Supplementary Material

Single-Step Fabrication of Polymer Nanocomposite Films

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**S1. Nanocomposite films with a low PVA solution concentration (C_p = 1/128 wt%)**

Figure S1 shows SEM cross-section images of a SiO_2–PVA nanocomposite film prepared in a single-step (Figure 1) using a low PVA concentration (C_p = 1/128 wt %) in the sprayed polymer solution and depositing for t = 4 min. Its average thickness (~370 nm, yellow arrows in Figure S1a) is as expected slightly thinner but similar to that of films prepared for same deposition duration where polymer solutions with higher C_p (1/16 and 1/32 wt %) are used (Figure 2). The planar surface seen in Figures S1a is identical to that obtained with higher C_p (Figure 2). Regardless of the low C_p of the sprayed polymer solution, the SiO_2 nanofiller (bright spots) is homogeneously distributed within the PVA matrix (Figure S1b) also in agreement with what is obtained in films where higher C_p is used (Figure 2).

Such films are expected to exhibit a filler content that is greater than 25 vol% as this is obtained already when more PVA (C_p = 1/32 wt %, Figure 2) is added. Such high filler loading with this small nanoparticle size (d_{SiO2} = 20 nm) is difficult to obtain [1] especially when homogeneity is demanded. The flexibility to add such high filler content significantly enhances the attractiveness of this already rapid and single-step fabrication.

![Figure S1](image.png)

**Figure S1.** SEM cross-section images of a SiO_2–PVA nanocomposite film prepared with a polymer solution containing C_p = 1/128 wt % PVA and depositing for t = 4 min on a glass substrate. Bright spots in a and b correspond to SiO_2 filler within the PVA matrix (light grey). Yellow arrows in a indicate the film thickness.
S2. Pure SiO$_2$ nanoparticle deposition

High versatility of single-step nanocomposite fabrication enables the preparation of pure nanoparticle films by spraying a polymer-free solution ($C_p = 0$ wt %) during nanoparticle deposition. Figure S2 shows SEM cross-section images of such a film at different magnifications prepared with SiO$_2$ nanoparticles ($t = 4$ min, $C_f = 0.25$ M). These films exhibit a rougher topography (Figure S2a) due to nanoparticle agglomerates protruding from its surface. Such a protrusion is enlarged in Figure S2c. There one can see the nanoparticulate features covering its surface. Their dimensions are in agreement with the expected nanoparticle size ($d_{SiO2} = 20$ nm).

These films exhibit a compact morphology where individual nanoparticles within the bulk film cannot be recognized. This contrasts starkly to the SiO$_2$–PVA nanocomposites (Figure 2 and Figure S1) where individual nanoparticles are seen throughout the entire film cross-section. The compact film morphology also differs substantially from the highly porous ones obtained during regular flame aerosol deposition [2].

![Figure S2. SEM cross-section images of a pure SiO$_2$ nanoparticle film prepared with a polymer-free PVA solution ($C_p = 0$ wt %) and depositing for $t = 4$ min. The topography is much rougher (a) due to protrusions (c) from its surface. The compact film morphology can be seen in b. The yellow arrows in a and b indicate the film thickness.](image-url)
S3. Theoretical nanocomposite film thickness

Changing the filler content in SiO$_2$–PVA nanocomposites by only varying the polymer solution concentration $C_p$ (i.e. identical flame synthesis precursor concentration $C_f$ and deposition duration $t$) leads to a constant total amount of deposited/incorporated nanoparticles (i.e. $m_{SiO_2} = \text{constant}$) but unavoidably alters the resulting film thickness (higher filler loading for lower $C_p$ of polymer solution).

Figure S3 shows the theoretical PVA nanocomposite thickness as a function of filler content (red line) for a film exhibiting $m_{SiO_2} = 0.115$ mg of SiO$_2$ and covering an area of $A_{NC} = 4 \text{ cm}^2$. This film thickness does not scale linearly with filler content. It changes drastically for <25 vol % nanoparticles. At higher loading this change becomes increasingly smaller until a compact SiO$_2$ layer is obtained (i.e. 100 vol %).

Experimentally derived values for SiO$_2$–PVA nanocomposites (circles) prepared with $C_p = 1/8$ and 1/32 wt % and depositing for $t = 4 \text{ min}$ (Figure 2c,e) are in good agreement with the theoretical trend. This indicates that the amount of SiO$_2$ filler depositing on the substrate is independent of added PVA. As a result, once the SiO$_2$ deposition rate (here: $\sim 7.2 \mu\text{g} \cdot \text{cm}^{-1} \cdot \text{min}^{-1}$) is determined, one is able to quickly predict the filler loading solely from the nanocomposite film thickness and deposition duration $t$.

![Figure S3](image)

**Figure S3.** The non-linear correlation of theoretical film thickness (red line) as a function of filler content for PVA nanocomposite films containing identical amount of SiO$_2$ nanoparticles ($m_{SiO_2} = 0.115$ mg = constant) and covering the same area ($A_{NC} = 4 \text{ cm}^2 = \text{constant}$). The thickness changes less at high filler content agreeing well with experimental measurements (circles) shown in Figure 2.
S4. Filler-free polymer deposition

Single-step fabrication of polymer nanocomposites (Figure 1) is capable of achieving agglomerate-free films with extreme variability of filler content. It is easily tuned by (1) increasing polymer solution concentration \( C_p \), (2) its feed-rate or (3) the rate at which nanoparticles are synthesized. On the one extreme, filler-free polymers can be prepared by either employing a particle-free flame or eliminating the flame altogether. Figures S4 shows SEM cross-section images of pure PVA films prepared on glass substrates with a particle-free flame. The deposition duration \( t \) is identical (2 min) for all three images whereas the polymer solution concentration \( C_p \) is varied between 1/8 (Figure S4a), 1/16 (Figure S4b) and 1/32 wt % (Figure S4c).

![Figure S4](image)

Figure S4. Filler-free PVA films prepared with a polymer solution concentration \( C_p =1/8 \) (a), 1/16 (b) and 1/32 wt % (c) exhibit an uneven surface topography. The yellow arrows indicate the strong variation in film thickness. The deposition duration \( t = 2 \) min) is same for all films. The scale bar shown in c is identical for all images.

In contrast to nanocomposites with filler (Figure 2-4, Figures S1), these exhibit a less planar surface topography for all \( C_p \). In fact, there even are areas where PVA does not cover the substrate. More planar film surface obtained with nanoparticle addition (Figure 2) stems from the surface wetting induced by nanoparticles [3]. Nevertheless, optimization of the fabrication by adjusting the substrate temperature or eliminating the particle-free flame may
improve the film formation for pure polymers [4]. Alternatively, the deposition can be carried out on a vibration-assisted substrate as this has shown efficacy for preparing homogeneous polymer films with and without fillers [5].
S5. References

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