Supplementary material (ESI) for Journal of Materials Chemistry

Fabrication of a Nanoparticle Gradient Substrate by Thermochemical Manipulation of an Ester Functionalised SAM

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Supplementary Information

Legend for figures

Fig. S1 Survey XPS spectra (0-700 eV) for (a) **MHBTE** (**I**), (b) **MHBME** (**II**) and **MHBA** (**III**) SAMs

Fig. S2 Survey XPS spectra (0-700 eV) for **MHBTE** (**I**) SAM after hydrolysis.

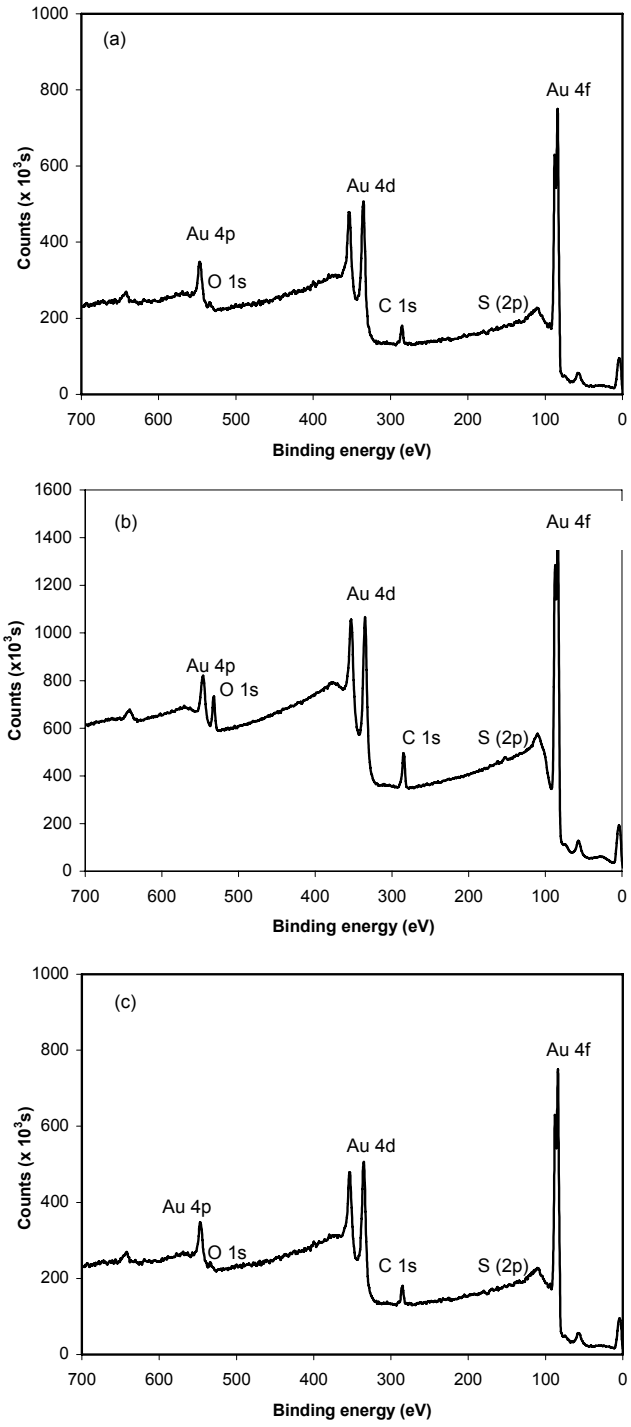

Fig. S1

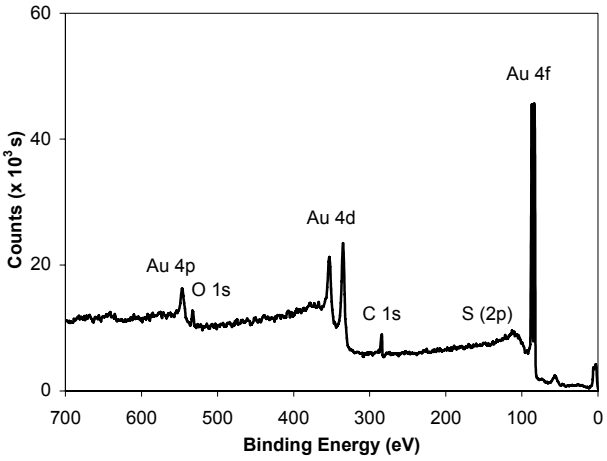

Fig. S2

Equations

$$d[MHBTE]/dt = k[H^+][MHBTE] \quad \textbf{equation 1}$$

where d[MHBTE]/dt denotes the rate of the hydrolysis

k denotes the second order rate constant

$[H^+]$ denotes the acid concentration

[MHBTE] denotes the concentration of **MHBTE (V)**

$$k = Ae^{-E_a/RT} \quad \textbf{equation 2}$$

where k denotes the rate constant

A denotes the frequency factor or the pre-exponential factor

E_a denotes the activation energy

R denotes the gas constant

T denotes the temperature

$$d[MHBTE]/dt = k'[MHBTE] \quad \textbf{equation 3}$$

Integrating **equation 3** with integrals of t and 0 gives **equation 4**.

$$\ln ([MHBTE]_t/[MHBTE]_0) = k't \quad \textbf{equation 4}$$

where $[MHBTE]_t$ denotes the concentration at time t

$[MHBTE]_0$ denotes the initial concentration

$$\cos\theta = f_1\cos\theta_1 + f_2\cos\theta_2 \quad \textbf{equation 5}$$

where θ denotes the contact angle of the heterogeneous surface.

θ_1 and θ_2 denotes the contact angle of the homogeneous surface for adsorbate 1 and adsorbate 2, respectively.

f_1 and f_2 are the fraction of coverage for the adsorbate 1 and 2 over the entire surface, respectively.

Table S1. Second-order rate constants of the acid-catalysed hydrolysis of **MHBTE (I)** SAM determined using the Cassie equation.

Temperature (°C)	k (x 10^{-4} dm^3 mol^{-1} s^{-1}) Cassie equation
80.4 ± 1	-10.00 ± 0.02
73.5 ± 1	-5.00 ± 0.01
64.4 ± 1	-3.00 ± 0.02
54.4 ± 1	-2.00 ± 0.04
48.4 ± 1	-0.50 ± 0.01