Supplementary Material (ESI) for Soft Matter

SUPPORTING INFORMATION

An Elegant and Facile Single-Step UV-curing Approach to Surface Nano-Silvering of Polymer Composites

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Materials. The reactive formulation for the preparation of conducting polymer composite membrane was based on a dimethacrylic monomer: bisphenol A ethoxylate (15 EO/phenol) dimethacrylate (BEMA, average M_n = 1700, Aldrich). The photo-initiator was 2-hydroxy-2-methyl-1-phenyl-1-propanon (Darocur 1173, Ciba Specialty Chemicals). Silver nitrate ($AgNO_3$, 99.5 %), methanol (CH_3OH, 99.8 %) and pyrrole (C_4H_5N, ≥ 98 %) from Aldrich were used as such.

Photo-polymerization procedure. A 50 % (v/v) CH_3OH + H_2O mixture enabled the dissolution of silver nitrate & pyrrole and homogenized the mixture with BEMA and initiator. Mixtures of the compositions given in Table 1 were poured into polypropylene moulds and then exposed to UV-irradiation for 6 minutes in 2 steps, each of 3 minutes. The photochemical curing was performed by using a medium vapour pressure Hg UV lamp (Helios Italquartz, Italy), with a radiation intensity on the surface of the sample of 28±2 mW cm^{-2}. For this process, the samples were held under a pure N_2 atmosphere in small sealed boxes equipped with a quartz window. Free films were later obtained by peeling them from the moulds. These conditions assure maximum curing (disappearance of the methacrylic double bonds, checked by FT-IR).[a]

Discussion. Silver has numerous applications in its different forms and matrices.[b-n] Our characterization was directed towards application of polymers with conducting surfaces in organic electronics along the lines of Southward and co-workers.[n] With respect to the existing reported findings, we have introduced a novel application of an industrially well-established process (i.e., free-radical photo-polymerisation, UV curing) to obtain conducting surfaces on a different substrate material (i.e., methacrylate). The process is rapid, versatile and can be easily extended to other metals and/or polymer matrixes. This opens up a new area for further research in such soft, flexible conducting composite materials.

Though formation of Ag particles with oxidative polymerization is well known, the novelty of the work described lies in its amalgamation with a photo cross-linked insulating polymer to obtain a conducting surface. Polymeric films with conducting surfaces are of importance in antistatic coatings and organic electronics. The phenomenon of obtaining surface silvered polymer films from a reactive broth is interesting and intriguing.

After thorough investigations, we found out that a 2:1 mole ratio of pyrrole to silver nitrate is sufficient to reduce all the silver ions to metallic form, which subsequently decreases the resistance of the sample E (compared to D). Film F, of course, demonstrates lower resistance than E by about 40 ohms, but it has twice the amount of silver as in sample E. This means, a 100 % increase of silver nitrate in the formulation leads to a decrease in resistance by about 25 % which is not very substantial as the drop is from 150 to 110 ohms. Our purpose in the present work was to obtain a sufficiently conducting surface with minimum amounts of silver and pyrrole. Hence, we consider 2:1 as optimum ratio.

The conducting surface with Ag nanoparticles is developed from the liquid reactive mixture upon UV irradiation. There, a migration phenomenon was observed due to which there is an accumulation of silver metal particles and polypyrrole towards the surface. This is an interesting and new observation unreported hitherto. Though it is not clear at the present stage as to how & why the “migration” happens, a plausible explanation has been provided for this on the manuscript.

SEM-EDX experiments. Morphological characterization of the films was performed employing a FEI Quanta Inspect 200LV Scanning Electron Microscope (max magnification of 1.5×10^5) equipped with an EDAX Genesis system with SUTW detector.

The surface of sample A is shown in Figure S1(a) in which it is clearly evident that without pyrrole the reduction of silver (i.e., the formation of silver nanoparticles at the surface) is very limited. Figure S1(b) shows the recrystallization of unreacted $AgNO_3$ due the lack of reductant (pyrrole). Similar structures were found in sample D, but to a much lesser extent, due to incomplete reaction.

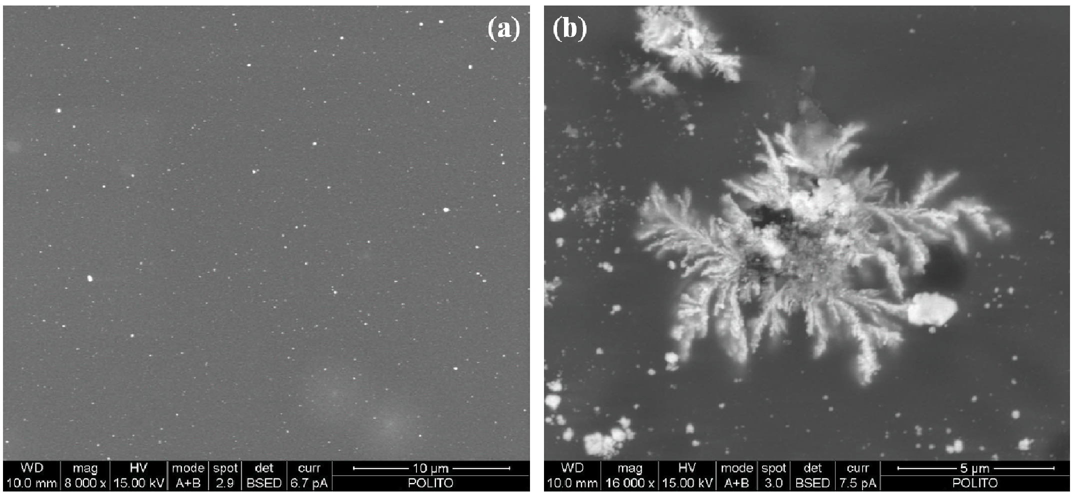

Figure S1. (a) Surface of film A, (b) recrystallized $AgNO_3$ in film A.

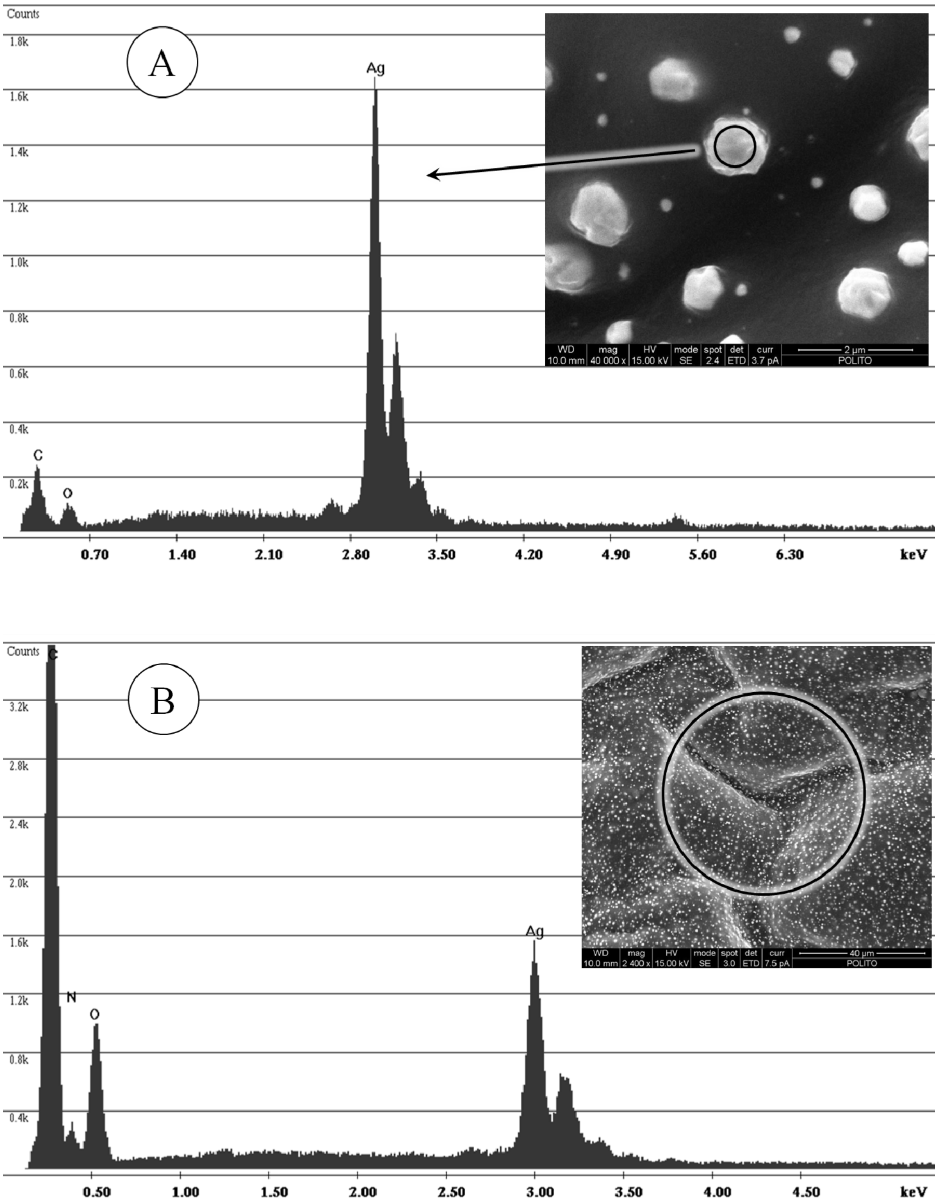

Figure S2. SEM-EDX analysis on sample E: (a) EDX spectrum of film surface (b) EDX spectrum focused on a silver agglomerate. Insets show the corresponding SEM micrographs.

STM experiments. A Rasterscope 3000 instrument from Danish Micro Engineering (DME) was used to map the topography and current density of sample E. Scanning area: 6.3µm × 6.3µm. Number of points for topography: 256 × 256. Number of points for spectroscopy: 64 × 64. Tunnel current used: 1.0 nA. Bias voltage for topography: 0.20 V. I-

V curves measured between – 0.2 V and + 0.2 V, but saturation of the current amplifier occurs at ±5.0 nA.

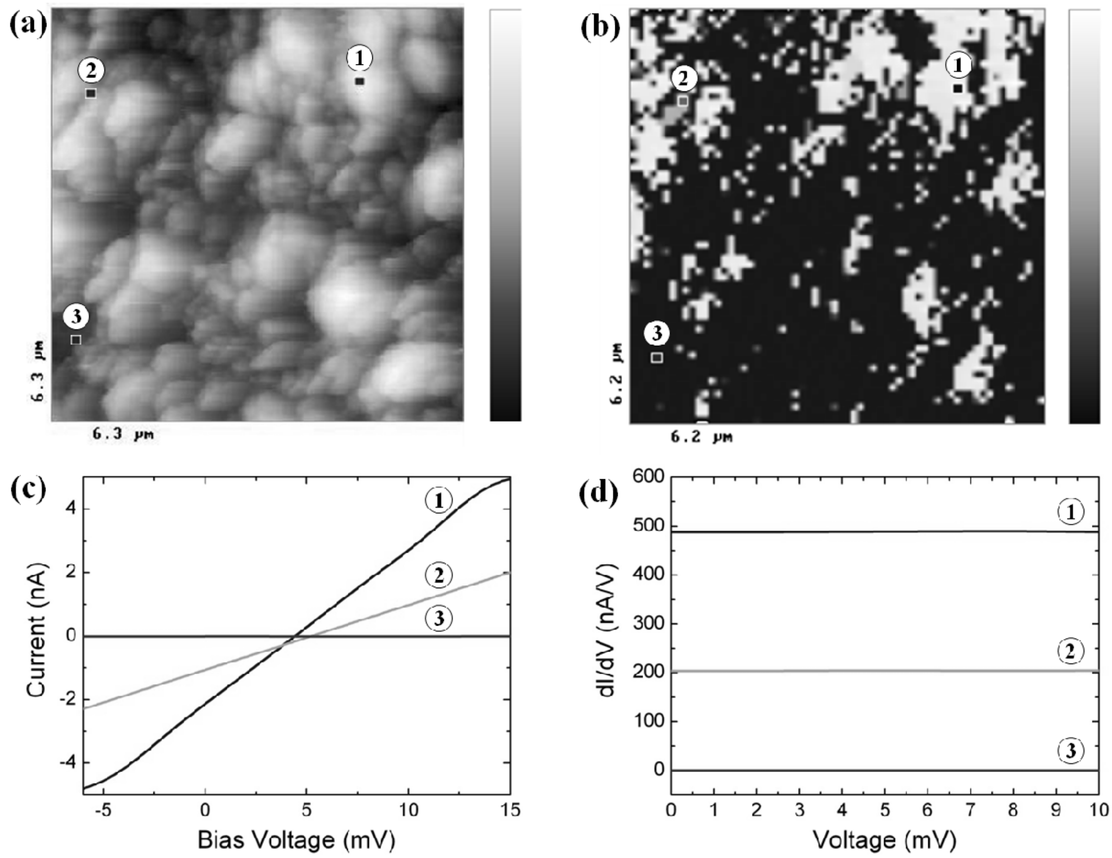

Figure S3. Scanning Tunneling Microscopy analysis of sample E; in the images, the lighter areas represent the regions with higher conductivity. (a) Topographic image, (b) current density image, (c) average of 20 I-V curves obtained by Scanning Tunneling Spectroscopy on the three kinds of areas with different conductivities at 20 different points each. Line (1) corresponds to the average of very high conducting regions, line (2) corresponds to the areas with lower conductivity and line (3) corresponds to the areas which have no conductivity at all. (d) Derivative plot of I-V curves reported in (c).

The similarity between the average I-V curves reported above and the single point I-V curves shown in Figs. 2(c,d) indicates a high reproducibility of the measurements. The present Figs. S3 (c, d) are not same as Figs. 2(c, d) reported in the manuscript, but similar. In fact, Fig. 2 refers to 3 individual points, while Fig. S3 refers to average of 20 such points. The close similarity in fact, attests the high reproducibility of the measurements, and this is also explained in the main manuscript.

The purpose of STM study was not only to "see" Ag particles, but also to have a deeper understanding of the surface conductivity. In fact, Scanning Tunnelling Spectroscopy (STS) revealed the presence of microscopic domains of varying conductivities, and this is discussed on the manuscript.

Electrical measurements. The surface resistances of the films were measured by a FLUKE 77 Multimeter with constant pressure spring loaded gold-plated pin probes (spring force 1.26 N, contact resistance 50 mΩ, P25-0822 Flat Head, Harwin). There was a fixed distance of 1.0 cm between the probes, and measurements were made at 6 different points on the surface of the films. The same probes were also used to record I-V curves over the range of ± 1.0 V with a CHI 760 D Electrochemical Work station, at ambient temperature. The results obtained for sample E at four different points on the surface are shown in Figure S3.

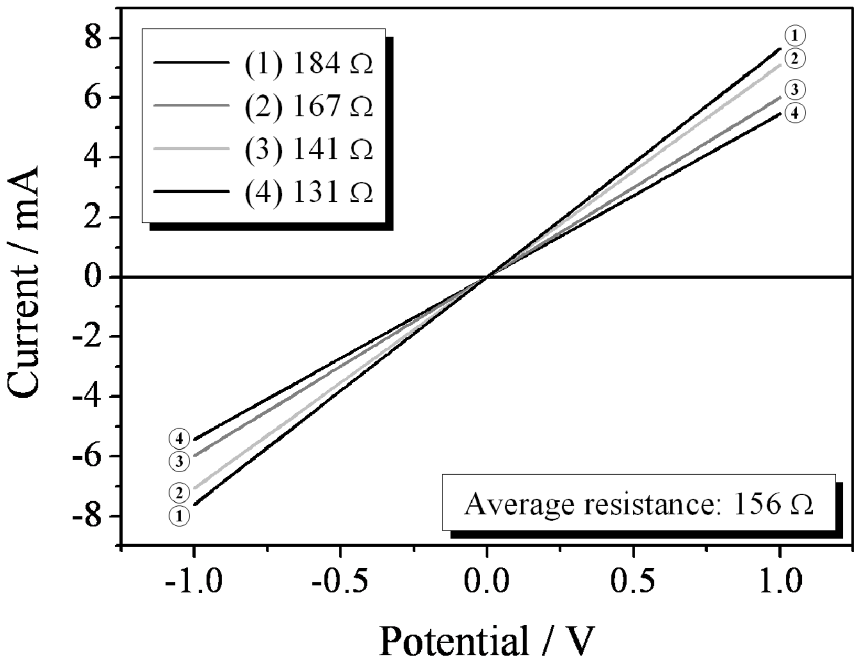

Figure S4. Current-voltage (I-V) plots at four different locations on the surface of film E.

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