

Supporting information:

Transparent, Luminescent, Antibacterial and Patternable Film Forming Composites of Graphene Oxide/Reduced Graphene Oxide

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Supporting information S1

a) Pre-oxidation of graphite

In a 250 mL beaker, concentrated H_2SO_4 (25 mL), 5 g of $\text{K}_2\text{S}_2\text{O}_8$ and 5 g of P_2O_5 were taken and heated to 90 °C with constant stirring. After all the reactants were completely dissolved, the reaction temperature was decreased to 80 °C. To this reaction mixture, 6 g of graphite powder was added slowly. Bubbling was observed initially and subsided subsequently, over a period of 30 min. Temperature of the reaction mixture was maintained at 80 °C for 5 h. Heating was stopped and the mixture was diluted with 1 L of distilled water and left undisturbed overnight. The resultant solution was then filtered and washed to remove excess acid. The solid product was dried in air overnight.

b) Oxidation to graphite oxide (GO)

230 mL of concentrated H_2SO_4 was maintained at 0 °C using an ice bath. Pre-oxidized graphite was then added to this and stirred. 15 g of KMnO_4 was added slowly making sure that the temperature never went beyond 10 °C. Then, the temperature was raised to 35 °C and allowed to react for 2 h. Subsequently, 1 L of distilled water was added carefully keeping the temperature below 50 °C. The reaction mixture was again stirred for 2 more hours and then 1.5 L of distilled water and 25 mL of 30% H_2O_2 were added. The mixture was kept at room temperature for a day and the supernatant was decanted. The remaining solution was centrifuged and washed with 10% HCl followed by distilled water. This was repeated several times. The resultant solid was dried and 2 % (w/w) dispersion was prepared in distilled water. This dispersion was put for dialysis for 3 weeks to remove all unwanted contaminants like salts and acid. Then the dispersion was diluted to 0.1 % (w/w).

c) Hydrothermal deoxygenation of graphene oxide (GO) to reduced graphene oxide nanosheets

Reduction of GO was done by the hydrothermal method. In a typical synthesis procedure, GO was sonicated for 45 min. (CREST TRU-SWEEP 27D, 50 Hz) to exfoliate the suspension completely and centrifuged at 5000 rpm to remove the unexfoliated GO. About 50 mL of the purified exfoliated GO solution (0.05 wt %) was transferred to a Teflon-lined hydrothermal reaction vessel and heated at 180 °C for 6 h. After 6 h, the vessel was cooled to room temperature. A black precipitate of RGO settles at the bottom. This was redispersed in distilled water by mild sonication. This sample will be referred to as purified reduced graphene oxide sheets (RGO).

d) Sulfonation of RGO

To increase the stability of graphene in water, sulfonic acid groups were introduced onto RGO surface through a simple sulfonation procedure. 20 mg sulfanilic acid and 8 mg sodium nitrite were firstly dissolved in NaOH solution (0.25%). Then 4 mL, 0.1 M HCl was added to the above mixture and kept in an ice bath under stirring. After 15 min, the aryl diazonium salt solution was added to 20 mL, 0.5 mg/mL RGO dispersion with continuous stirring for 2 h in an ice bath. After 2 h, the solution was filtered and washed and redispersed in distilled water with a final concentration of 0.05 wt %. The pH of the solution was measured to be around 6.

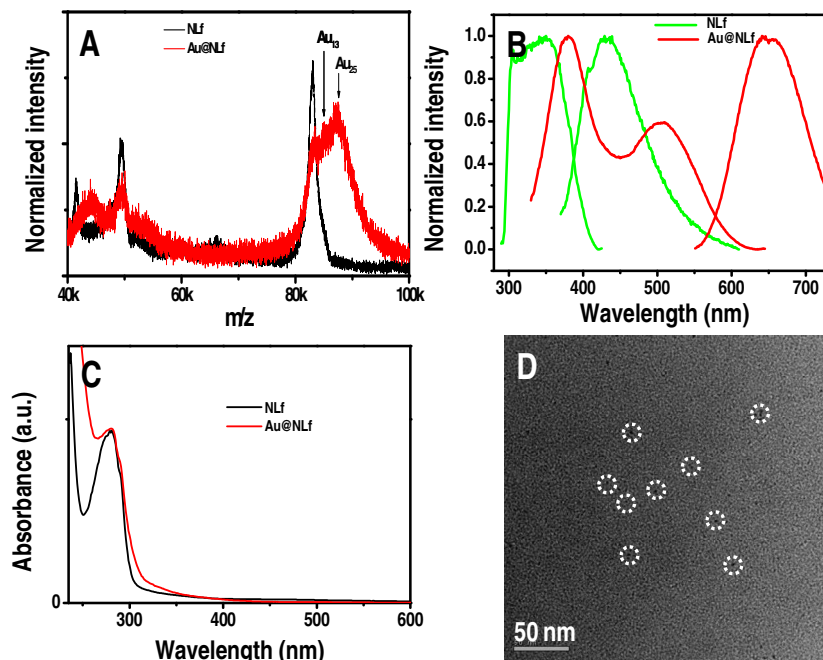


Figure S2. A) MALDI mass spectrum of Nlf and Au@Nlf. B) photoluminescence spectra Nlf and Au@Nlf, C) UV/Vis spectra of the evolution of clusters, Nlf and Au@Nlf and D) TEM image of Au@Nlf. Due to the small size, clusters are not clearly visible. Some clusters are marked by white dotted circles.

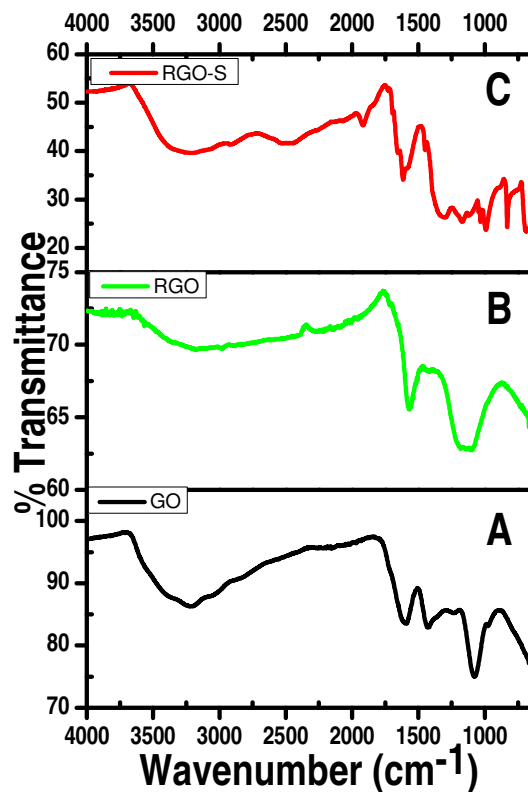


Figure S3. IR spectra of A) GO, B) RGO, and C) sulfonated RGO.

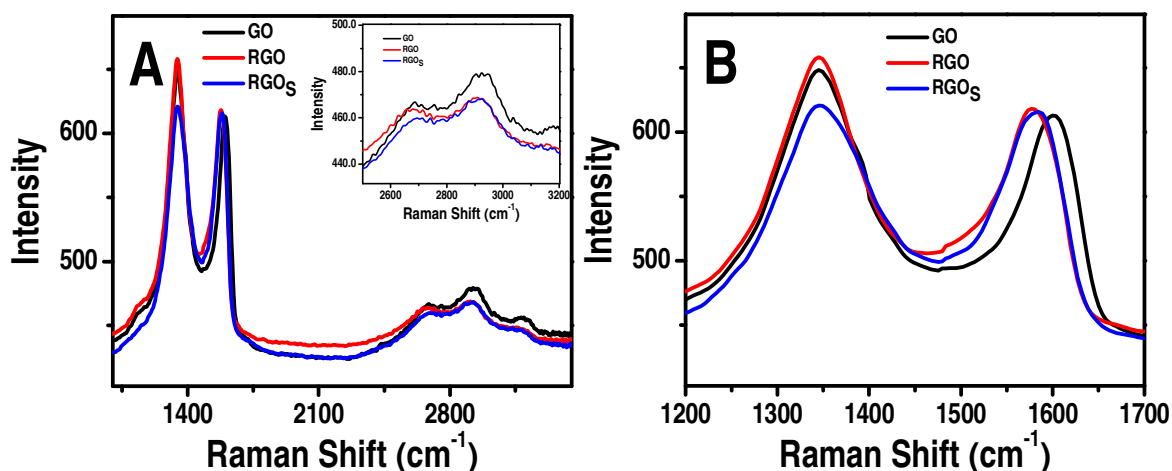


Figure S4. Raman Spectra of GO, RGO, RGO_s. A) Full range spectra from 1000 cm^{-1} to 3400 cm^{-1} . B) Enlarged portion showing the D and G band and corresponding shift. Inset in A shows the enlarged view of region from 2500- 3200 cm^{-1} showing the low intense 2D band.

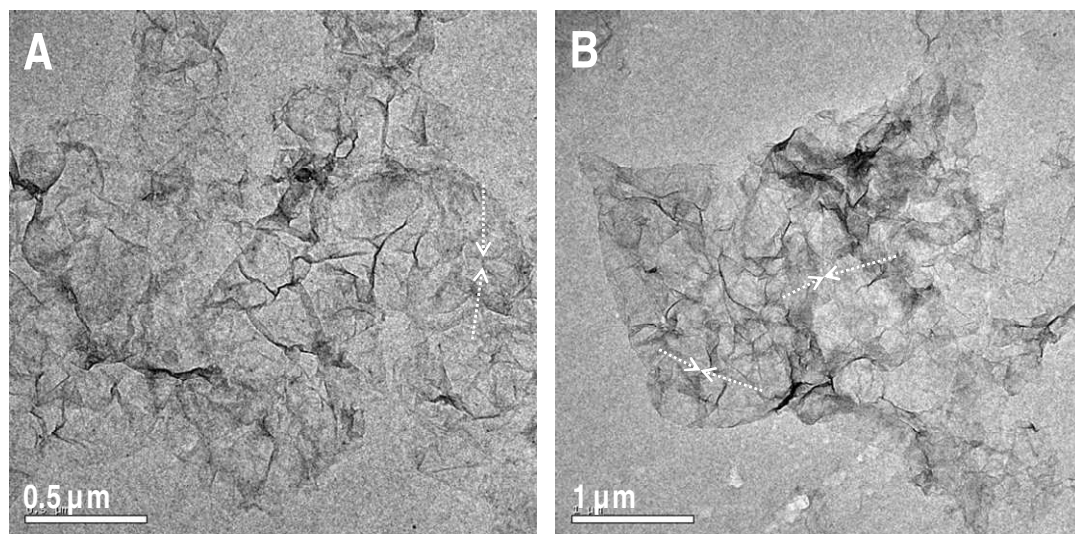


Figure S5. TEM images of A) GO and B) RGO. Large area sheets with characteristic wrinkles can be seen.

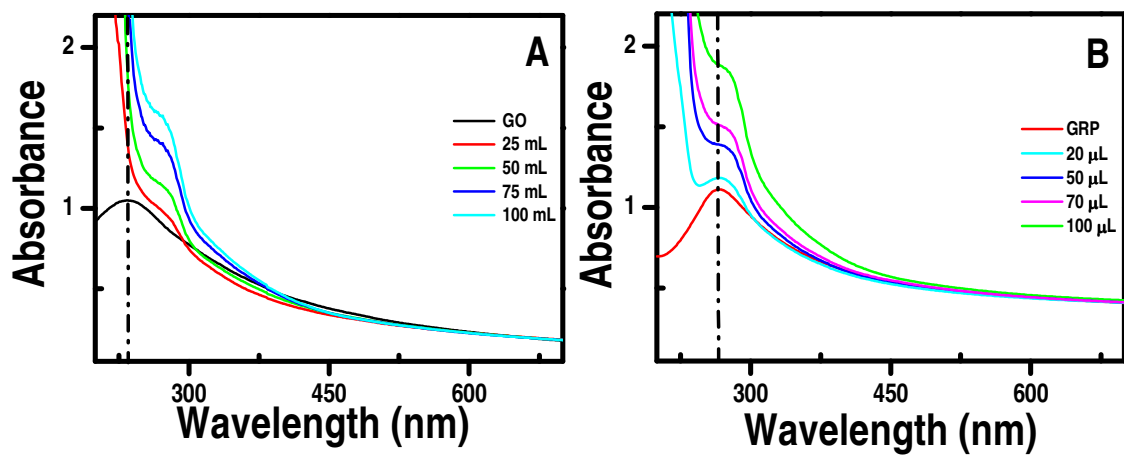


Figure S6. UV/Vis spectral changes of A) GO and B) RGO upon addition of different amounts of Au@NLF.

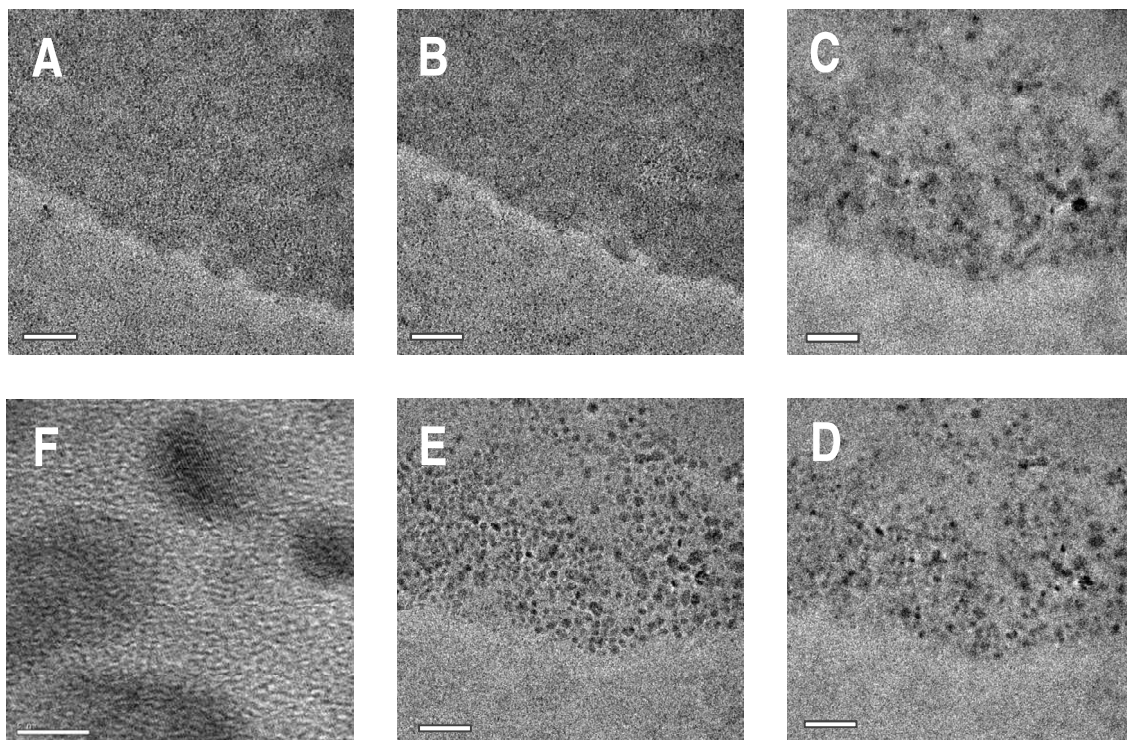


Figure S7. Time dependent TEM images of RGO-Au@NLf composite upon e-beam exposure. Image taken every 5 min interval.

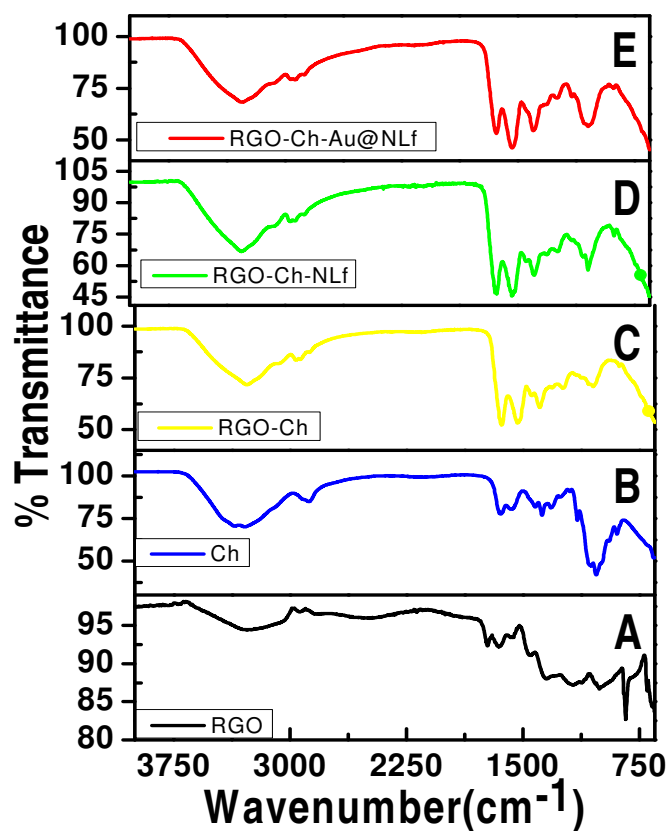


Figure S8. IR Spectra of A) RGO, B) Ch, C) RGO-Ch, D) RGO-NLf-Ch, and E) RGO-Au@NLf-Ch.

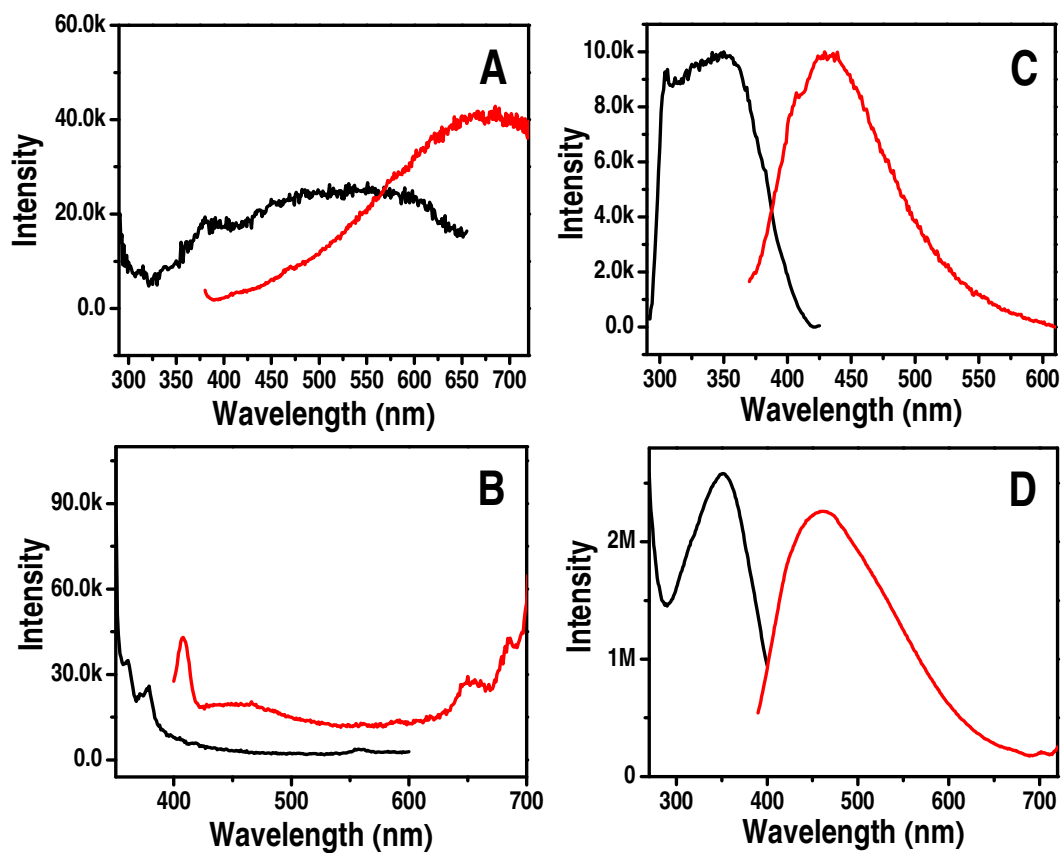


Figure S9. Photoluminescence profiles of A) GO, B) RGO, C) NLf and D) Au@NLf.

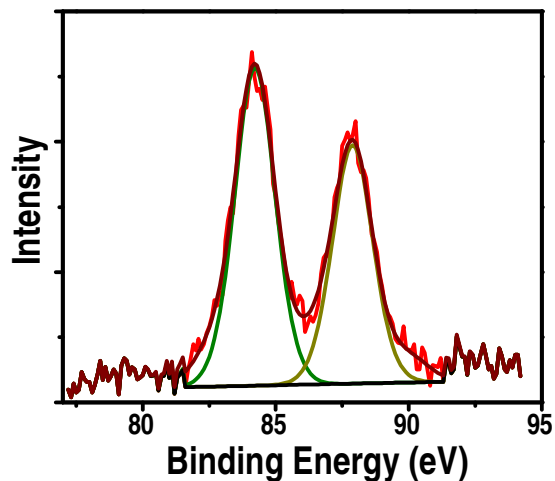


Figure S10. Au 4f core level photoelectron spectrum of the RGO-Au@NLf-Ch composite. The components are fitted to the respective components (Au 4f_{7/2} and 4f_{5/2}).

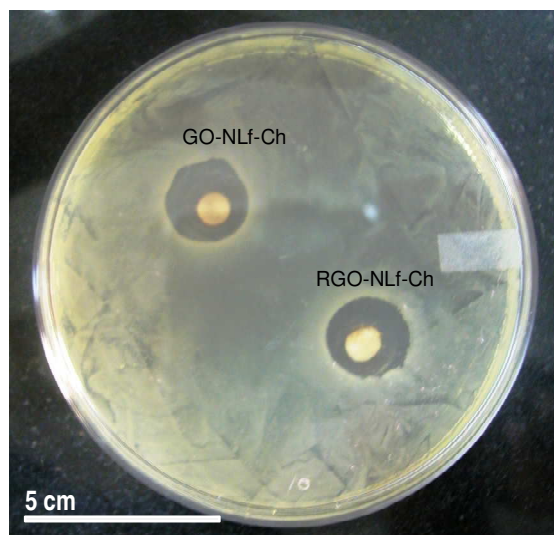


Figure S11. Kerley-Born diffusion test conducted for the RGO/GO composites showing the zone of inhibition depicting the antibacterial activity. OD is plotted in the text.

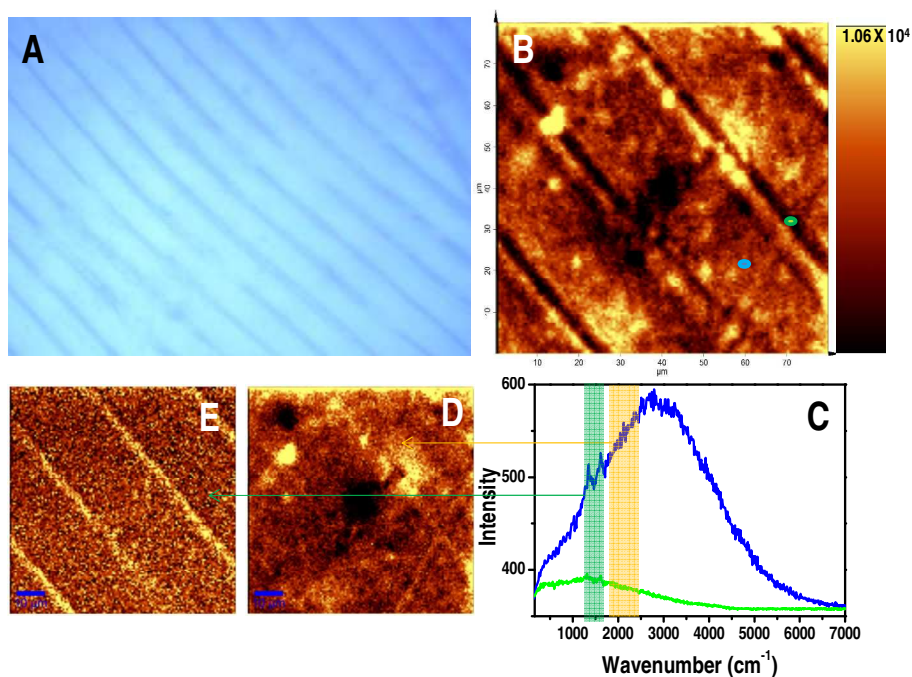


Figure S12. Characterization of large area luminescent patterns. A) Optical image of the pattern, B) Raman spectral image collected from the pattern and C) spectra from two locations of the image marked in B. Color of the spectral traces corresponds to the locations, indicated in image B. Raman spectral images generated D) from the fluorescence of Au@NLf and E) from the frequency range of 1300-1600 cm^{-1} corresponding to D- and G- bands of RGO.

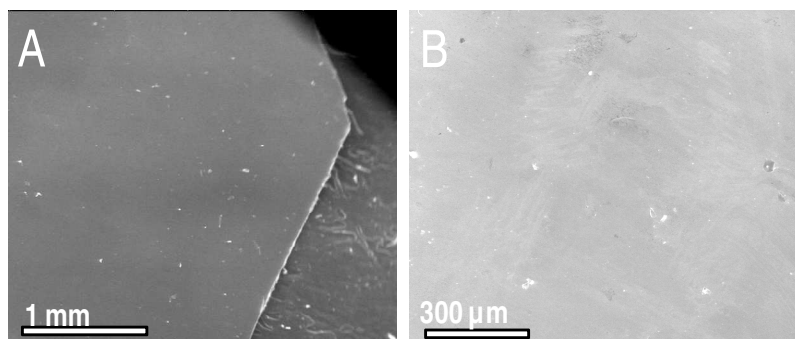


Figure S13. SEM images of film after 3 times patterning- and erasure. A) low-magnification image and B) higher magnification image of the inside portion. No trace of pattern can be seen.