Electronic Supplementary Information

Introducing the concept of pulsed vapor phase copper-free surface clickchemistry using the ALD technique

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Experimental Section

General. As a substrate for the pulsed vapor phase surface modification processes ZnO powder (Honeywell-Fluka) was used. The organic precursors (reagents) were propiolic acid (PA) (98 %, Acros Organics) and benzyl azide (BA) (94 %, Alfa Aesar). All purchased materials were used as received. Prior to modification, a homogeneous paste of ZnO powder (300 mg/mL) in absolute ethanol was prepared by ultrasonic agitation, and dropped on top of a silicon wafer. All substrates were air dried and were kept at a temperature of 130 °C in the ALD reaction chamber for 2 hours before processing.

ALD processing. Vapor phase modification was carried out using a Cambridge Nanotech Savannah S100 atomic layer deposition tool. Nitrogen (≥99.99% N₂) was used as the delivery and purge gas. During the processing, the pressure in the reaction chamber was 0.75 Torr, and all gas lines were kept at 120 °C to avoid cold spots and condensations of the precursors. In order to investigate the chemical functionalization of the ZnO surface with PA, a series of experiments were conducted applying different processing temperatures (70 °C – 150 °C), the pulsing and exposure times of the PA, and the number of cycles used. Optimum *in-situ* two-step pulsed vapor phase surface modification conditions for the investigated click reaction were performed by applying the following pulsing/purging sequences: 40 pulses of PA (pulse duration for each pulse 2 seconds), 120 seconds N₂ purging. The PA and BA containers were kept at room temperature and 45 °C, respectively. The temperature of the ALD reaction chamber was kept at 130 °C.

X-ray photoelectron spectroscopy (XPS). Photoemission spectra of all samples were measured by using a SPECS system equipped with a non-monochromatized source of Al K α X-rays of 1486.74 eV and a Phoibos 100 hemispherical electron analyzer. Spectra around the C 1s state were recorded at a pass energy of 20 eV, and spectra around the N 1s level were taken at a pass energy of 25 eV. The typical pressure in the UHV chamber during the XPS analysis was in the 10⁻¹⁰ Torr range. The spectra were analyzed by the Unifit software¹, and simulated with several sets of mixed Gaussian-Lorentzian functions, while the background was subtracted according to the Shirley's method.² The position of the C 1s peak, adjusted to the binding energy of 284.5 eV, was used for the energy calibration.

Fourier Transform Infrared Spectroscopy (FTIR). FTIR spectra in the range of 4000 to 600 cm⁻¹ were acquired at room temperature in air with a FTIR spectrometer PerkinElmer Frontier. All the spectra were obtained in the Attenuated Total Reflection (ATR) mode with a resolution of 4 cm⁻¹ and 30 scans per spectrum with air as background.

Field Emission Scanning Electron Microscopy (FE-SEM). The Scanning Electron Microscope (SEM) images were taken by a Jeol JSM-7800F SEM instrument. The surface morphology was analyzed applying a gentle beam mode with the electron beam acceleration voltage of 0.7 kV and at a working distance of 2 mm. Dark-field, scanning transmission electron imaging of samples supported on a lacey carbon film on 300 mesh copper grids was achieved using transmission electron detector at 30 kV accelerating voltage (STEM mode).

2 D. A. Shirley, *Phys. Rev. B*, 1972, **5**, 4709.

¹ R. Hesse, T. Chassé, R. Szargan, *Fresenius' J. Anal. Chem.*, 1999, **365**, 48.



Fig. S1. Full FTIR-ATR spectra of ZnO modified with PA (dotted line), and ZnO modified with PA and BA (continuous line) during the optimized ALD process at 130 °C. The inset shows an expansion of the region around 3000 cm⁻¹ after the addition of BA. The usually low-intensity aromatic C-H stretching bands cannot be seen due to the overlapping with the broad O-H stretching band centered at ~3300 cm⁻¹ owing to water adsorbed on the ZnO surface after exposure to ambient conditions during the measurements. Apart from the peak at 1410 cm⁻¹, another broadening of the COO stretching bands at around 1550 cm⁻¹ is highlighted and attributed to the C=C stretching of the aromatic ring.



Fig. S2. Comparison of normalized C 1s core-level XPS spectra of ZnO (PA+BA) measured *ex-situ*: (a) immediately after the ALD processing, and (b) four days after ALD processing upon storage at ambient conditions. The relative intensities of carbon peaks at 284.5 eV, 286.0 eV, and 288.5 eV alter with time as a consequence of adventitious carbon adsorption.



Fig. S3. Comparison of areas of N1s core level XPS spectra of ZnO (PA+BA) measured *ex-situ* four days (dotted curve), and two months (plain curve) after ALD processing upon storage at ambient conditions. The preservation of peak intensity and position confirms that time-dependent organic decomposition does not occur during these periods.