Importance of Co-catalyst Dispersion in Pt-functionalized Graphitic Carbon Nitride Photocatalysts

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Graphitic carbon nitrides (g-CN's) demonstrate immense potential for efficient photocatalytic hydrogen generation, attributed to their high surface area and ability to absorb visible light [1]. Due to kinetic limitations afforded during synthesis, involving calcination of N-rich precursors, g-CN's contain a range of residual hydrogen, perturbing structural condensation [2]. Efforts to improve the efficiency of g-CN's have focused on reducing H-content to give higher hydrogen evolution rates (HER's), suggesting that amine ($N-H_x$) defects hinder charge transfer [2]. However, the need of Pt remains as g-CN_xH_y must be functionalized with ~1-5 wt% Pt to achieve appreciable HER's. Recently, g-CN's with supported single Pt atoms and very low loadings (<0.2 wt%) have been shown to give improved HER's on a per-Pt-atom basis [3]. Yet, low-loading, highly-dispersed Pt co-catalysts still cannot surpass the high HER's 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 HER's. 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-CN's.

To capture a range of support structural disorder, 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, determined by Scherrer analysis. When loaded with ~5 wt% Pt via PD, the HER of g-CN:2 (at 1600 μmol/h/$g_{catalyst}$) is >2x higher than both g-CN:1 (at 750 μmol/h/$g_{catalyst}$) and g-CN:3 (at 600 μmol/h/$g_{catalyst}$). Figure 1 compares the Pt nanoparticle size distributions of each used photocatalyst based on ADF-STEM imaging at 200 kV (insets). As shown in Figure 1, each sample 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, g-CN:1 contains ~45% <2 nm particles with larger particles up to 50 nm in size (Figure 1(a)) whereas g-CN:3 has the lowest proportion of <2 nm particles at ~25% (Figure 1(c)) giving specific surface areas of 10 and 17 m^2/g_{Pt}, respectively. By normalizing HER of each 5 wt% Pt/g-CN by the number of exposed surface Pt atoms (based on the SSA's and loading), 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 hydrogen evolution 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 utilizing $NaBH_4$ as a reducing agent for aqueous Pt^{4+} ions was employed to stabilize single Pt atoms on g-CN:1 [4]. 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 show through ADF-STEM imaging and the corresponding histogram in Figures 2(b)-(c). Using MIPAR image analysis software, the equivalent diameter of each Pt nanoparticle from several images of 0.5 wt% Pt/g-CN:1 were calculated yielding the

particle size histogram pictured in Figure 2(c). For the 0.5 wt% Pt/g-CN:1 photocatalyst, an SSA of 155 m^2/g_{Pt} is achieved giving a total surface area increase of 31% when the decrease in Pt loading is accounted for. Structure-activity relationships in Pt-functionalized g-CN's will be discussed as well as ongoing efforts to improve the photocatalytic performance in this system [5].

References:
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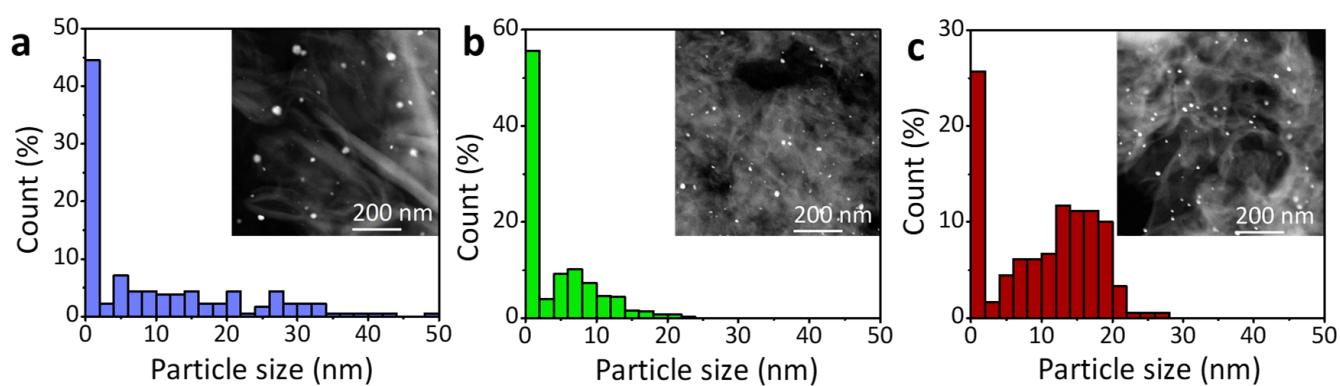
Figure 1. Co-catalyst particle size distributions of 5 wt% Pt/g-CN's after undergoing ~5 hours of visible-light hydrogen evolution photoreactions: (a) g-CN:1, (b) g-CN:2, and (c) g-CN:3. Insets depict representative ADF-STEM images of each photocatalyst.
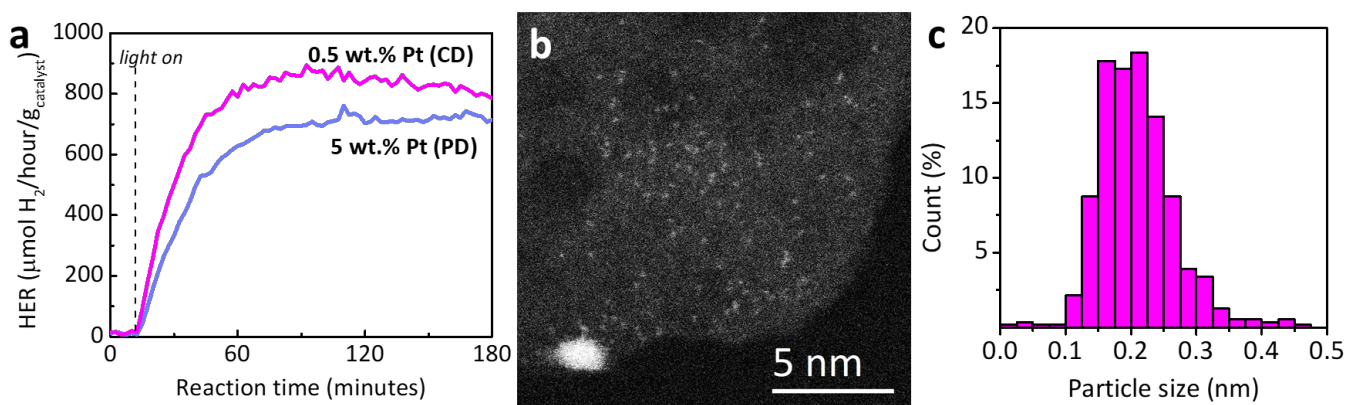

Figure 2. (a) Hydrogen evolution rate comparison for two different Pt loading methods on g-CN:1 – low loading (0.5 wt%) using chemical deposition (CD) and high loading (5 wt%) using photodeposition (PD). (b) ADF-STEM image of the 0.5 wt% Pt/g-CN:1 and (c) corresponding Pt particle size histogram.