

# Flexible urea sensor fabrication by localized laser - induced pyrolysis of Kapton

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## Introduction

We present a fabrication method of enzymatic urea sensor employing new, low-cost, lithography free, one-step process of laser-induced carbonization [1-4] and compare it to glassy carbon [5].

Here, we report fabrication of two types of enzymatic urea sensors by immobilization of urease:

- directly on carbon;
- via intermediate biopolymer (chitosan) layer.

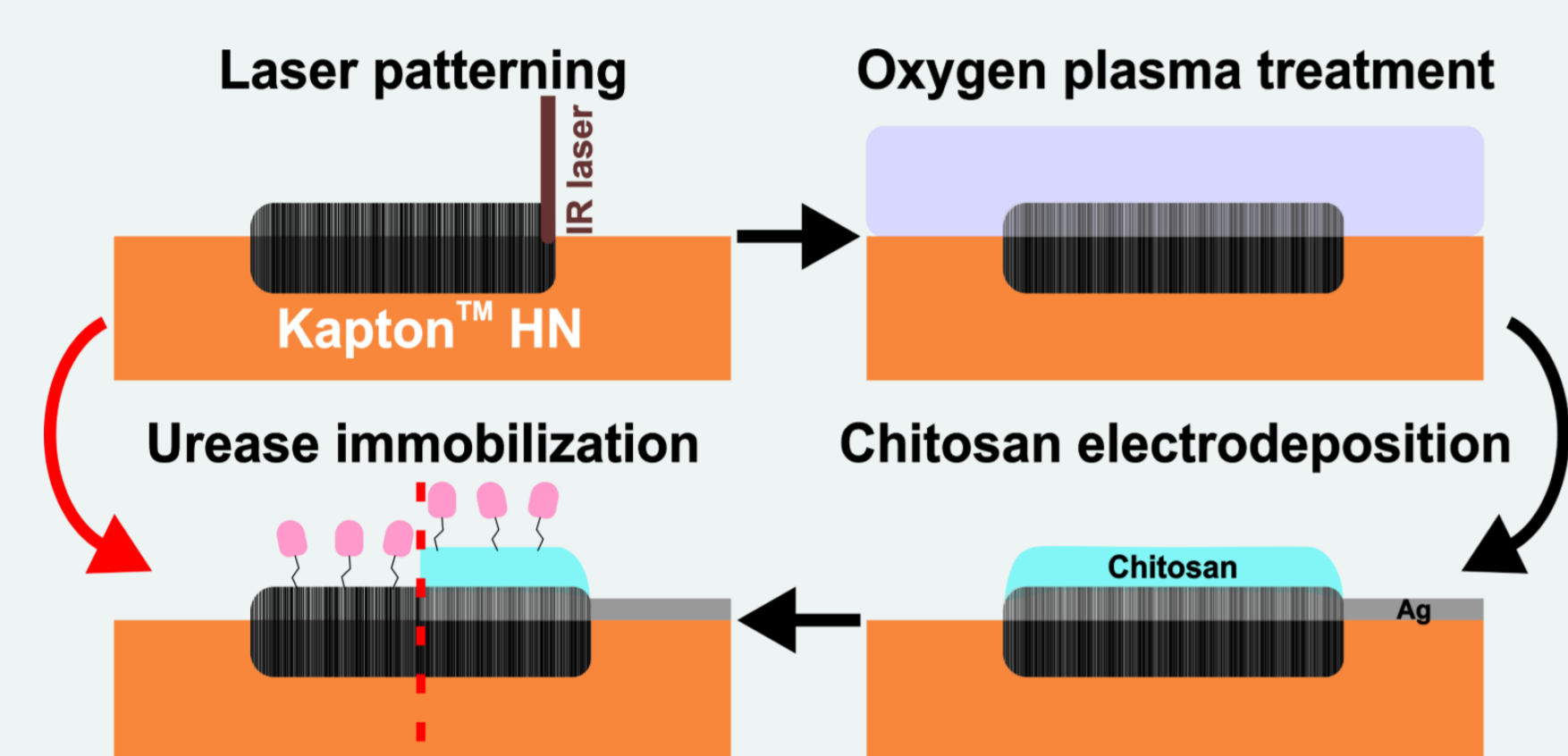


Fig. 1. Flow chart of the process

## Carbon electrode fabrication and characterization

### Fabrication:

- Kapton™ HN 125±13µm;
- CO<sub>2</sub> laser, wavelength 10.6µm;
- Power 4.8 W, speed 10 cm/s.

### Properties:

- High porosity:
  - BET surface area – 255 m<sup>2</sup>/g;
  - Surface porosity – 15.2%;
- Composition:
  - XPS: C – 76.1%, N – 1.0%, O – 23.0%;
  - Combustion analyzer: C – 93%, N–0.9%, H – 0.4%;
- Conductivity – 7.1±0.7 S/cm;
- d-spacing – 3.48Å; L<sub>a</sub> = 4.0nm; L<sub>c</sub> = 7.1nm;
- Raman ratio (I<sub>D</sub>/I<sub>G</sub>) – 0.8;
- Hydrophilicity (contact angle 70°).

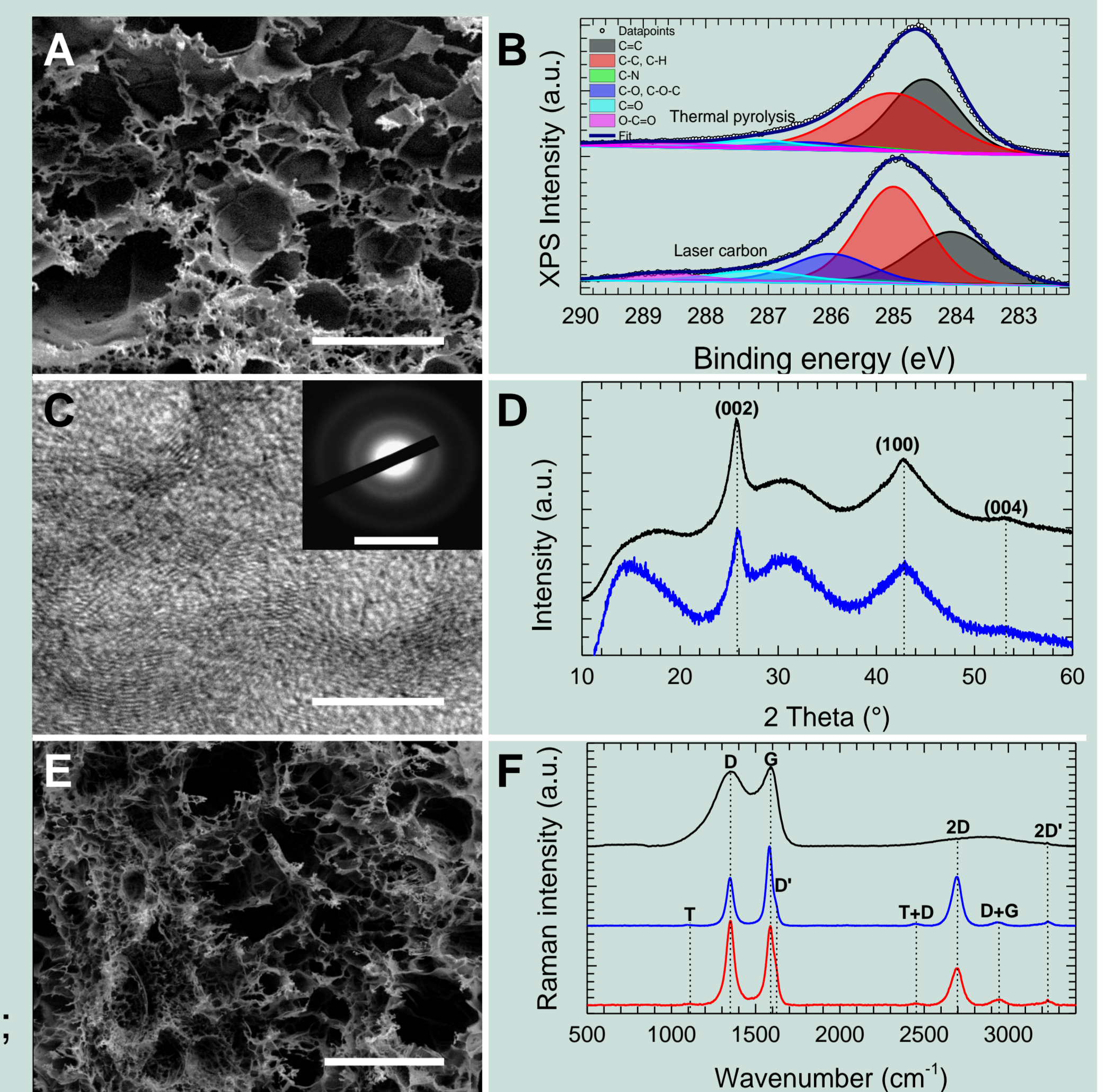


Fig. 2. (A) SEM image of fabricated laser carbon ([scale bar]=10µm); (B) XPS spectra C 1s line; (C) TEM image of laser carbon and corresponding selected area diffraction, ([scale bar]= 10 nm, [SAED]=10 1/nm) (D) powder X-ray diffractogram collected from powder; (E) morphology after oxygen plasma treatment ([scale bar]= 10 µm); (F) Raman spectra. In all cases in black thermally pyrolysed Kapton at 900°C, blue - laser carbon, red – laser carbon after oxygen plasma treatment

## Chitosan electrodeposition and process optimization

- Chitosan preparation: chitosan solution 1 % w/v, pH 5.5 in diluted HCl (0.2 M) and filtered,
- Improvement of hydrophilicity
  - Oxygen plasma treatment at 100 W for 120s
  - Contact angle <10°;
  - Retention over 5 days;
- Highest deposition quantity at current direction perpendicular to laser patterning;
- Optimal deposition duration is 15 min at 4 A/m<sup>2</sup>. Increase of the time leads to chitosan self-peeling;
- Chitosan film thickness ~2 µm after drying.

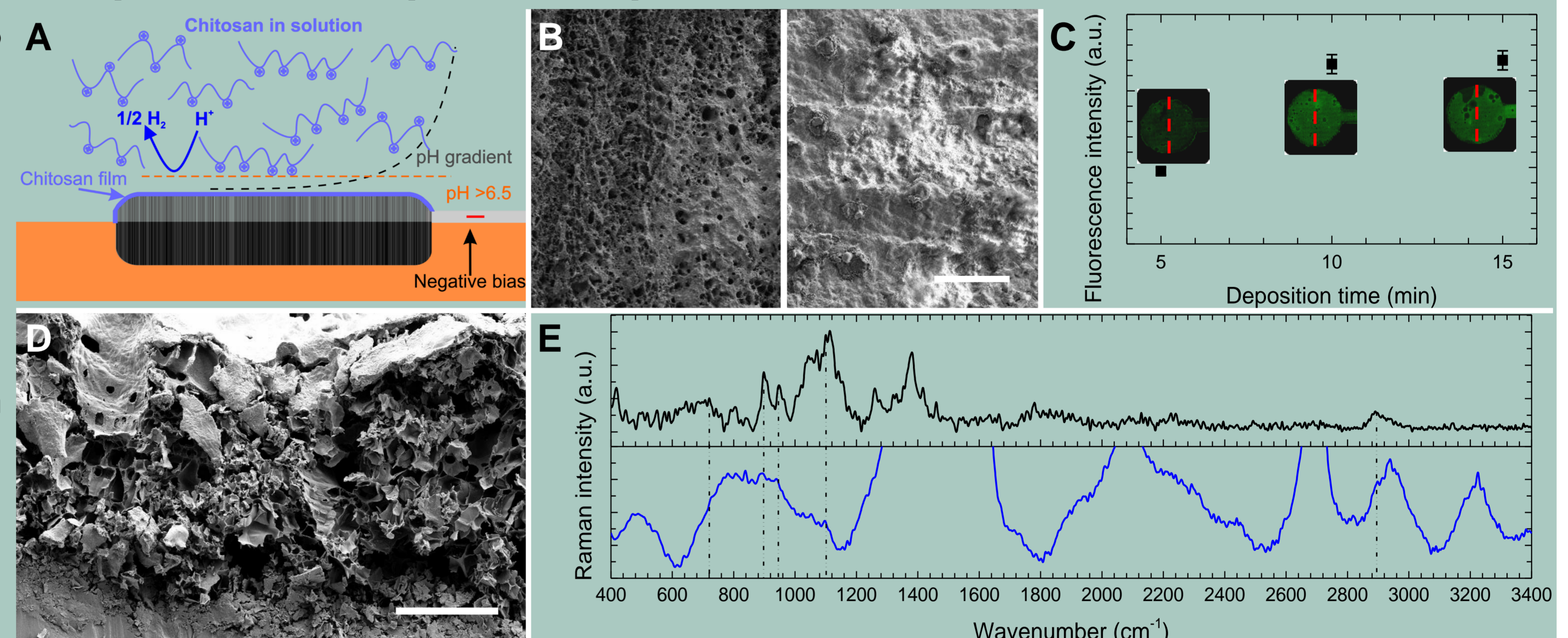


Fig. 3. (A) Scheme of chitosan electrodeposition. (B) Electrodeposited chitosan on laser carbon with applied current (left) parallel and (right) perpendicular to laser patterning ([scale bar] = 50 µm). (C) Quantity of chitosan deposition over time of attached chitosan determined with fluorescence microscopy. (D) Cross-sectional SEM. (E) Raman spectra collected from chitosan film deposited on gold (black) and on carbon electrode (blue)

## Urea sensor fabrication and analysis

- Urease from Jack Beans (*Canavalia ensiformis*):
  - Covalently coupled to chitosan with glutaraldehyde (Sigma Aldrich 25% in water) [6];
  - All sensors were immobilized in 1 mg/ml urease solution overnight;
- Activity tested by urea hydrolysis and ammonia release [7,8].

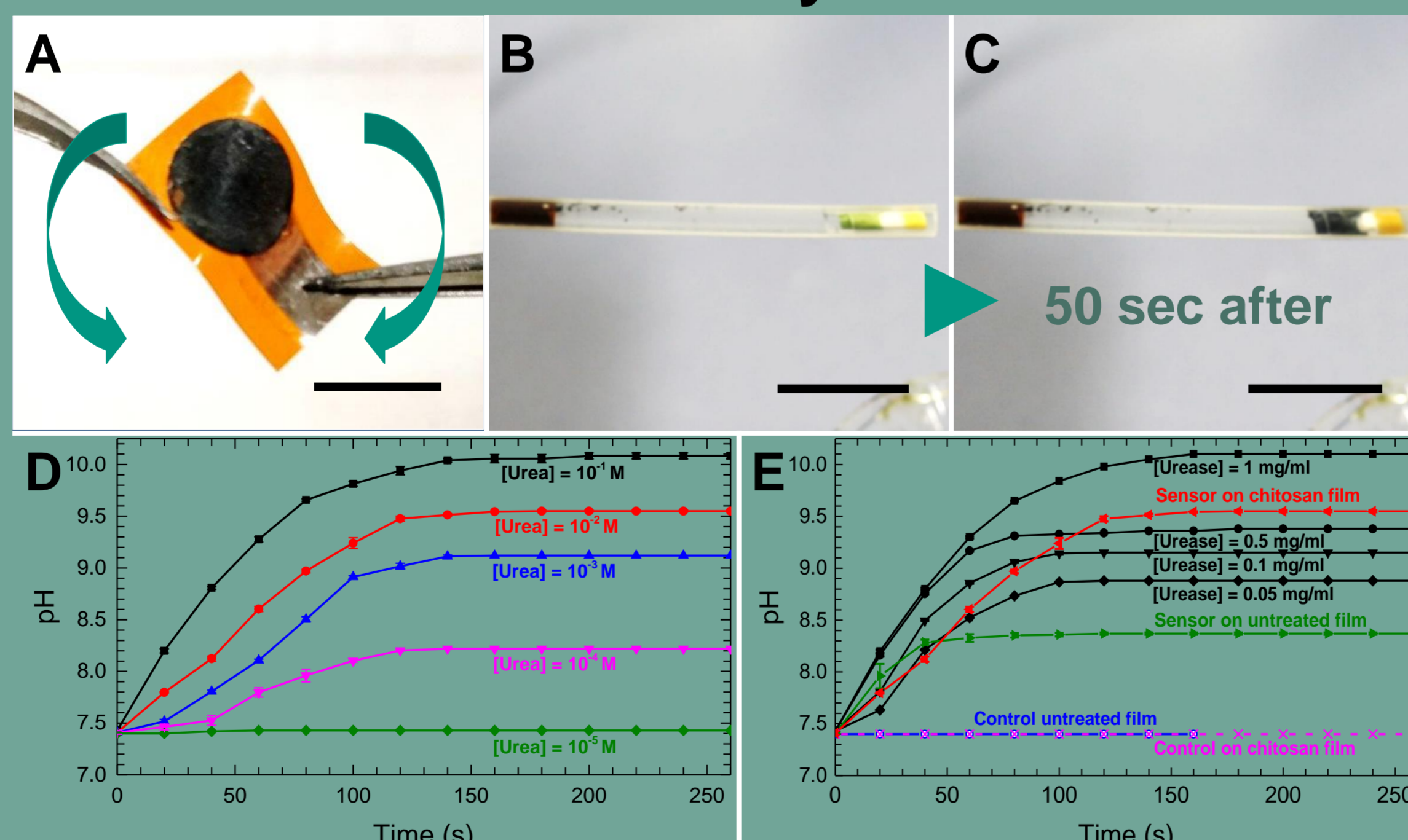


Fig. 4. (A) Circular assembly of urease-chitosan-laser carbon ([scale bar] = 10 mm); (B-C) qualitative test with pH indicator ([scale bar] = 20 mm). (D) Comparison of urease concentrations, each sensor was coated with 1 mg/ml of initial urease concentration. (E) Comparison of urease activity to control solutions of various urea concentrations (black) and test sensors: urease-chitosan-laser carbon (red) and urease - laser carbon (green)

## Conclusions

Material exhibits electrical, mechanical and physical properties different from glassy carbon. Simplicity, flexibility and versatility of such method enable:

- fabrication of the patterns of various designs;
- variation of the properties dependent on applied laser parameters;
- electrodeposition of chitosan can be utilized for immobilization of other enzymes;
- determined urea detection limit at 10<sup>-4</sup>M, which is in two orders below risk values for a healthy human;
- integration with other biomedical devices, e.g. in catheter tube (4 mm diameter tested).

## References

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