CuO/TiO_2 - Low cost semiconductor photocatalysts for solar hydrogen production

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CuO/TiO_2 photocatalysts (CuO loadings 0-15 wt.%) were prepared, characterized and evaluated for H_2 production from ethanol-water mixtures (80 vol.% ethanol, 20 vol.% H_2O) under UV excitation. Degussa P25 TiO_2 (85 wt.% Anatase, 15 wt.% Rutile) was used as the support phase. XRF, EDAX, EPR, Raman and TGA measurements showed that the CuO content in the samples increased linearly with nominal CuO loading. XPS and Cu L-edge NEXAFS analyses verified that Cu(II) was the dominant copper species in the near surface region of the photocatalysts. At CuO loadings < 5 wt.%, no CuO crystallites were seen by TEM, indicating that the CuO was highly dispersed over the TiO_2 support, possibly as a monolayer dispersion. At CuO loadings > 5 wt.%, CuO crystallites of diameter 1-2 nm were identified. Photoluminescence studies established that CuO deposition strongly suppresses electron-hole pair recombination in TiO_2. The photocatalytic activity of CuO/TiO_2 photocatalysts was highly dependent on the CuO loading, with 1.25 wt.% CuO being optimal (H_2 production rate = 21 mmol g^{-1} h^{-1}). Above 1.25 wt.% CuO, the H_2 production activity of the CuO/TiO_2 photocatalysts decreased sharply with increasing CuO loading. The decrease in activity at higher CuO loadings coincided with the onset of CuO nanoparticle formation, which is postulated to alter electronic properties the CuO/TiO_2 interface in a manner detrimental to H_2 production. CuO itself was inactive as a photocatalyst under the applied testing conditions. Results suggest that sub-monolayer coverages of CuO on TiO_2 are highly beneficial for H_2 generation, and support the development of a sustainable H_2 economy.

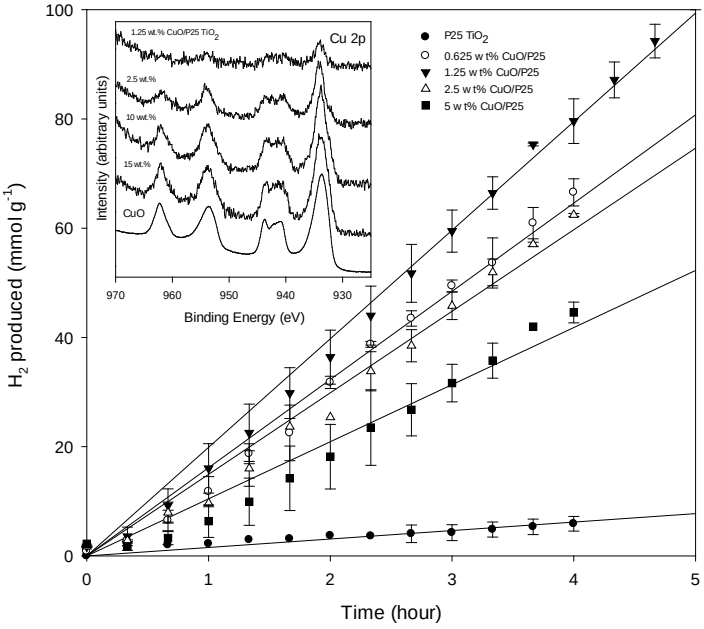

Fig. 1. Plots of H_2 production versus time for various CuO/TiO_2 photocatalysts. The inset shows Cu 2p XPS spectra for selected CuO/TiO_2 photocatalysts and bulk CuO.

The Cu 2p XPS spectra for the CuO/TiO_2 photocatalysts were similar to data collected for a CuO reference powder, with Cu $2p_{3/2}$ = 933.7 eV and Cu $2p_{1/2}$ = 953.6 eV (2:1 area ratio). The presence of characteristic "shake up" satellites ~7 eV above the Cu 2p peaks, provide further evidence for the presence of paramagnetic Cu^{2+} species (formally $3d^9$). No CuO reduction occurred under UV excitation.