

## Efficient cocatalyst design: a study of Pt photodeposition on WO<sub>3</sub>

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For efficient usage of photocatalysis, semiconductor systems need to be developed which i) are able to absorb visible light, ii) have proper band positions, iii) have a low overpotential, and iv) repress electron/hole recombination. To tackle the latter two issues, cocatalytic nanoparticles can be loaded on semiconductor materials. These nanoparticles will lower the overpotential of the photocatalytic system and act as a beacon for the charge carriers, thereby effectively improving charge carrier separation and thus repressing electron/hole recombination.<sup>1,2</sup> In water splitting, noble metals (*e.g.* Pt, Pd) can be employed as hydrogen evolution cocatalysts, whereas metal oxides (*e.g.* RuO<sub>2</sub>, IrO<sub>2</sub>) are very suitable cocatalysts for water oxidation.

Photodeposition is often considered to be a convenient, effective and green technique to deposit cocatalytic nanoparticles on semiconductor materials. However, on a fundamental level, photodeposition is not as simple as it seems. This is reflected in a limited amount of studies demonstrating that physicochemical properties of as-deposited nanoparticles, such as the oxidation state, size and dispersion, are dependent on *e.g.* the employment of a sacrificial reagent or adjustment of the pH.<sup>3,4</sup> Research on photodeposition should be stimulated, as it is a promising technique to engineer cocatalytic nanoparticles with desired physicochemical properties.<sup>5</sup>

In this work, we investigated the influence of the sacrificial reagent methanol in the photodeposition of platinum (Pt) on tungsten oxide (WO<sub>3</sub>), which is a suitable water oxidation photocatalyst. We demonstrate that the employment of methanol has drastic consequences for i) the amount of Pt deposited, ii) the oxidation state of as-deposited Pt, and iii) the size and dispersion of the Pt nanoparticles. Furthermore, we demonstrate that small, metallic Pt particles can be engineered by employing photodeposition with the right conditions, followed by hydrogenation. The mechanisms behind the photodeposition process will be thoroughly discussed, as well as the lessons we can learn from these findings for further design of more efficient photocatalyst/co-catalyst systems. Furthermore, we are investigating charge carrier kinetics of as-synthesized samples by femtosecond transient absorption spectroscopy, which further demonstrates the need to carefully engineer the physicochemical properties of photodeposited Pt co-catalytic nanoparticles.

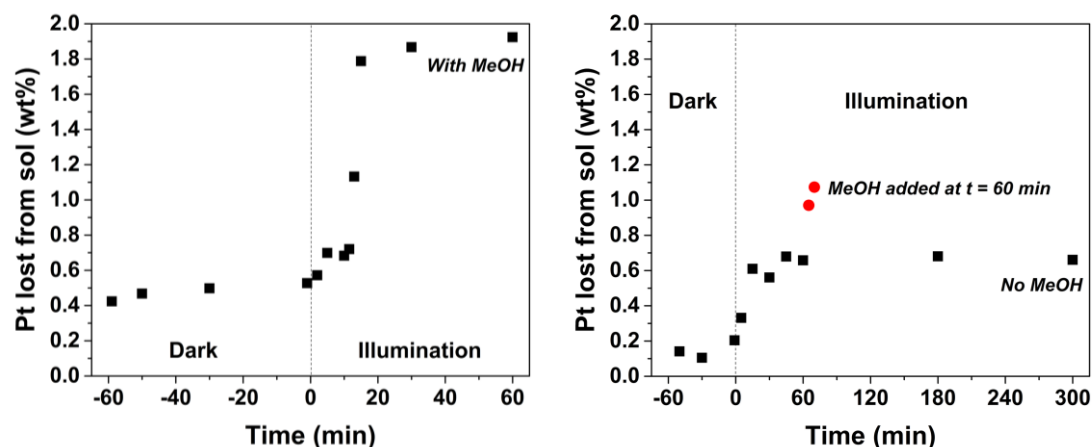


Figure 1. Amount of Pt lost from a  $\text{H}_2\text{PtCl}_6$  solution in wt% after (left) photodeposition with methanol and (right) photodeposition without methanol (or MeOH added after 1 hour of illumination)

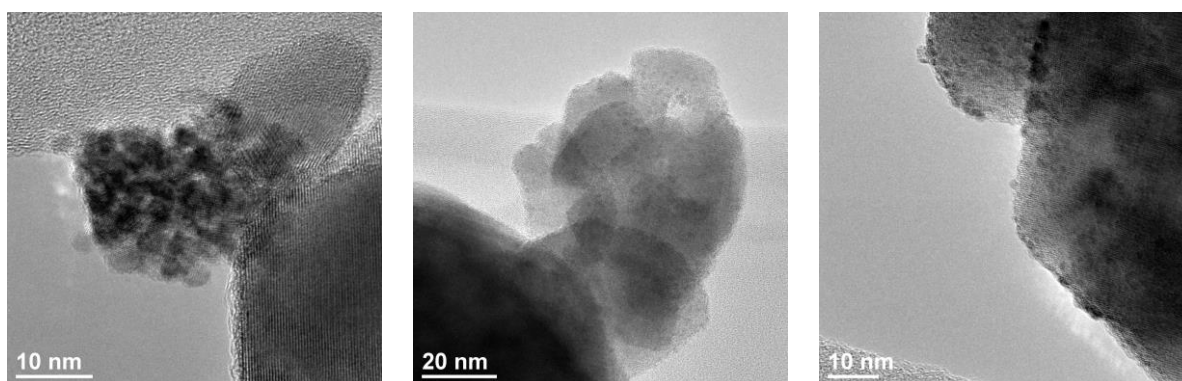


Figure 2. HR-TEM images of Pt/WO<sub>3</sub> obtained by (left) 1 hour of photodeposition using MeOH (aim: 2 wt% Pt, loaded: 1.92 wt%), (middle) 5 hours of photodeposition using no MeOH (aim: 2 wt% Pt, loaded: 0.66 wt%) and (right) 5 hours of photodeposition using no MeOH (aim: 10 wt% Pt, loaded: 1.4 wt%)

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