

### 7.4 % Efficient Solar to Chemical Conversion with a Pt Nano-dotted and Surface-methylated n-Si Electrode

Susumu Takabayashi and Yoshihiro Nakato

Division of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan, and CREST, JST, Japan

The main target of recent solar-cell studies is to lower the fabrication cost without reducing the conversion efficiency. The remarkable merit of solar to chemical conversion is that it is not necessary to use expensive, not-enough-conductive TCO (transparent conductive oxide) films. In the present work, we report that 7.4 % efficient solar to chemical conversion is achieved through photodecomposition of HI into H<sub>2</sub> and I<sub>2</sub> with a Pt nano-dotted and surface-methylated n-Si electrode.

We reported before<sup>1</sup> that Pt nano-dotted n-Si electrodes showed very high photovoltages ( $V_{OC}$ ) of 0.62-0.64 V in 8.6 M HBr / 0.05 M Br<sub>2</sub>, exceeding that of p-n junction Si solar cells, owing to a unique effect of metal nano-contact. Unfortunately, the n-Si electrodes degraded within 1 h due to surface oxidation. Alkylation of Si surfaces has lately attracted considerable attention from the standpoint of surface modification. A merit is that surface alkyl groups can prevent the Si surface from oxidation.<sup>2</sup> However, the surface methylation retarded interfacial electron transfer reactions. This dilemma could be removed by a combination with Pt nano-dot coating, which acted as an efficient catalyst.

The n-Si used was (111) oriented single crystal wafers with a 825  $\mu$ m thickness and a 1-5  $\Omega$ cm resistivity. The surface methylation was carried out by a photo-chlorination / Grignard reaction technique, reported by Bansal *et al.*<sup>3</sup> and Okubo *et al.*<sup>4</sup> Pt nanoparticles were deposited electrochemically on the methylated n-Si(111) surface in an aqueous solution of 5 mM K<sub>2</sub>PtCl<sub>6</sub> and 0.1 M LiClO<sub>4</sub> at -1.0 V vs. Ag|AgCl (*sat.* KCl). The electricity passing across the n-Si surface was 83 mC cm<sup>-2</sup>. Photodecomposition of HI was performed using an electrochemical cell equipped with a methylated and Pt-dotted n-Si electrode and a Pt-plate counter electrode, both immersed in 7.6 M HI / 0.05 M I<sub>2</sub>, under simulated solar (AM 1.5G, 100 mW cm<sup>-2</sup>) illumination, with no external bias.

Figure 1 shows SEM images of (a) the Pt-dotted and H-terminated n-Si(111) and (b) the Pt-dotted and methylated n-Si(111) surfaces. Pt was distributed relatively homogeneously all over the n-Si(111) surface. Figure 2 shows photocurrent density ( $j$ ) vs. potential ( $U$ ) curves under the simulated solar illumination. Interestingly, the  $V_{OC}$  for Pt-dotted and methylated n-Si(111) (0.55 V) is much higher than that for the Pt-dotted and H-terminated n-Si(111) (0.30 V). Moreover, the Pt-dotted and methylated n-Si(111) showed good stability even for 24-h continuous illumination.

Figure 3 shows the solar-to-chemical conversion efficiency ( $\phi_{Chem}^S$ ), obtained through photodecomposition of HI into H<sub>2</sub> and I<sub>2</sub>, as a function of the HI concentration of the electrolyte solution. The  $\phi_{Chem}^S$  was calculated by using equations below,

$$\phi_{Chem}^S = \frac{(\Delta G/e) \cdot j}{W}$$

$$(\Delta G/e) = E_{eq}(I_3^-/I^-) - E_{eq}(H^+/H_2)$$

where  $\Delta G$  is the Gibbs energy (in eV) for the

decomposition of HI into H<sub>2</sub> and I<sub>2</sub> (or I<sub>3</sub><sup>-</sup>),  $e$  the elementary charge (in C),  $j$  the observed photocurrent density (in mA cm<sup>-2</sup>), and  $W$  is the input solar energy (in mW cm<sup>-2</sup>). Experiments showed that the maximum  $\phi_{Chem}^S$  of 7.4 % was achieved in 3.2 M HI. This is the highest efficiency ever reported, apart from values reported for MOCVD-made high-quality multilayered electrodes.

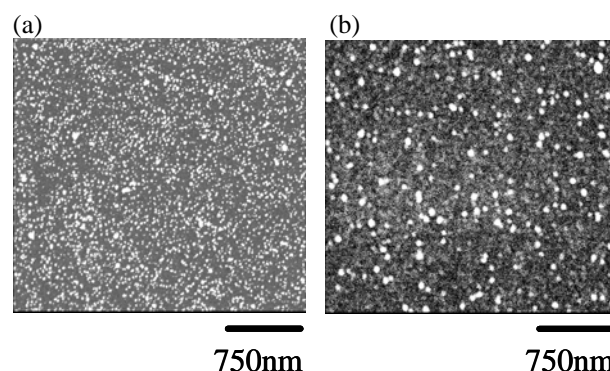


Figure 1 SEM images of (a) the Pt-dotted and H-terminated n-Si(111) and (b) the Pt-dotted and methylated n-Si(111) surfaces.

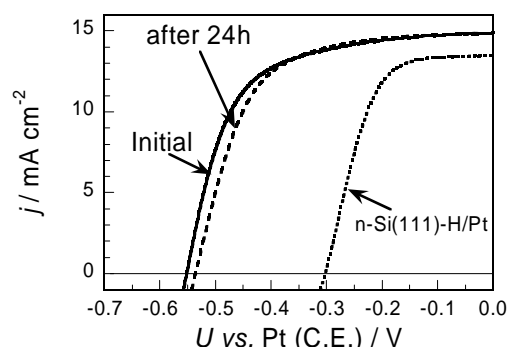


Figure 2  $j$ - $U$  curves (solid and broken curves) for n-Si(111)-CH<sub>3</sub>/Pt in 7.6 M HI / 0.05 M I<sub>2</sub> under simulated solar (AM 1.5G, 100 mC cm<sup>-2</sup>) illumination, compared with that (dotted curve) for n-Si(111)-H/Pt.

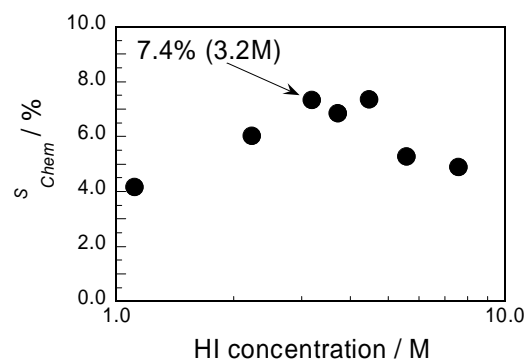


Figure 3 The solar-to-chemical conversion efficiency ( $\phi_{Chem}^S$ ) as a function of the HI concentration.

#### References

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