In Situ Fabrication of Flexible, Thermally Stable, Large-Area, Strongly Luminescent Copper Nanocluster/ Polymer Composite Films

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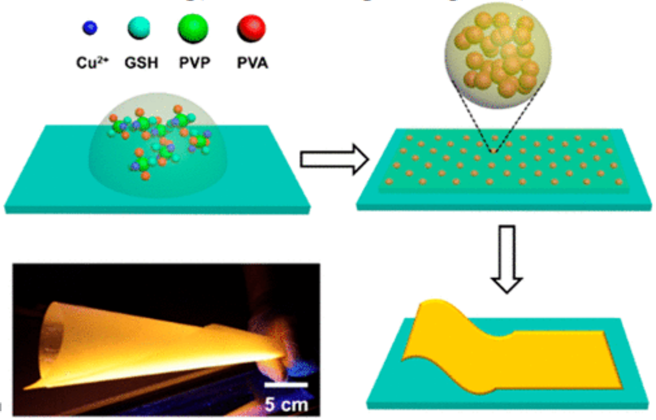

CHEMISTRY OF MATERIALS

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Jyoti Sarita Mohanty
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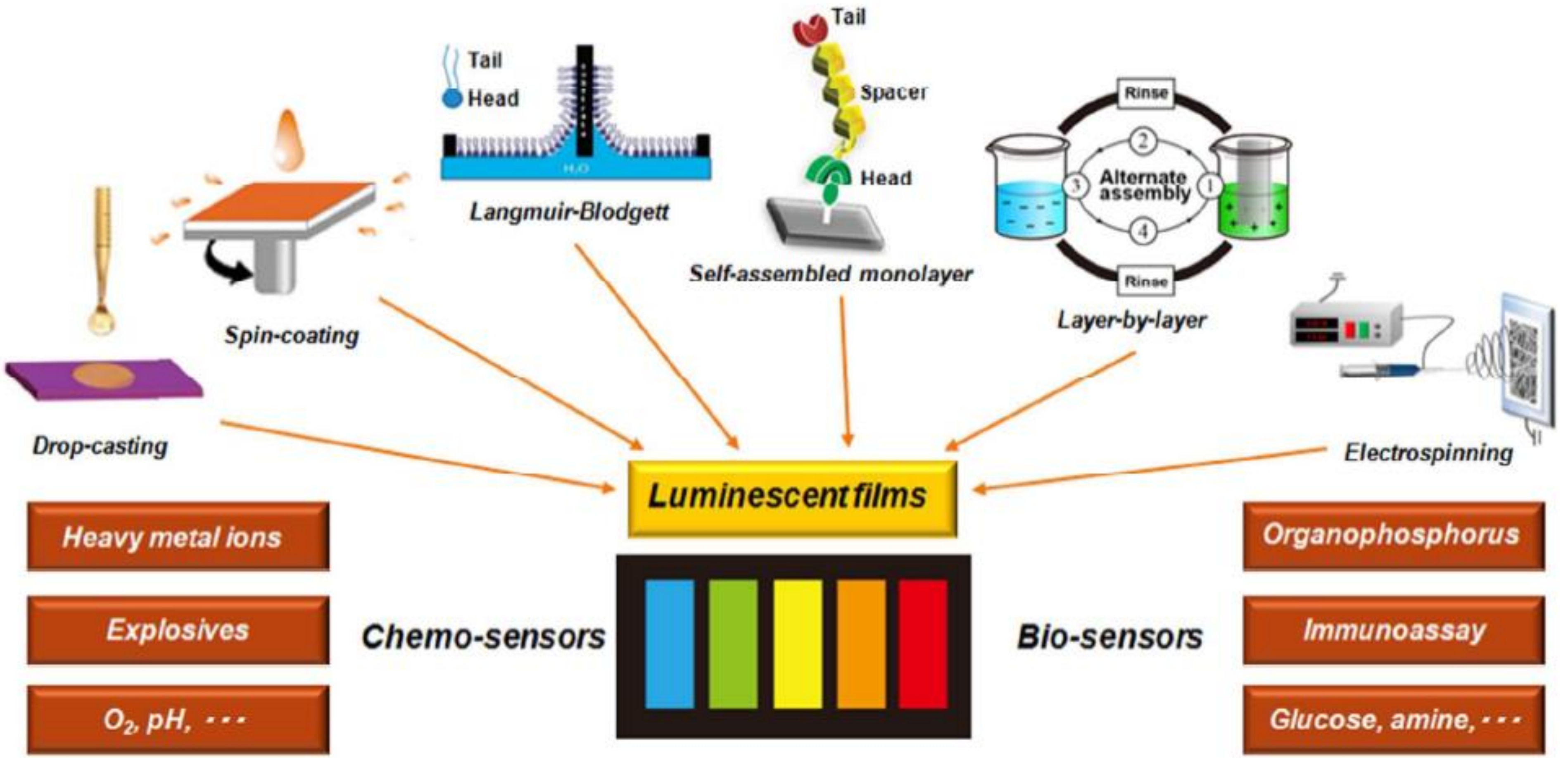
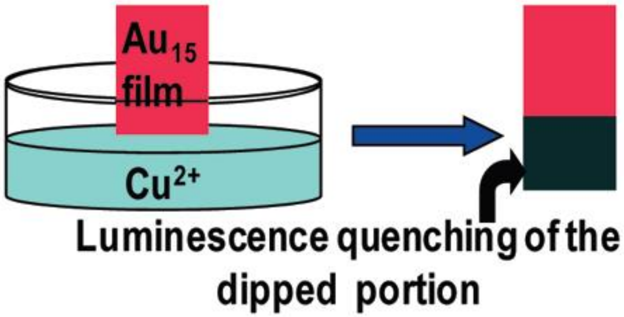
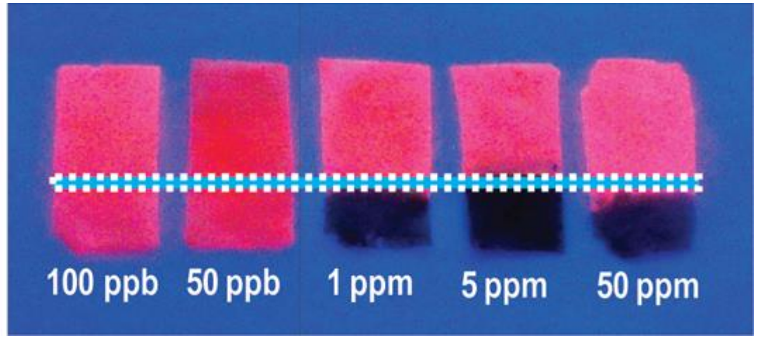
Different fabrication method in designing various luminescent film for chemo-/ bio- sensing

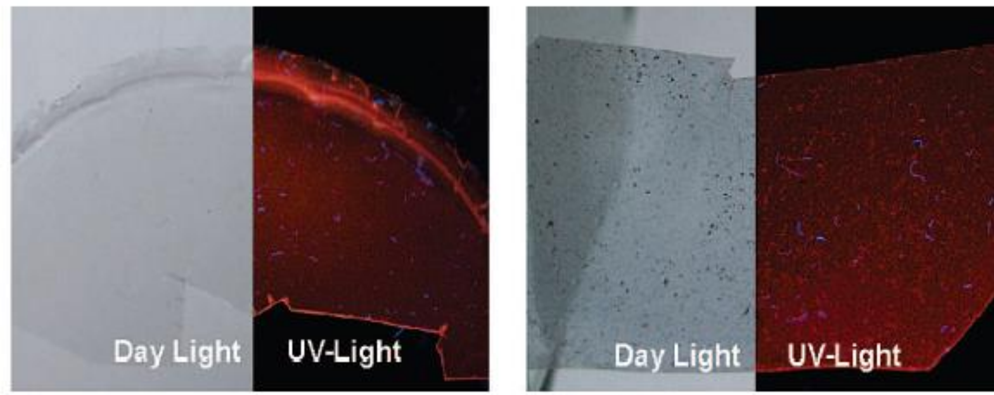




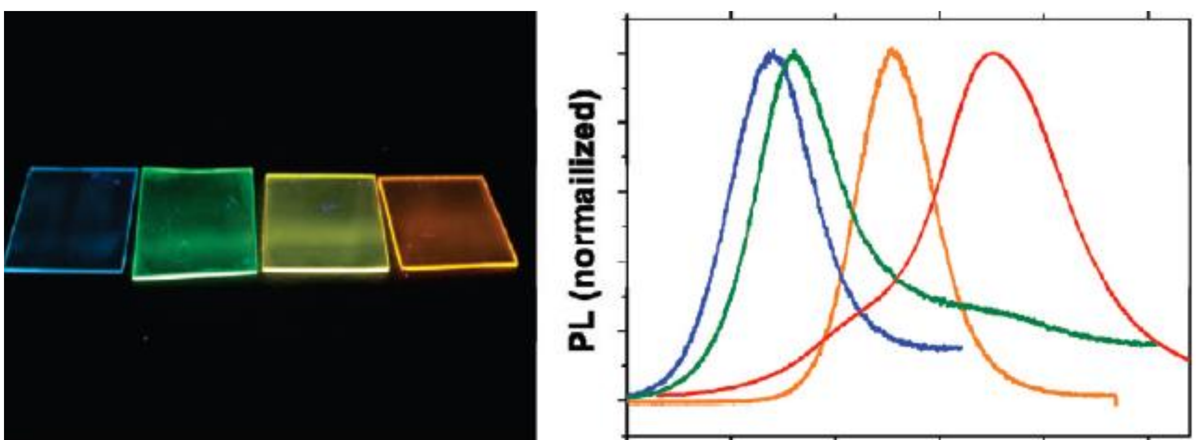


Luminescent, freestanding composite films of Au_{15} cluster for Cu^{2+} sensing.

Strongly luminescent films fabricated by thermolysis of gold-thiolate complexes in a polymer matrix.



Feldmann et al., chem. Mater. **2008**, 20, 6169-6175



(a) (b)

Strongly luminescent and highly loaded CdSe QD-silica film composite.

Kim *et al* ., J. Phys. Chem. C. , **2010**, 114, 14362-14367.

Advantages of using film over the luminescence probes in solution:

Luminescent films can be transformed easily into the device format with several unique advantages:

- luminescent films with any shape and size (dependent on the substrate pattern) can be easily fabricated for various applications.
- they are easy to store and transport as a result of the good chemical stability of luminophores in the solid state.
- It enable real-time detection of the analyte.
- It can be regenerated by washing them with suitable solvents.

Why This paper….

❖ It shows the simple method to synthesize thin film along with luminescent cluster .

❖ This approach avoids use of any heavy or expensive metal elements and toxic organic solvents, and can easily be adapted to produce large-area films.

Introduction:

Polymer-based luminescent films are frequently used in sensors, solar concentrators, and LEDs. Fabrication of such composite films often involves two processes:

(i) synthesis of the luminescent component, such as an organic dye, semiconductor quantum dots (QDs), or metal nanoclusters (NCs) in solution, and

(ii) dispersion of these in a monomer or a dissolved polymer, followed by polymerization/evaporation of the solvent.

However, widespread application of this approach is in part hindered by several limitations:

- Sometimes poor dispersion of luminescent components in the polymer, leading to the phase segregation which makes it difficult to fabricate large-area uniformly.
- Deterioration of the photoluminescence (PL) quantum yield (QY) of the luminescent component during the fabrication process of the film.
- Poor PL stability, particularly when the films are exposed to heat, oxygen, or moisture.

In this paper…..

❑ They proposed a strategy to fabricate composite polymer films with incorporated Cu NCs which are grown in situ in a 3D hydrogel network formed by cross-linked polyvinylpyrrolidone (PVP) and poly(vinyl alcohol) (PVA) molecules in aqueous solution.

Synthesis of In Situ Fabrication of the Cu NC Composites Films

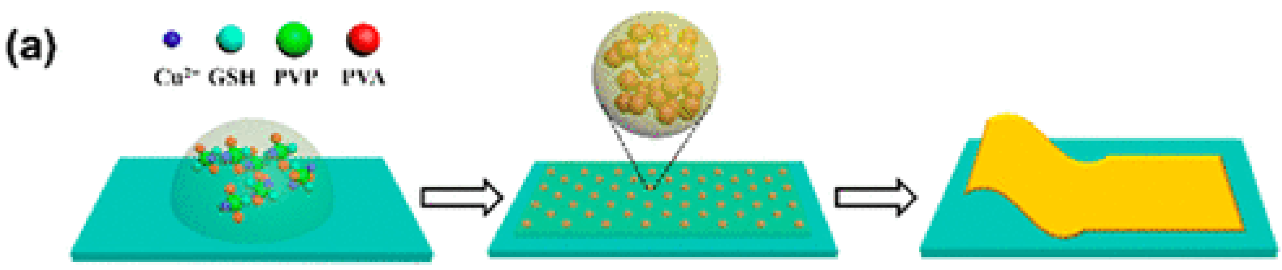
PVA was dissolved in DI H_2O at 80 °C at a concentration of 60 mg/mL.
6 mL aq. solution of PVA + 1mL of PVP (60 mg/mL) under stirring.

0.1 M of 2.5 mL of GSH + into the polymer mixture

↓

0.5 mL of $Cu(NO_3)_2$ (0.1 M) was added

The mixture was dropped onto the surface of cleaned glass slides, which were then kept in vacuum at 40 °C for 10 h.



(a) Schematic illustration of the in situ fabrication method of Cu NC/polymer composite films.

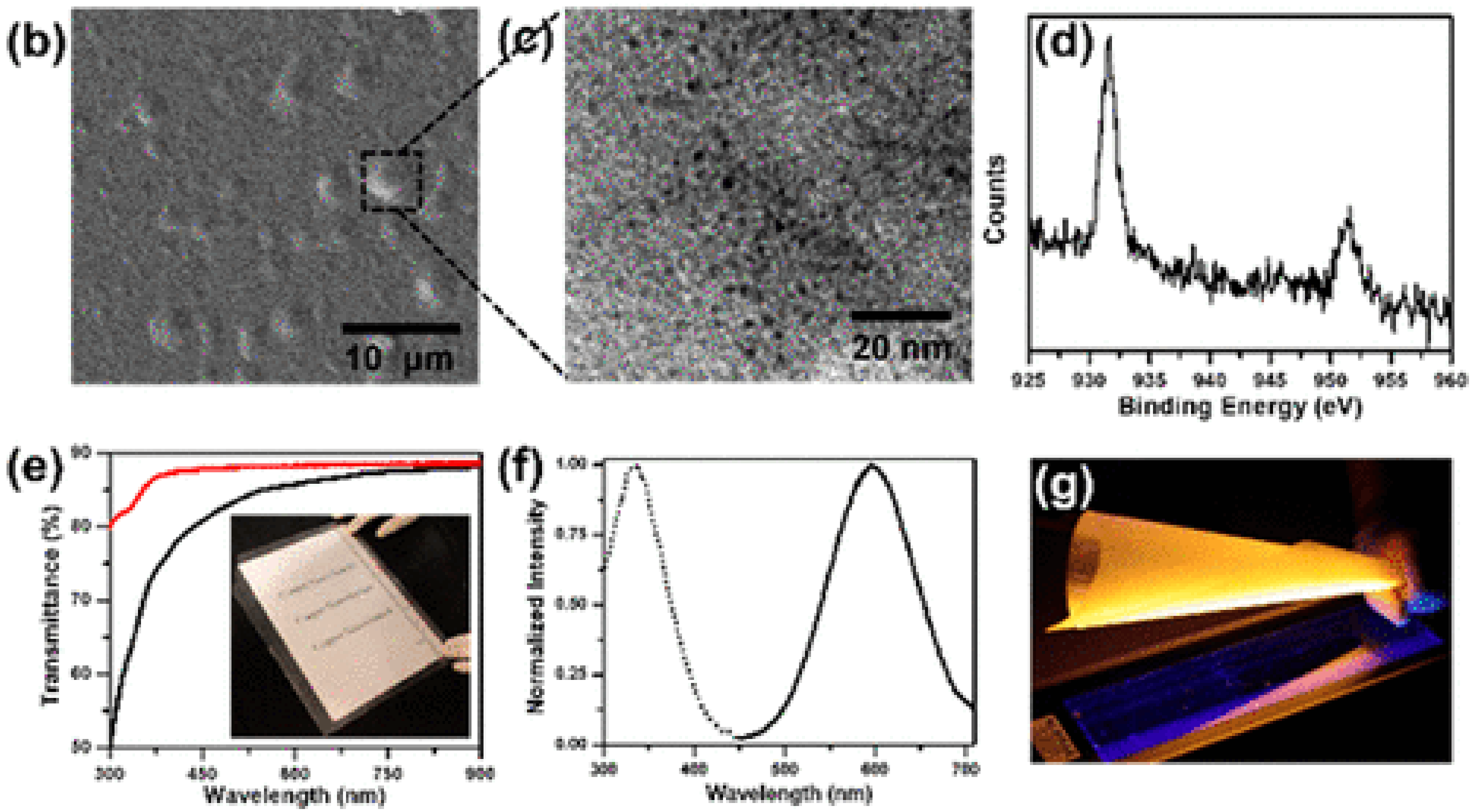


Figure 1. (b) SEM images. (c) TEM images. (d) XPS spectra of the composite films. (e) Transmittance spectra of the Cu NC/polymer composite film (black) and of the bare PVP/PVA film (red), inset shows the photograph of a film with a size bigger than an A4 sheet of paper. (f) PL (solid) and PLE (dotted) spectra of Cu NC/polymer composite film. (g) Photograph of an orange-emittingCu NC/polymer composite film under UV light.

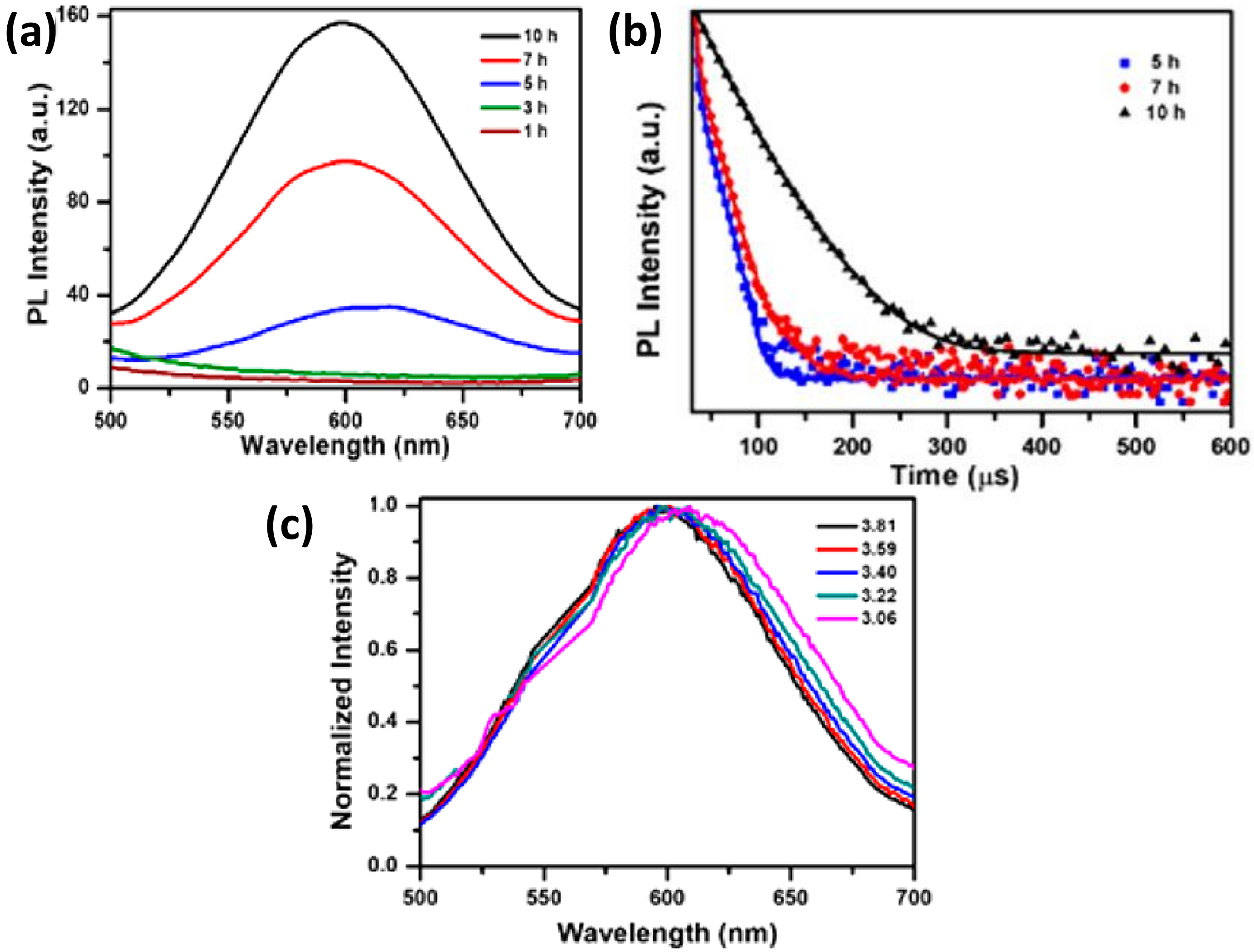


Figure 2. Evolution of PL spectra (a) and PL decay curves (b) of Cu NC/polymer composite films obtained with different thermal treatment times. (C) PL spectra of Cu NC/polymer composite films under different excitation energies (as indicated on the frame, in eV).

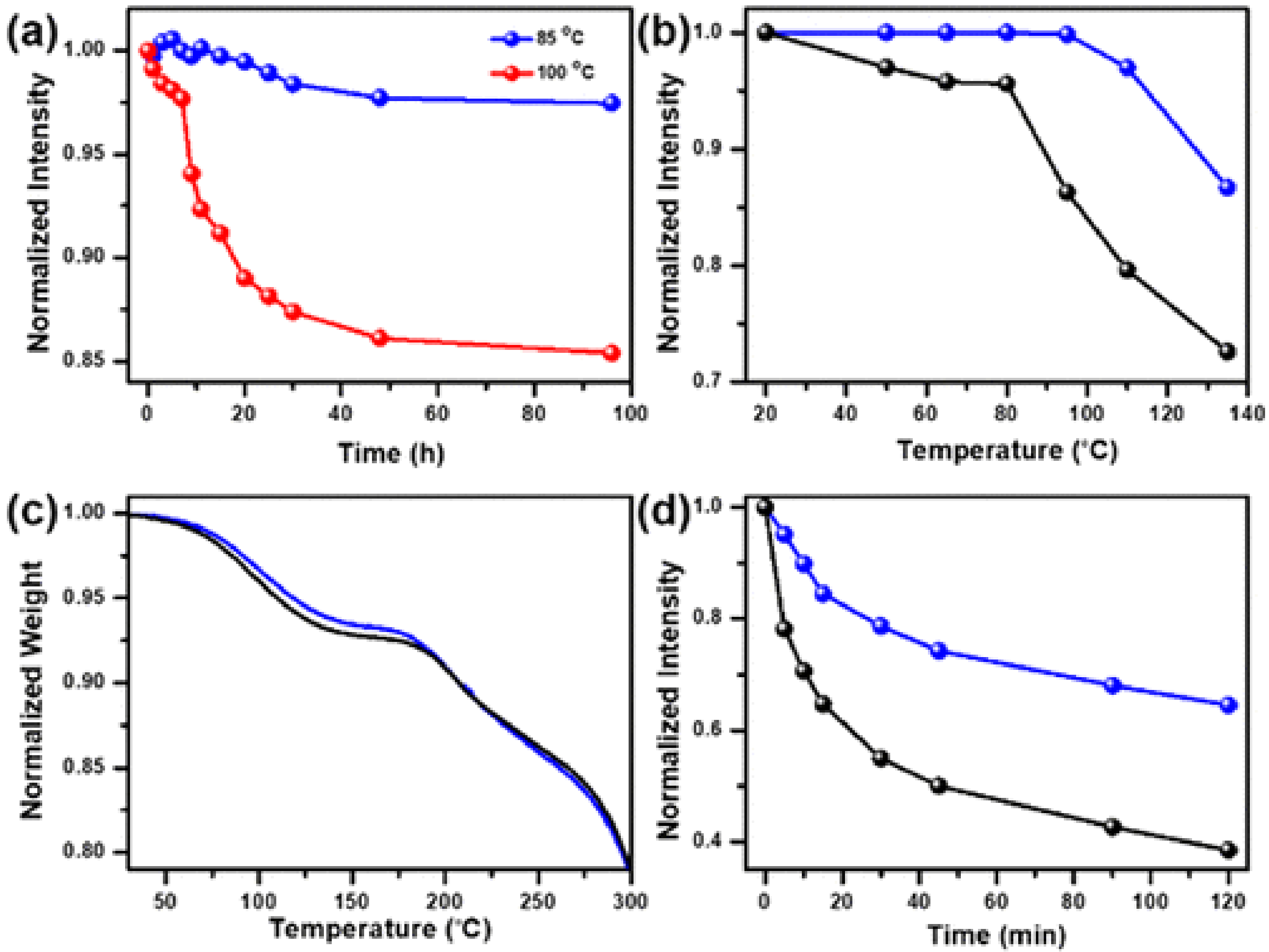


Figure 3. (a) Relative PL intensity of Cu NC/polymer composite films kept for up to 96 h at 85 °C (blue) and 100 °C (red). (b) Relative PL intensity of Cu NC/polymer composite films (blue) and the similar films fabricated without PVP (black) kept for 3 h at the temp. indicated. (c) TGA curves of the Cu NC/polymer composite films (blue line) and similar films fabricated without PVP (black). (d) Relative PL intensity of Cu NC/polymer composite films (blue) and similar films fabricated without PVP (black), under UV radiation. All the PL intensities were recorded at 600 nm, under 365 nm excitation.

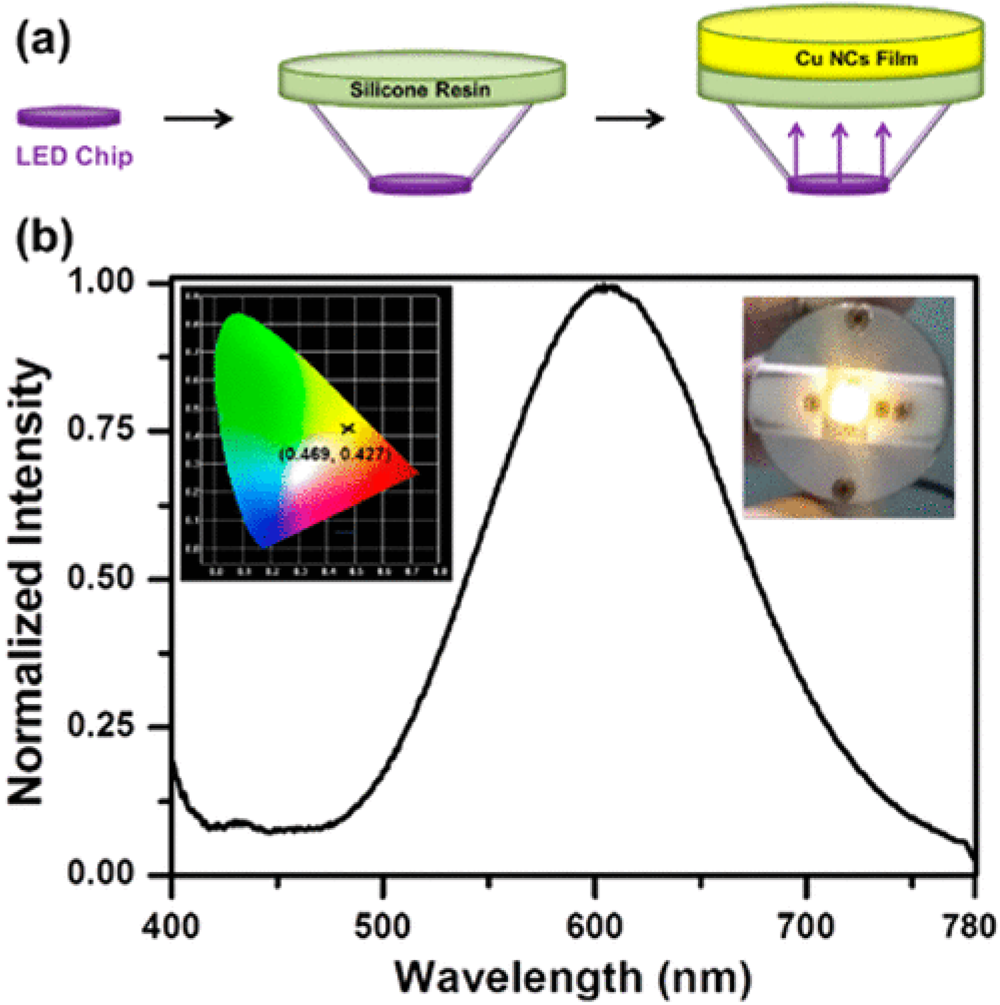


Figure 4. (a) Fabrication of a down-conversion LED with a Cu NC/ polymer film placed on top of a silicone resin layer at a distance from a UV excitation chip. (b) Emission spectrum of an orange LED; inset shows the CIE chromaticity coordinate of the LED (left), and a photograph of the operating device (right).

Summary:

- In situ fabrication of Cu NC composite films, by encapsulating Cu NCs in 3D hydrogels of PVP/PVA, and by dehydration-induced AIE processes in aqueous solution, is reported.

- This approach avoids use of any heavy or expensive metal elements and toxic organic solvents, and can easily be adapted to produce large-area films.

- Bright (PL QY of up to 30%) orange luminescence of the films is achieved.

- The composite Cu NC/polymer films show high thermal stability and favourable mechanical properties, and have been employed as a color converter for fabricating downconversion orange LEDs.