Electronic Supplementary Material (ESI) for RSC Advances.

PVA/PANI/rGO Ternary Electrospun Mats as Metal-Free Anti-Bacterial Substrates

Supplementary Information

Statistical Analysis of antibacterial property investigation

In order to depict the significance and the extent of influence from each factor on the antimicrobial properties, the main effect and interaction analyses was conducted on the data set. The main effect and interaction analyses between graphene content and treatment type (Fig. S1-a, and b), revealed that the high, 2 wt%, graphene content as well as the cross-link/acid doping treatment types were the most effective conditions in order to achieve reliable antibacterial property. The reason being is that via addition of graphene the mean value of scanned bacteria population was reduced by over 60%. Additionally, the main effect study of treatment type showed almost 30% overall improvement in antibacterial property by using cross-link/acid doping treatment compared to the thermal treatment method.

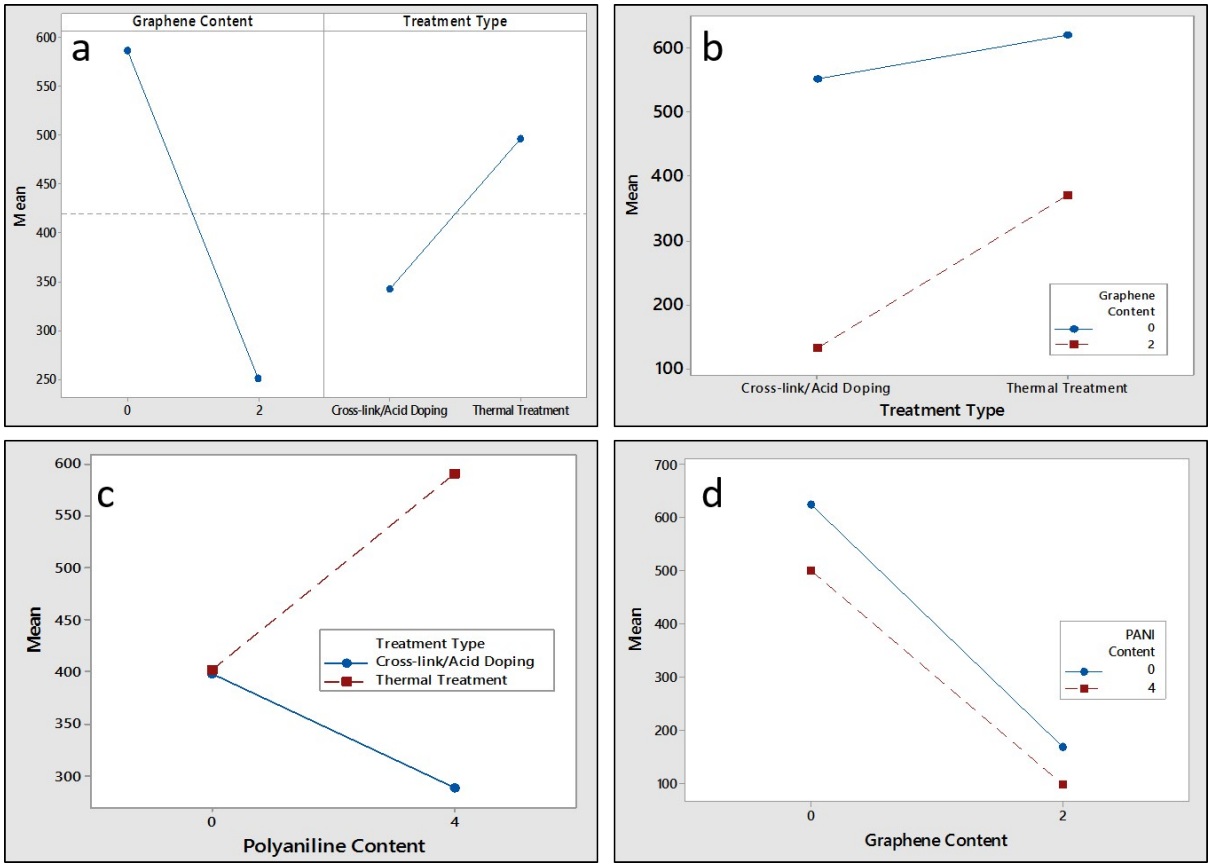

Figure S1 a) Main effect analysis, and b) interaction effect study of graphene content and treatment type, and interaction effect study on polyaniline content versus c) overall treatment type, and d) graphene content in cross-link/acid doped samples

After clarifying the best conditions in terms of graphene content, the polyaniline content effect was studied in interaction with the treatment type (Figure S1-c). The mean bacteria population was significantly lowered by using the cross-linking/acid doping method at the highest PANI of 4 wt%.

The interaction investigation among PANI and rGO content clarified their synergistic effect treated by HCl acid solution. The study shown in Figure S1-d showed that the specimen with highest amount of rGO and PANI loading successfully suppressed the bacteria culture expansion by 80%. The CG2P4 sample including 2 and 4 wt% rGO and PANI contents, respectively, benefited from both antibacterial mechanisms of additive materials. Thus the

mentioned trial showed the lowest average bacteria population of 98 mm^{-2} indicating success of preparation of antibacterial cross-linked/ acid doped hybrid nanocomposites with minimal additive material.

Scanning Electron Microscopy of Polyaniline Nanofibers.

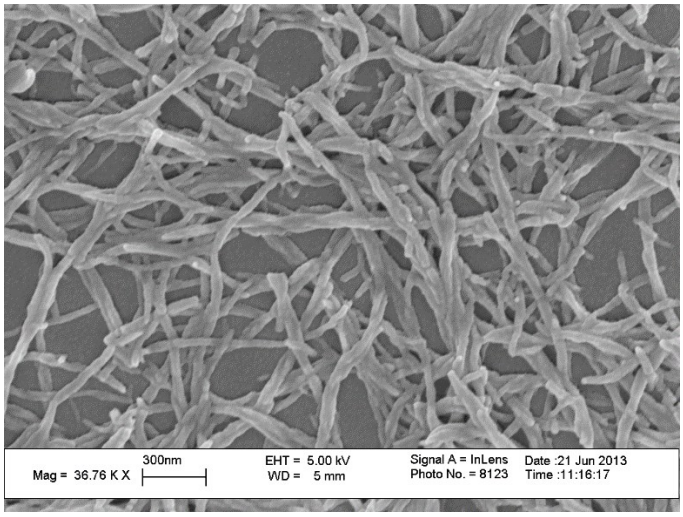

Figure S2 The SEM image of the PANI nanofibers.

As shown in the figure above, the synthesized PANI aspect ratio was over 40 (average length: 700 nm) indicating that formation of PANI was in nanofiber shape. The percolation network of PANI nanofibers can also be detected in the figure.

Rheological Behavior of Electrospinning Suspensions

Rotational Rheometry Based on the rotational rheometry analyses (Fig.1), the shear thinning behavior in all of the samples was observed where a decreasing trend of apparent viscosity with respect to shear rate increase was consistently recorded[14]. As described elsewhere[3c],the samples containing DMF as co-solvent and other additive materials (rGO and PANI in this case), had higher viscosity values compared to the pristine sample. This effect was found to be due to both the hydroxyl interactions among PVA's side groups and DMF solvent, which leads to

form a hydrogel structure among them, as well as the effect of high viscosity additive materials addition.

Additionally in order to have further insight on the relation between apparent viscosity and shear rate, a quantitative study was conducted via non-linear fitting of the power law model on the data set (Table 1). The least-square curve fitting method was used for this study. The Power law equation is known as the following:

$$\eta = K\gamma^{n-1} \text{(Eq. 1)}$$

Where η is the apparent viscosity, γ is the shear rate, K and n are the fluid consistency coefficient and non-Newtonian index, respectively. Considering the observed change in the fitted power law equation parameters, K and n values respectively, among the electrospinning suspensions, following results can be reported.

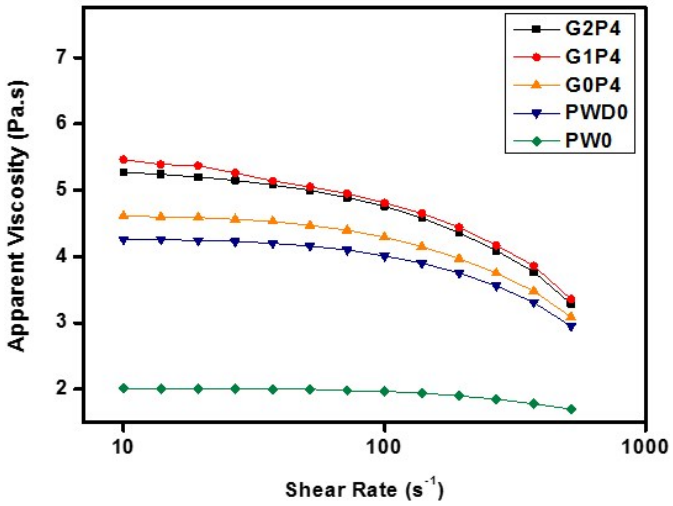

Figure S3. Apparent viscosity vs. shear rate of selected samples obtained via rotational viscometry analysis

Table 1 Power law parameters of selected samples calculated by curve-fitting on rotational viscometry results

Sample	K value	Non-newton index, n	Standard Error of Fitting
Neat (DI Water)	2.25	0.97	0.05
Neat (Water/DMF)	5.31	0.93	0.20
G0P4	5.86	0.92	0.23
G1P4	7.17	0.90	0.24
G2P4	6.92	0.91	0.26

Firstly, Newtonian behavior of pristine sample was confirmed as its relative n value was 0.97 concluding that the sample's viscosity was independent from shear rate. However, the mentioned equation parameter value started to decrease in the rest of samples by addition of DMF co-solvent and the additive materials, respectively. As a result, the deviation of suspension behavior from the Newtonian behavior was shown in the samples with added substances as there was a decreasing behavior of non-Newtonian Parameter, n, among them compared to the neat electrospinning suspension.

Secondly, by studying the increasing pattern of the K value from the neat PVA suspension towards multi-component samples, it can be seen that the viscosity of electrospinning suspensions containing additive materials would be higher than the neat one. This estimation was confirmed by the experimental results where the viscosity of rGO and PANI containing samples was at least two times-fold higher than the pristine PVA sample. This phenomenon

was the result of both hydrogel formation among PVA chains and DMF co-solvent as well as addition of ultra-high viscosity rGO nanosheets and PANI nanofibrous additive materials to the media.

As the suspension behavior of tri-component rGO/PANI/PVA samples deviated from Newtonian behavior and their respective viscosity was increased in comparison with the pristine PVA sample, this effect caused a drastic exacerbation of electrospinning process which resulted in formation of irregular morphologies in their relative as-spun electrospun mats.

Extensional Rheometry. The normalized diameter versus time diagram of tri-component samples (Fig.2–A), obtained via extensional viscometry, showed that through the set of experiments, with different material compositions, the suspension column breaking behavior followed the same behavior. As an index for suspension jet behavior in electrospinning process, the mentioned behavior showed that the prepared suspensions had a consistent behavior during the electrospinning.[3c]

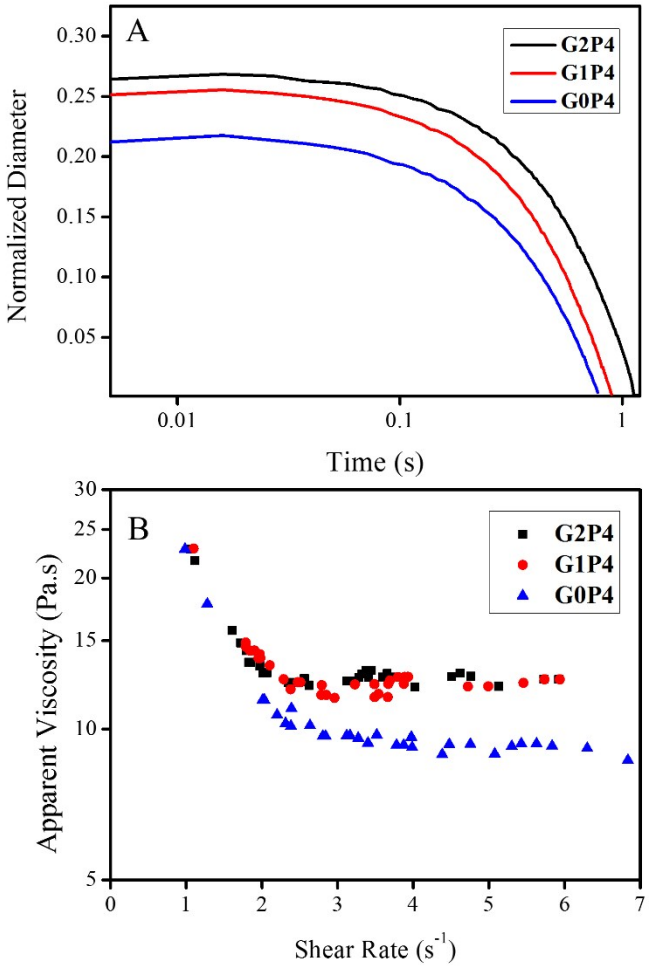

Figure S4 A) Normalized diameter vs time dependence, and B) Apparent viscosity vs. shear rate of selected samples obtained via extensional viscometry

Complemented by the rotational viscometry analyses results (Fig 2-B), it was shown that for tri-component samples by increasing the rGO content, during the extensional rheology studies an increasing trend in apparent viscosity with respect to strain rate for the mentioned samples was shown. Indicating that the effective dispersion of additive materials was achieved during their suspension preparation process. As it was reported before by this team[3c], for the suspensions containing DMF co-solvent and rGO nanosheets higher apparent viscosity values in comparison with pristine sample was recorded