Sub 1 nm aggregation-free AuPd nanocatalysts for visible-light-driven hydrogen evolution from formaldehyde

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Abstract: Novel amino-functionalized organosilica nanotubes were facilely synthesized. By using the unique nanotube as the supports, a series of AuPd alloy nanoparticles with the average size of sub 1 nm could be synthesized and were applied for the hydrogen evolution from formaldehyde aqueous solution. These bimetallic AuPd nanocatalysts exhibited remarkably improved catalytic activity under visible light irradiation and the highest initial TOF value of 241.7 h^{-1} could be achieved at the room temperature. Furthermore, these ultrasmall nanocatalysts exhibited high reaction stability and no aggregation of metal nanoparticles was observed even after 5 recycles.
Keywords: organosilica nanotubes, AuPd alloy, photocatalytic hydrogen evolution.

1. Introduction

Hydrogen is widely utilized in the petroleum and chemical industries.[1,2] Many studies have confirmed that small metal nanoparticles can act as catalysts and significantly accelerate the hydrogen evolution rate from formaldehyde alkaline solution.[3,4] However, using small metal nanoparticle as catalysts suffers from the aggregation, leading to the decreased activity. Herein, we report the synthesis of benzene-bridged organosilica nanotubes containing amino groups in the framework and its encapsulation of AuPd alloys in the nanotube channels for the visible-light-driven hydrogen evolution from formaldehyde.[5]

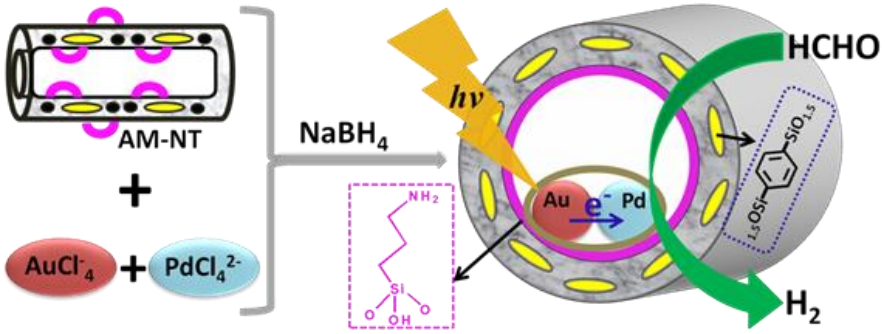

Figure 1. Synthetic routes and photocatalytic hydrogen evolution of amino-functionalized organosilica nanotubes supported AuPd alloy nanoparticles.

2. Experimental (or Theoretical)

100 mg nanotube was dispersed in 30 mL water, then $HAuCl_4$ and H_2PdCl_4 was added, and then stirred for 24 h at room temperature. 2 mL 1.0 M $NaBH_4$ was added and stirred for 4 h. The mixture was filtered, washed and dried at room temperature.

In a typical experiment, 0.04 mmol AuPd immobilized on nanotubes was added to a fresh HCHO and NaOH solution (100 mL) after being purged with N2 for 0.5 h. The reaction was operated at room temperature with a visible light ($\lambda > 420$ nm) illumination.

3. Results and discussion

The TEM images of the as-prepared Au, Pd and AuPd show that almost all the nanoparticles are homogeneously distributed on the surface of amino-functionalized organosilica nanotubes with an ultrafine size distribution of about 0.8 nm (Figure 2).

The photo absorption properties of Au and AuPd nanoparticles on nanotubes were studied by the UV/vis diffuse reflectance spectrometry. The organosilica nanotube support did not contribute to any visible

light absorption. In contrast, the Au and AuPd alloy nanoparticles supported on the nanotubes exhibited obvious absorption ability in visible-light region. The characteristic absorption peak at 520 nm due to the LSPR effect of Au nanoparticles could be easily observed.

The catalytic hydrogen evolution from alkaline formaldehyde of all the as-prepared samples was tested in a 100 mL 0.3 M formaldehyde solution containing 0.04 mmol AuPd at room temperature. It was found that the catalytic activity of bimetallic AuPd were higher than that of monometallic Au or Pd and gave the highest hydrogen amount of about 130 mL. The higher activity of AuPd nanocatalysts could be primarily attributed to the shorter tube length (~ 60 nm) and much smaller well-dispersed particle size (sub 1 nm), which can reduce the diffusion limitation of reactants and increase the active sites.

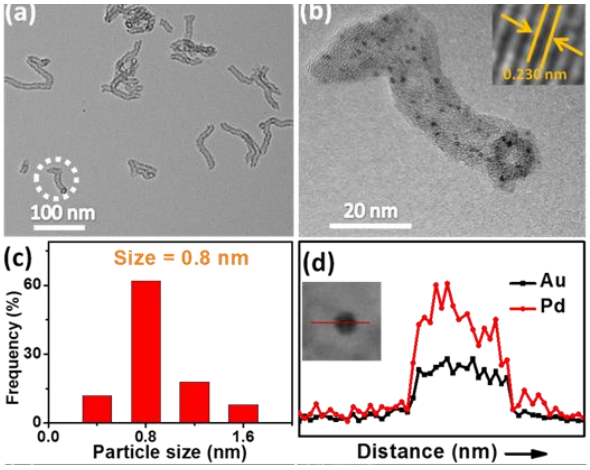

Figure 2. TEM images of AuPd nanocatalysts.

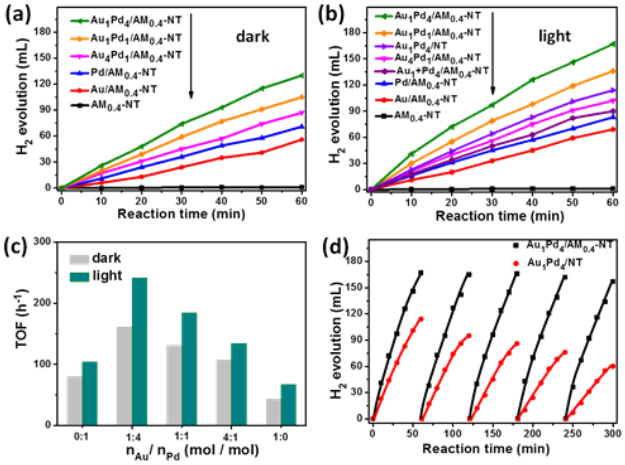

Figure 3. Time-dependent hydrogen evolution curves.

4. Conclusions

In summary, the novel cut-shorted robust amino-incorporated organosilica nanotubes with large mesopores have been successfully synthesized under facile conditions. By using the unique amino-functionalized origanosilica nanotubes as the supports, a series of well-dispersed and ultrafine AuPd alloy nanoparticles were designed and prepared. The as-prepared heterogeneous catalysts exhibited superhigh hydrogen evolution performance from formaldehyde aqueous solution under visible light illumination, which was attributed to the ultrafine AuPd alloy nanostructures and the efficient electron transfer from Au with LSPR effect to active Pd sites. To the best of our knowledge, this is the first study of AuPd alloy nanoparticles for hydrogen evolution from formaldehyde aqueous solution under visible light illumination. We believe that this work might open up a new way to obtain H_2 from formaldehyde and provides an integration platform for the heterogeneous catalysis in artificial photosynthesis systems.

References

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