Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information

Borate Cross-Linked Graphene Oxide-Chitosan as Robust and High Gas Barrier Films

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Characterization

X-ray photoemission (XPS) spectra was collected by using an Escalab 250Xi (Thermo Fisher Scientific, UK) spectrometer, equipped with a monochromatic Al Kα excitation source, electron and ion flood guns for charge neutralization and a 6-channeltron detection system. The photoemission spectra were collected at 20 eV pass energy, and the diameter of analyzed area was about 1 mm.

A 300 MHz Bruker AVANCE magnet, equipped with a 4 mm Wide Bore MAS probe (operating at the 11B frequency of 75.4 MHz), has been adopted to collect 11B NMR spectra by Cross Polarization Magic Angle Spinning (CPMAS) technique. Each sample (70-90 mg) has been packed in 4 mm zirconia rotors with Kel-F caps prior to be loaded in the magnet and spun at a rate of 13000±1 Hz. All spectra have been processed and elaborated by using the Bruker Topspin software (v.2.1) (Bruker Biospin, Rheinstetten, Germany).

Scanning electron microscope (SEM) observation was performed using an Inspect F model FEI apparatus at an accelerating voltage of 10 KV. The chitosan films were frozen and fractured in liquid nitrogen, and then the cross sections were sputter coated with gold for observation.

Cross-sections of the chitosan composite films were imaged with a FEI Tecnai G2 F20 S-Twin TEM, operating at an accelerating voltage of 200 kV. Film was embedded into epoxy resin, supporting for sectioning with a microtome.

The crystalline structure of chitosan polymer as well as the morphology of graphene oxide in the polymer matrix was determined by WAXD measurements. An Anton Paar SAXSess diffractomer (40 kV, 50mA) equipped with a Cu-K radiation (λ= 0.1542 nm) source and an image plate detector was used. The spectra were collected in transmission mode by scanning the 2θ range from 2.5o to 40o. The samples were mounted with the casting surface perpendicular to the incident X-rays pathway. All spectra were corrected only for the dark current and the empty holder background.

Uniaxial tensile test was performed at room temperature with universal testing machine (Instron 3360) according the ASTM D-412. The specimens were cut into rectangular shape with dimension of 80mm ×10mm×0.04mm, mounted in between two grips with a gauge length of 40mm, and stretched at the extension rate of 5mm min-1. For each samples, the tensile properties are obtained from average value of five parallel measurements.

The dynamic mechanical properties of the composite films (strips 7×10mm) were investigated in the tensile mode by using the DMA (Q800) of TA Instrument. The strips were heated at 3°C/min under a flow of dry nitrogen from 30oC to 250oC and simultaneously stretched at a frequency of 1Hz. Before the test, all the chitosan samples were previously thermal treated at 90oC for 50min in vacuum oven in order to remove the free water.

Oxygen transmission rate (OTR) was evaluated by using a standard permeabilimeter (Extra solution, MULTIPERM), in accordance with ASTM D-3985, at 23^{o}C and 0% and 75% relative humidity (RH) at both downstream and upstream side of the film.

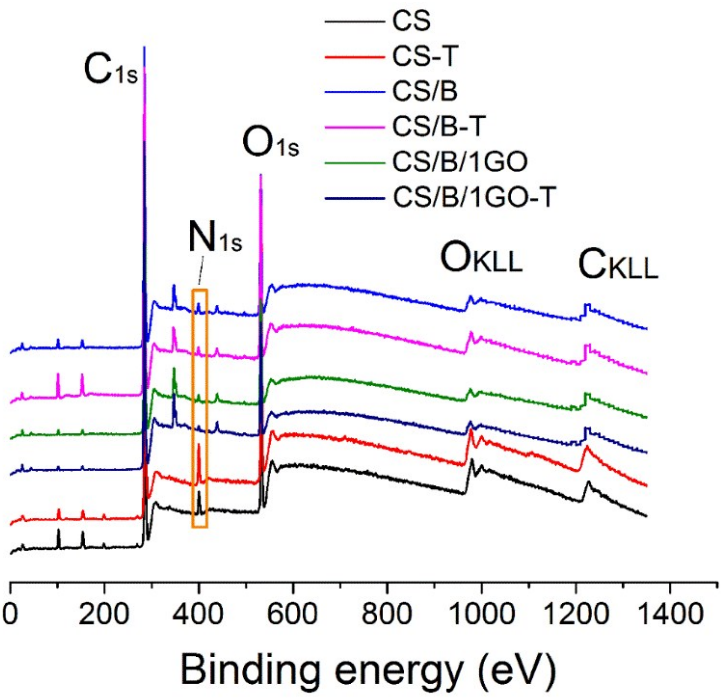

Figure S1. XPS spectra for pristine chitosan and chitosan composite films before and after thermal treatment.