

Pt-Au-ZnO hybrid nanostructures: Effect of crystal structure on photocatalytic properties.

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Metal-semiconductor hybrid nanoparticles have attracted wide interest for many applications such as photoelectrochemical water splitting, photocatalysis, biomedical imaging, photodetectors, drug delivery and so on, owing to their promising optical and optoelectronic properties. In many instances, new collective properties emerge in hybrids differing significantly from a simple linear combination of the individual component's properties. The ultimate properties of hybrid nanoparticles largely depend on the structure, morphology, the ratio between hybrid components and to a greater extent on the nature of the metal-semiconductor interface. The synthetic approach has a considerable effect on the structure, morphology and therefore the physical properties of hybrid nanoparticles.

In the present study, we employed (HR)TEM, HAADF-STEM and EDX to measure and characterize Pt-Au-ZnO three component heterostructures prepared by two different methods. Then we evaluated how the structure, morphology and the nature of the metal-semiconductor interface influence the photocatalytic performance of different Pt-Au-ZnO nanostructures. Pt-Au-ZnO heterostructures were prepared by two distinct techniques. In technique 1, Au-ZnO particles were first prepared using a Au seed mediated heterogeneous nucleation approach, where the growth of ZnO crystals occurred at Au seeds at 175 °C. TEM analysis confirmed ZnO particles have a hexagonal pyramidal shape where the Au nanoparticle was attached to the center of hexagonal basal facet. HRTEM confirmed that an epitaxial connection exists at Au-ZnO interface. Afterwards, Pt nanoparticles were deposited at Au-ZnO utilizing a photodeposition approach (s-Pt-Au-ZnO - Figure 1a). TEM imaging and HAADF STEM imaging showed that small Pt nanoparticles were deposited only at the Au site of Au-ZnO hybrid nanoparticles. In technique 2, a multistep photodeposition approach was utilized to deposit Au and then Pt at pre-synthesized prolate shaped ZnO crystals (p-Pt-Au-ZnO - Figure 1b). TEM revealed that several Au nanoparticles deposited at ZnO crystals during the 1st deposition step, however the connection at the Au-ZnO interface was non-epitaxial. Interestingly, during the 2nd photodeposition step small Pt nanoparticles deposited at all over Au-ZnO surface at both Au and ZnO sites as confirmed by TEM and DF-STEM imaging. HAADF-STEM imaging combined with EDX mapping was employed to identify each chemical component in both Pt-Au-ZnO systems. Furthermore, XPS analysis confirmed that Au and Pt in both hybrid systems were in metallic form.

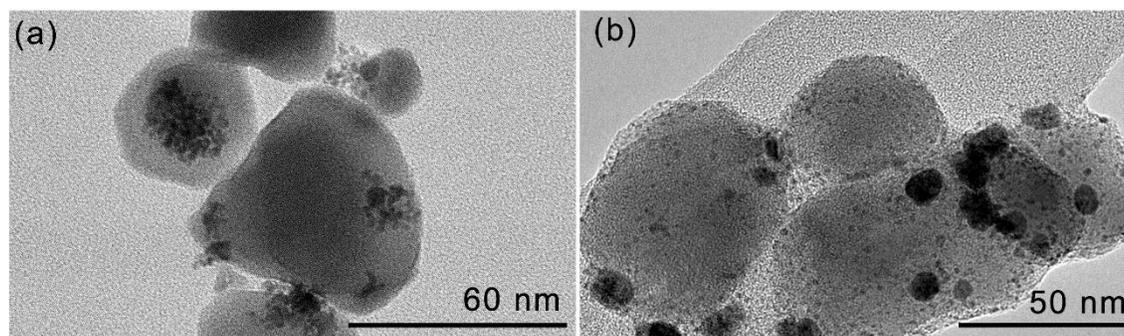


Figure 1. TEM images of (a) s-Pt-Au-ZnO and (b) p-Pt-Au-ZnO

Then we evaluated the photocatalytic properties of s-Pt-Au-ZnO and p-Pt-Au-ZnO by studying the photocatalytic colour loss of an organic dye molecule, toluidine blue. *In situ* ultra violet-visible spectroscopy was used to measure the change in absorption over time, under UV illumination of a mixture of catalyst and toluidine blue.

The photocatalysis experiments revealed that s-Pt-Au-ZnO hybrids possess superior catalytic properties compared to p-Pt-Au-ZnO. The property enhancement could be attributed to the efficient electron transfer at the epitaxial interface in s-Pt-Au-ZnO particles. This conclusion is further corroborated by the fact that Pt exclusively deposited at Au sites when Au-ZnO interface was epitaxial. On the other hand, Pt deposited all over Au-ZnO surface when Au-ZnO interface was non-epitaxial. This study highlights the importance of identifying the structure-property relationships in nanomaterials to assess their suitability for prospective applications.