Unstained native PAGE showing crude and purified R-PE.

f) Silver stained native PAGE showing crude and purified R-PE.

g) Silver stained SDS PAGE showing crude and purified R-PE.

Table S1. Determination of spectrophotometric purity of R-PE from *Solieria robusta* at each stage of purification.

	Crude extract	Fractional precipitation with $(NH_4)_2SO_4$ (35-55% saturation)	Preparative native PAGE
A_{280}	2.534	1.577	0.521
A_{562}	1.852	2.827	2.899
Purity index	0.73	1.79	5.56
Total R-PE (mg)	52.6	38.1	29.3
Yield (%)	100	72.4	55.7
Total Protein (mg)	528.4	198	30.8
R-PE from total protein (%)	9.95	19.2	95.1
Impurities (%)	90.05	72.8	4.9

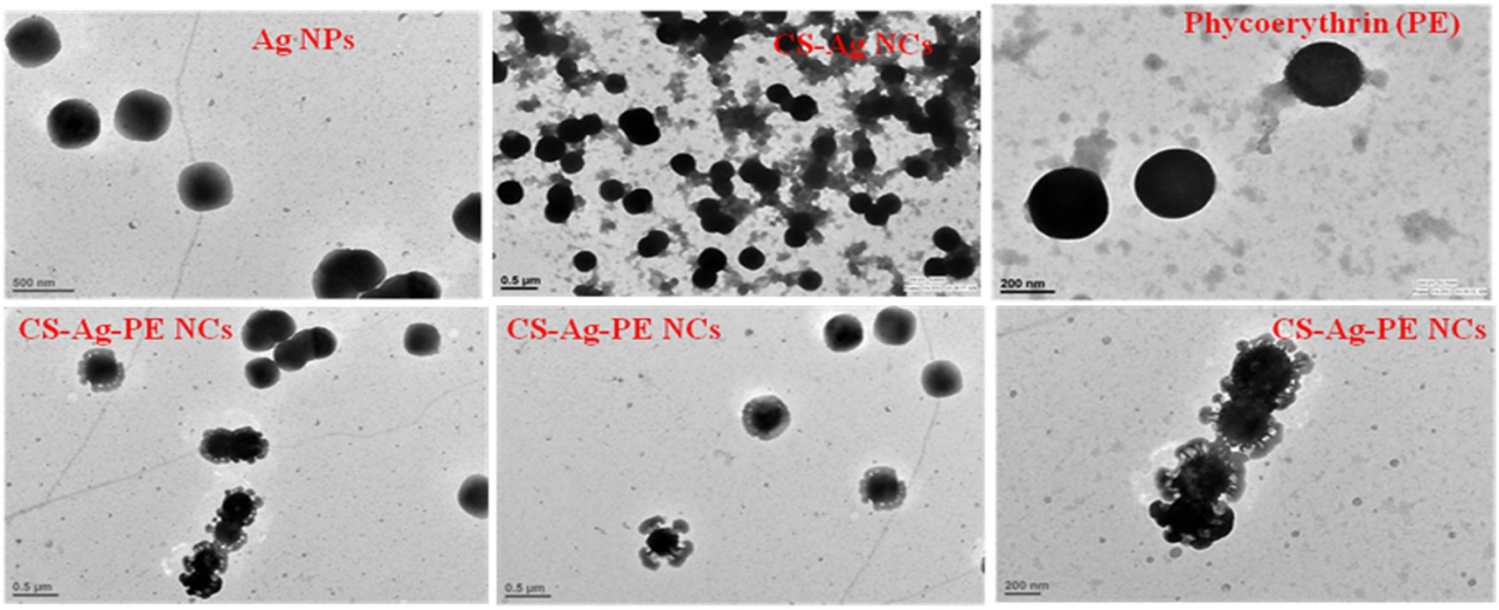


Figure S3. TEM images of the Phycoerythrin and synthesized nanocomposites.

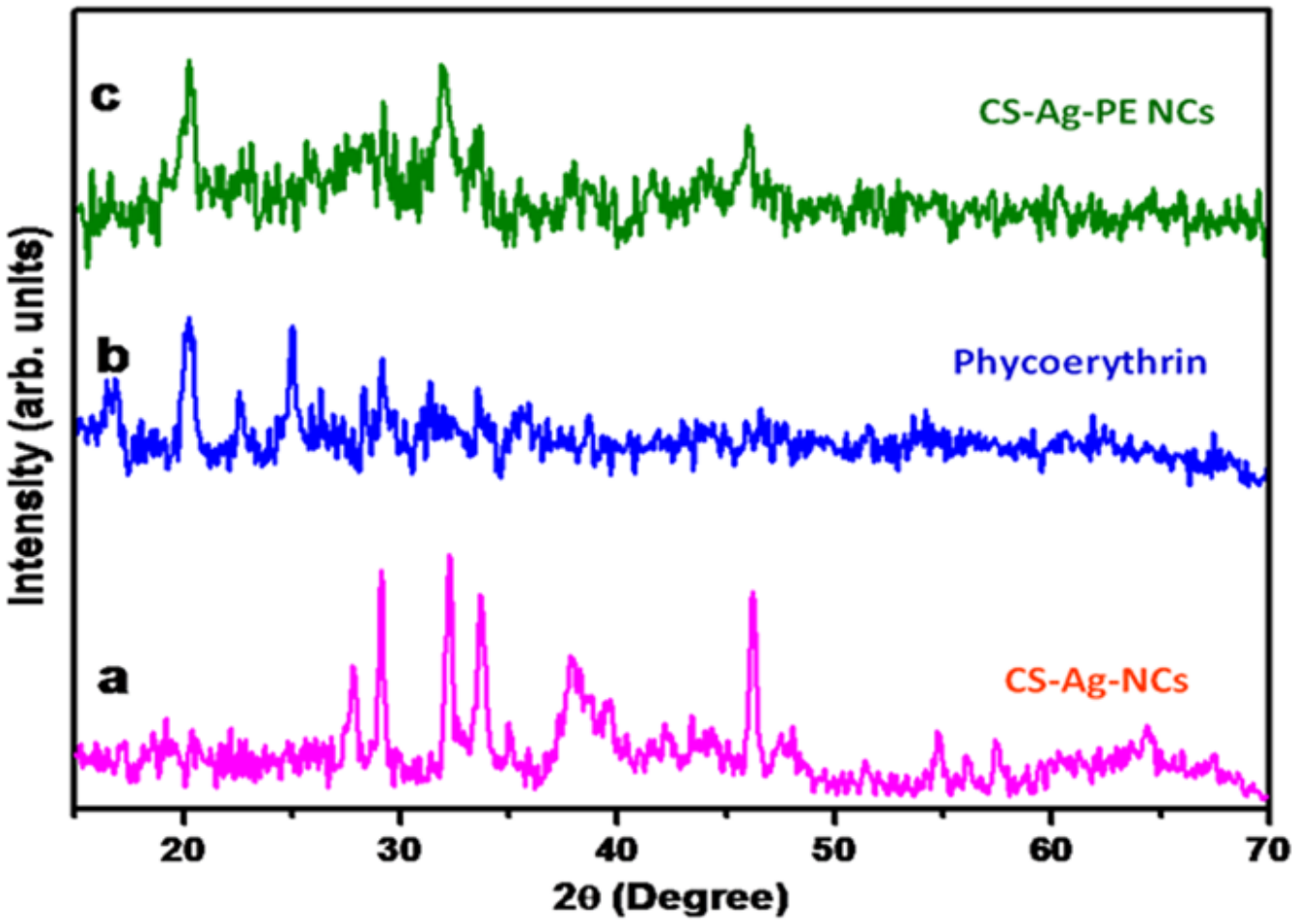


Figure S4. XRD patterns of phycoerythrin, CS-Ag NCs and CS-Ag-PE NCs.

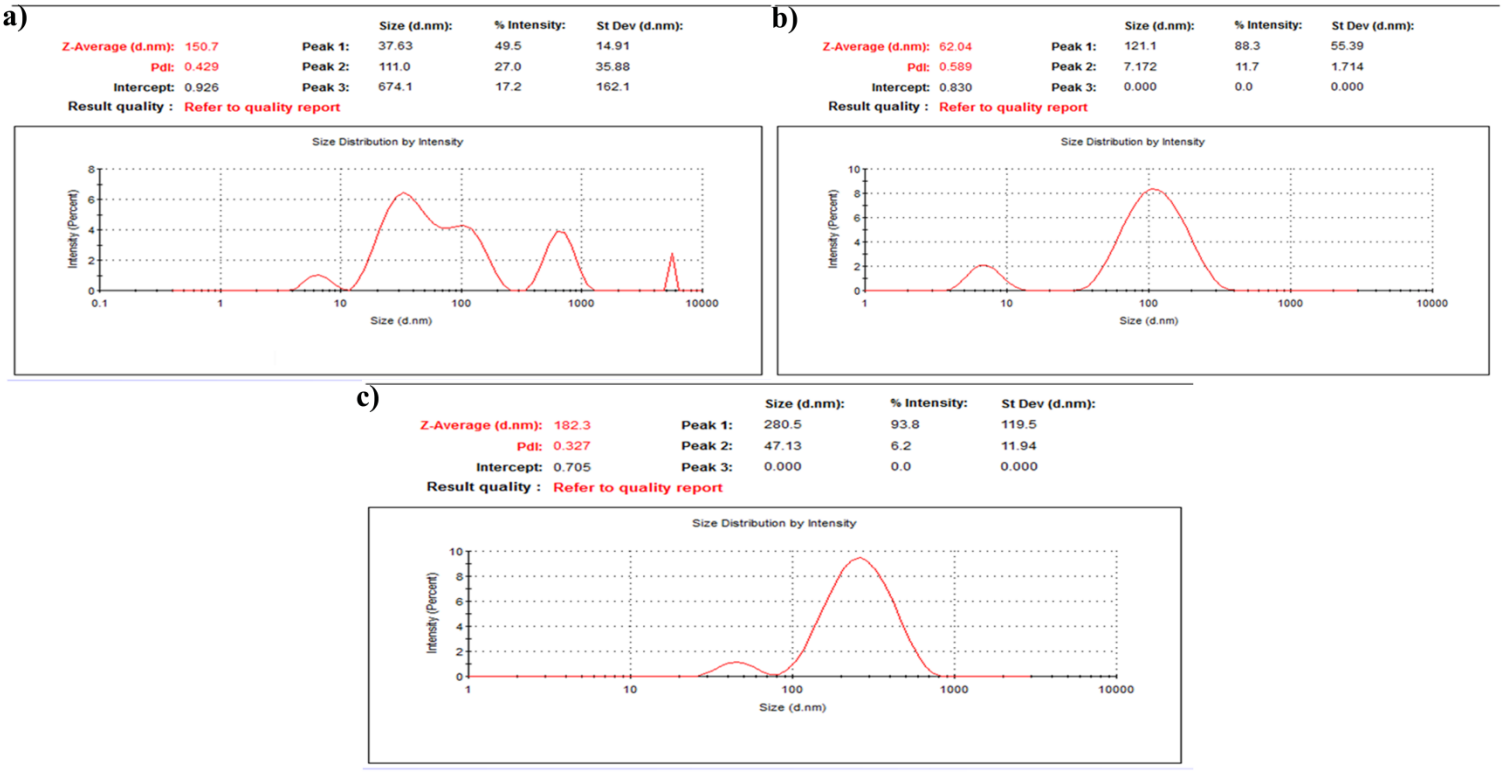


Figure S5. DLS analysis for particle size distribution of the nanocomposites **(a)** Phycoerythrin (PE) **(b)** CS-Ag NCs and **(c)** CS-Ag-PE NCs.

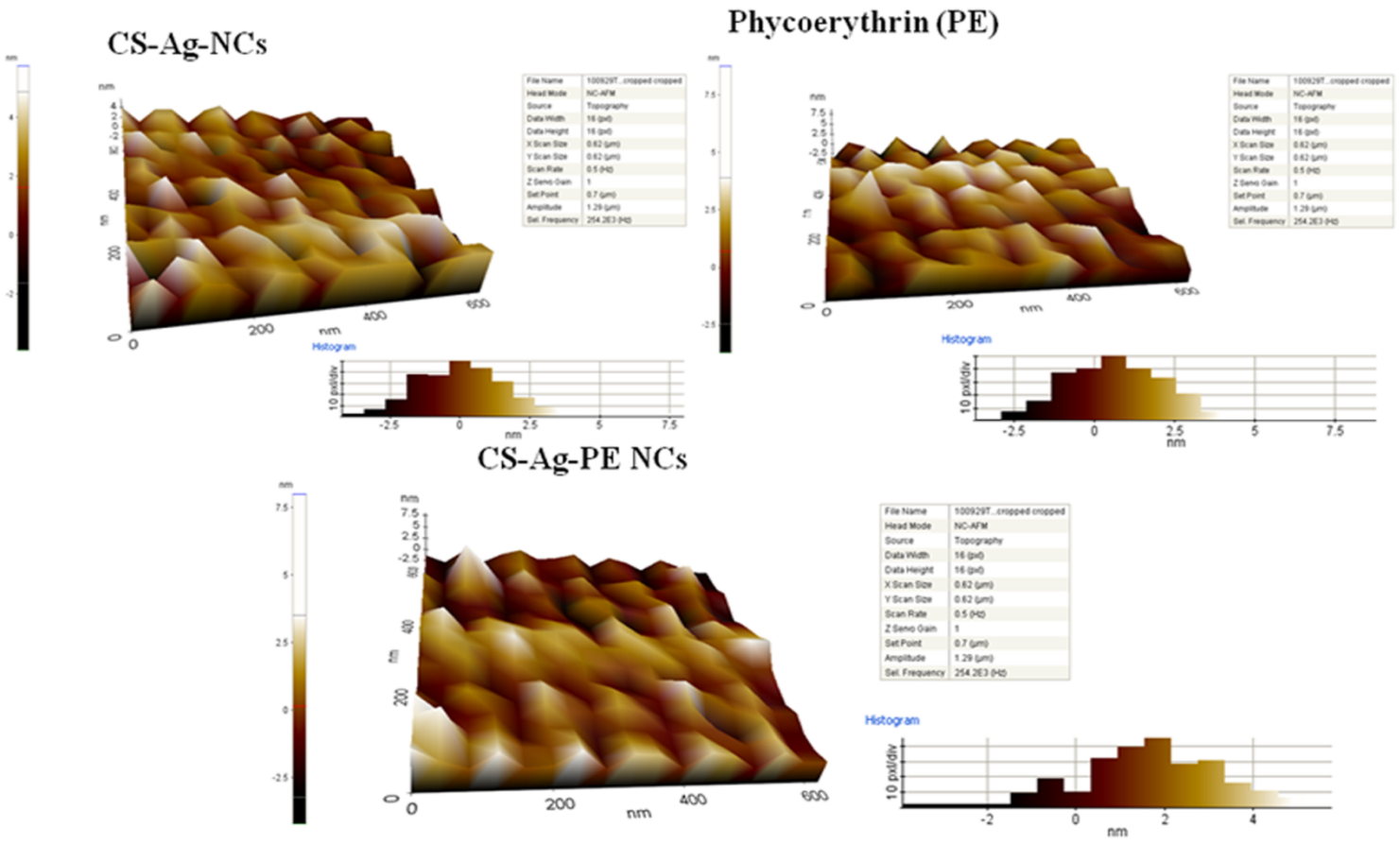


Figure S6. AFM Images of the PE and synthesized nanocomposites.

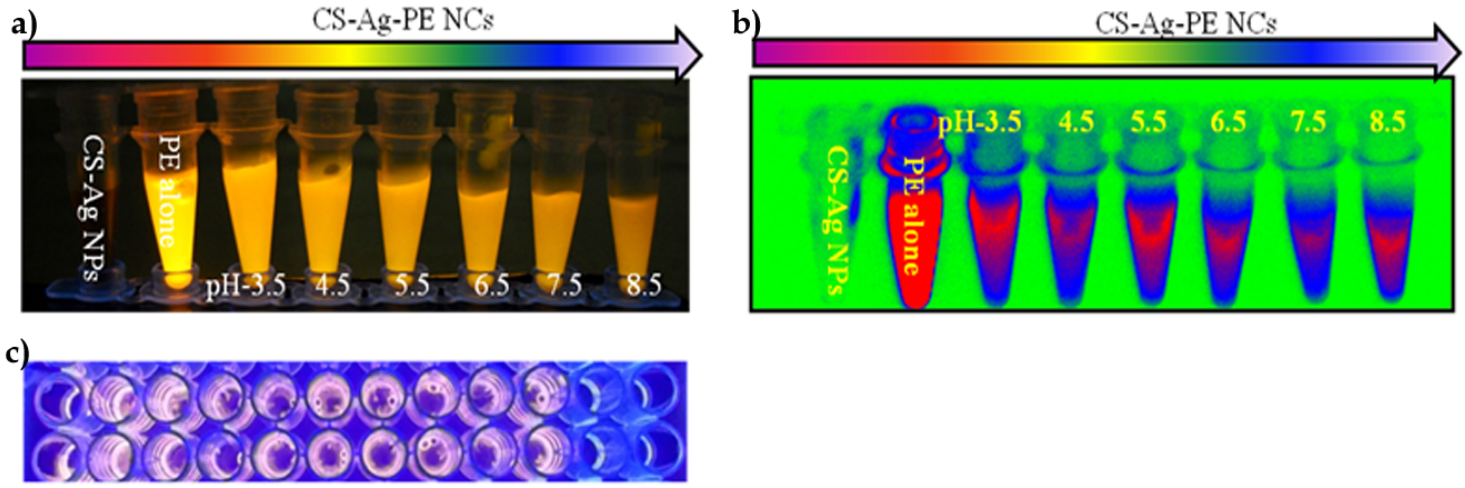


Figure S7. Synthesized nanocomposites emit fluorescence upon UV visualization (a, b) and fluorescence emission due to MDA-MB-231 cell uptake of CS-Ag-PE NCs with different concentration (c).

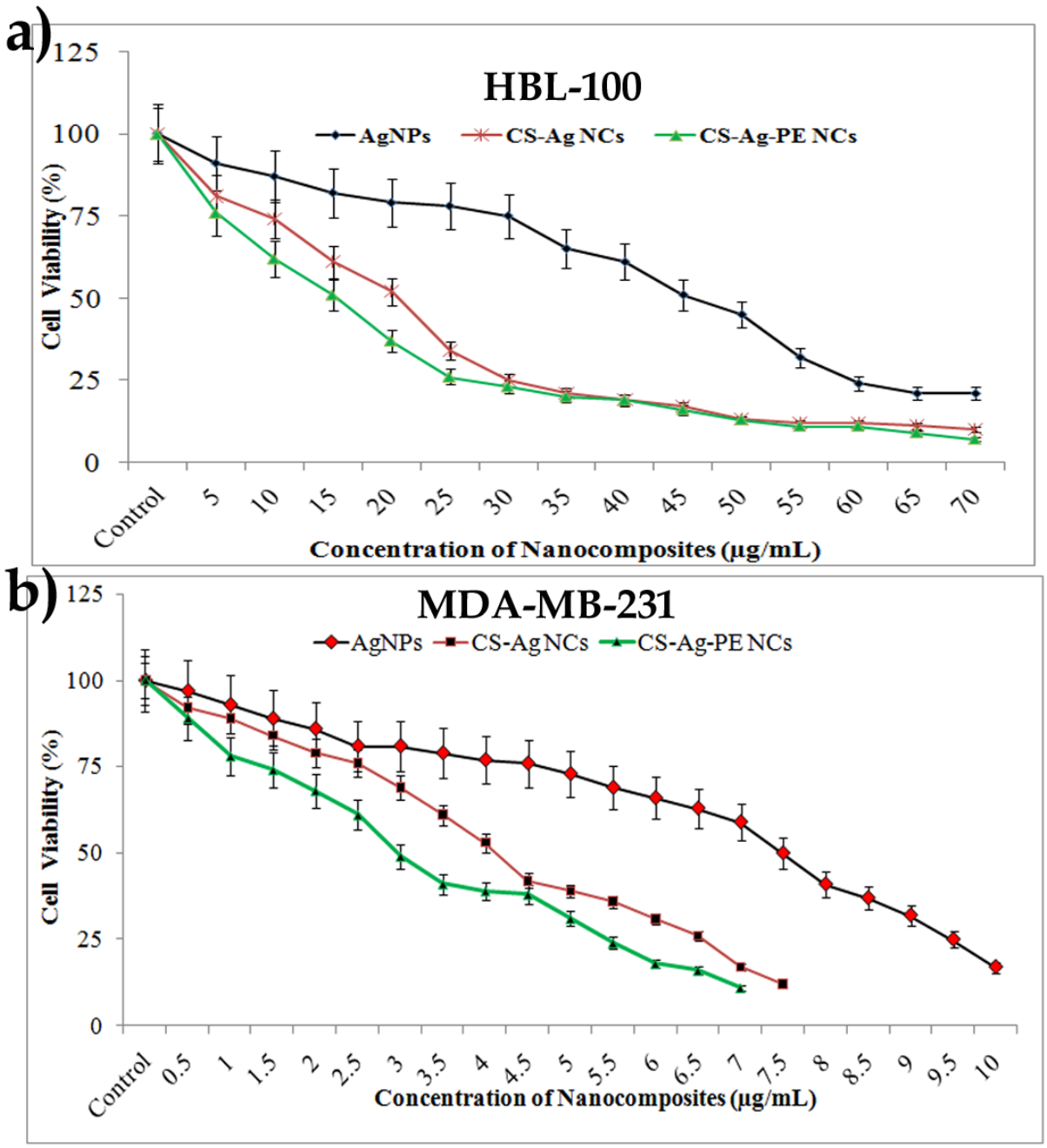
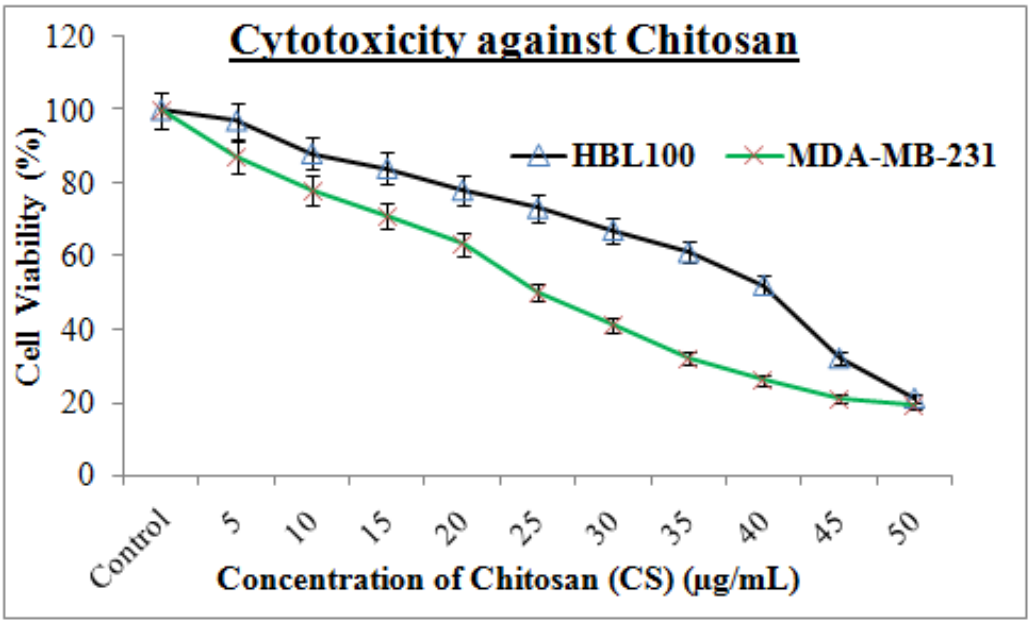


Figure S8. Viability (%) of (a) HBL-100 cells and (b) MDA-MB-231 cells treated with nanocomposites in 24 h.

a)



b)

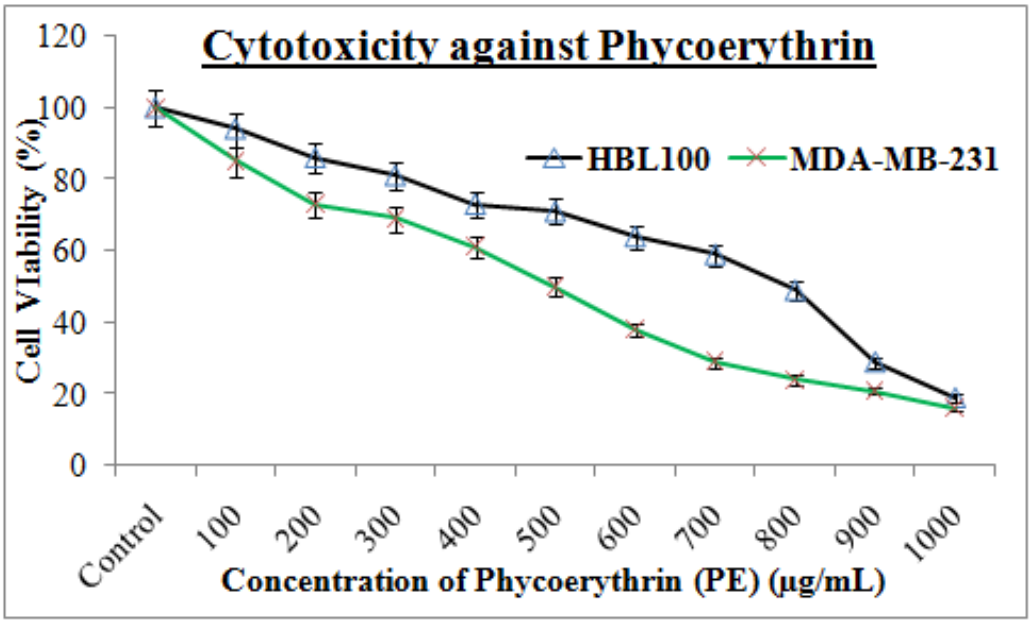


Figure S9. Viability (%) of cells treated with (a) Chitosan, (b) Phycoerythrin in 24 h. The figures show that Chitosan and Phycoerythrin are non toxic materials.