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Understanding the Formation of Bimetallic Pd-Au Co-catalysts on TiO₂

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Transition metal modified titania (M/TiO₂, M = Pd, Pt or Au) photocatalysts have shown excellent activity for H₂ production in alcohol-water mixtures under UV excitation [1, 2]. Recently, we have found that a 0.25 wt.% Pd-0.25 wt.% Au/TiO₂ photocatalyst demonstrated a superior H₂ production rate of 68 mmol g⁻¹ h⁻¹ compared to monometallic 0.50 wt.% Pd/TiO₂ (43.0 mmol g⁻¹ h⁻¹) or 1.00 wt.% Au/TiO₂ (34.2 mmol g⁻¹ h⁻¹) photocatalysts evaluated in 80 vol.% ethanol solutions at a UV flux (365 nm, 6.5 mW cm⁻²) comparable to that present in sunlight at the Earth's surface. To rationalise the high H₂ production activities of the Pd-Au/TiO₂ photocatalysts, we characterize the materials using UV-Vis absorbance, TEM, XRD, XRF, N₂ physisorption and lab-XPS. Preliminary data strongly suggests the formation of bimetallic Pd-Au nanoparticles on the surface of TiO₂ responsible for the increased H₂ evolution rates. Using higher resolution instrumentation, such as synchrotron XPS, XAS and HR-STEM, we further probed the question of 'what is the Pd-Au nanoparticle structure (random, core-shell, ordered binary alloy)?' Synchrotron Pd 3d and Au 4f XPS data (hν = 1486.7 eV) confirmed the presence of Pd(0)-Au(0), whilst HR-STEM/EDS showed Pd-Au nanoparticles of size 2-5 nm composed of randomly arranged Pd and Au atoms with a near 1:1 atomic ratio. Pd K-edge and Au L3-edge EXAFS analyses found the onset of alloy formation to occur around 160 °C in a 1 vol.% H₂ atmosphere and nearest neighbour Pd-Au bond lengths of 2.08-2.35 Å were intermediate to that of Pd and Au metal in good agreement with HR-STEM data (Figure 1). Results here guide the rational design of new and improved M/TiO₂ photocatalysts for H₂ production.

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Figure 1. A-HRTEM, B-STEM-EDS, C-Pd and D-Au L3 FT-EXAFS.

References:

[1] Al-Azri, Z.H.N.; Chen, W.T.; Chan, A.; Jovic, V.; Ina, T.; Idriss, H.; Waterhouse, G.I.N. *J.Catal.* 2015, 329, 355-367.

[2] Chen, W.T.; Chan, A.; Al-Azri, Z.H.N.; Dosado, A.G.; Nadeem, M.A.; Sun-Waterhouse, D.; Idriss, H.; Waterhouse, G.I.N. *J.Catal.* 2015, 329, 499-513.

Keywords or phrases (comma separated)

Bimetallic, Pd, Au, titania, TiO₂, Photocatalyst, XPS, TEM, XAS, EXAFS

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What is your gender?

Male

Primary author(s) : Mr CHAN, Andrew (The University of Auckland)

Co-author(s) : Dr SUN-WATERHOUSE, Dongxiao (School of Chemical Sciences, The University of Auckland, New Zealand); Dr WATERHOUSE, Geoffrey (School of Chemical Sciences, The University of Auckland, New Zealand); Prof. IDRIS, Hicham (SABIC, Corporate Research and Innovation (CRI), KAUST, Saudi Arabia)

Presenter(s) : Mr CHAN, Andrew (The University of Auckland)

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