Importance of co-catalyst dispersion in Pt-functionalized graphitic carbon nitrides for solar fuel generation

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Graphitic carbon nitrides (g-CNs) demonstrate immense potential for efficient photocatalytic hydrogen generation, attributed to their high surface area and ability to absorb visible light.[1] Recently, g-CN's with supported single Pt atoms and very low loadings (<0.2 wt%) have been shown to give improved hydrogen evolution rates (HERs) on a per-Pt-atom basis.[2] Yet, low-loading, highly-dispersed Pt co-catalysts still cannot surpass the high HERs of the traditional photodeposition (PD), high-loading routes. Moreover, the unique g-CN support structure and morphology affects the resultant co-catalyst dispersion making structure-activity relationships difficult to establish based solely on HERs. By combining annular-dark-field scanning transmission electron microscopy (ADF-STEM) and photoreaction data, we systematically determine the contribution of co-catalyst dispersion and support structure on the photocatalytic performance of Pt/g-CNs.

To capture a range of support structures, three g-CN samples are selected based on the broadening of the (002)-peak observed in powder x-ray diffraction. Here, g-CN:1, g-CN:2, and g-CN:3 refer to g-CN materials with average domain sizes of 9.9, 4.5, and 3.2 nm, respectively. When loaded with ~5 wt% Pt via PD, the HER of g-CN:2 is >2x higher than both g-CN:1 and g-CN:3. Figure 1 compares the Pt nanoparticle size distributions of each used photocatalyst based on ADF-STEM (insets). Each photocatalyst shows a bimodal distribution and g-CN:2, with ~55% of Pt particles <2 nm in size (Figure 1(b)), possesses the highest co-catalyst dispersion characterized by a specific surface area (SSA) of 25 m^2/g_{Pt}. On the other hand, the SSA of Pt on g-CN:1 and g-CN:3 are 10 and 17 m^2/g_{Pt}, respectively. By normalizing the HER of each 5 wt% Pt/g-CN by the number of exposed surface Pt atoms, the turn over frequency (TOF) of each g-CN material can be derived and are found to correlate with the g-CN average domain size.

With a TOF of 133/hr, g-CN:1 is the most 'active' photocatalyst but suffers from a low surface site density meaning that co-catalyst dispersion in Pt/g-CN's can be a limiting factor for photocatalytic performance. To reduce Pt consumption and maximize co-catalyst dispersion, a chemical deposition (CD) approach was employed to stabilize single Pt atoms on g-CN:1.[3] As shown in Figure 2(a), the HER of g-CN:1 can be improved by ~13% with a nominal 10x reduction in Pt loading. This improvement is attributed to the presence of predominately sub-nanometer Pt particles, as shown through ADF-STEM imaging and the corresponding histogram in Figures 2(b)-(c). Structure-activity relationships in Pt-functionalized g-CNs will be discussed as well as ongoing efforts to improve the photocatalytic performance in this system.

1. X. Wang et al. *Nat. Mater.* **2009**, *9*, 76-80.

2. X. Li et al. *Adv. Mater.* **2016**, *28*, 2427-31.

3. Z. Chen et al. *Adv. Funct. Mater.* **2017**, 1605785.

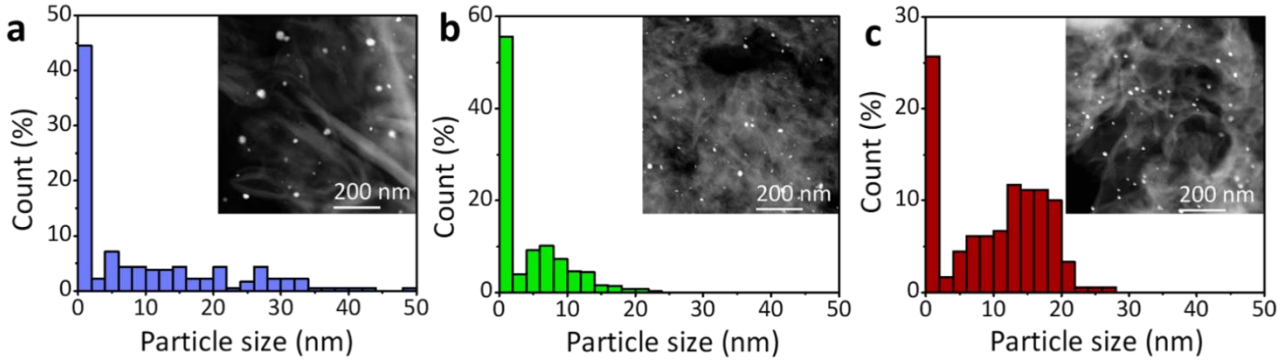

Figure 1: Co-catalyst particle size distributions of used 5 wt% Pt/g-CN's: (a) g-CN:1, (b) g-CN:2, and (c) g-CN:3. Insets depict representative ADF-STEM images of each photocatlyst.

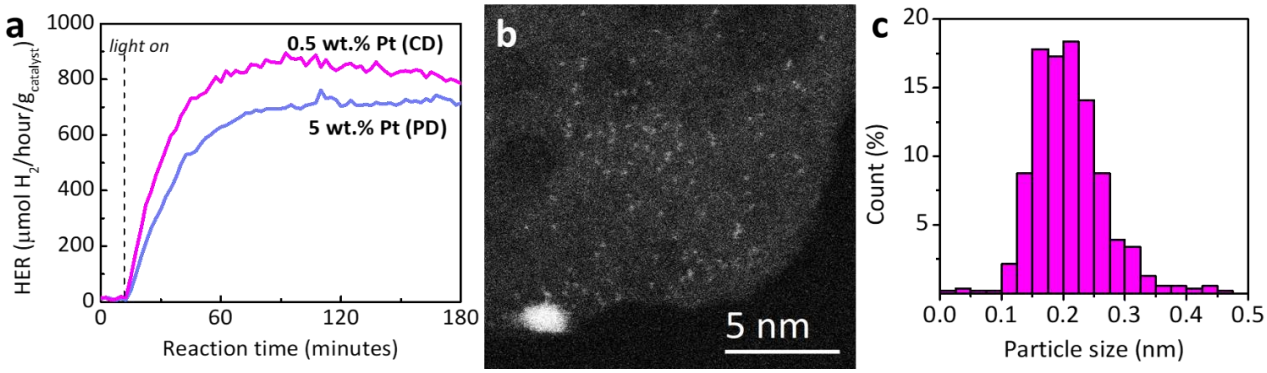

Figure 2: (a) Hydrogen evolution rates for two different Pt loading methods on g-CN:1. (b) ADF-STEM image of fresh 0.5 wt% Pt/g-CN:1 and (c) corresponding Pt particle size histogram.

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