Copper Nanowires: A Substitute for Noble Metals in Enhancing Photocatalytic H_2 Generation

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Abstract: Microwave-assisted hydrothermal approach was developed as a general strategy to decorate copper nanowires with nanorods or nanoparticles (NPs) of oxides, metal sulfides and metal organic frameworks (MOFs). The microwave irradiation induced local “super hot” dots generated on the CuNWs surface, which initiated the adsorption and chemical reactions of the metal ions, accompanied by the growth and assembly of NRs (NPs) building blocks along the metal nanowires’ surfaces. This work shows the utilization of low cost copper nanowires as a substitute for noble metals in enhanced photocatalytic H_2 generation. It also exhibits a general strategy for fabricating highly active H_2-production photocatalysts.

Keywords: Microwave synthesis, copper nanowires, TiO_2

1. Introduction

Nanocomposites have received increasing attention owing to the enhanced activity resulting from synergic effects.[1-3] Most nanocomposites are usually fabricated by uniformly mixing different components via either physical or chemical methods. Both theoretical predictions and experimental results demonstrate that the controlling assembly of nanoparticle building blocks onto the substrates usually generates fascinating properties owing to the unique structure and morphology,[4, 5] such as butterfly wing, fishscale, and lotus leaf for cold-proof, selective light absorbance, and self-cleaning usually found in nature. Herein, we developed a general strategy to decorate copper nanowires (CuNWs) with nanorods (NRs) or nanoparticles (NPs) of metal oxides, metal sulfides and metal organic frameworks (MOFs). Learning from nature that plants grow *via* photosynthesis in which light is harvested by leafs and photoelectrons are generated and transferred through chlorophyll, such TiO_2/CuNWs hybrid photocatalyst, with the morphology of TiO_2 NRs directly growth from the ultralong copper nanowire (CuNWs), also favors the photocatalytic process. The well-assembled TiO_2 NRs promote the light harvesting via multiple reflections to generate photoelectrons while the one-dimensional CuNWs facilitate the transfer and gathering of photoelectrons, leading to the high H_2-production rate via photocatalytic water reduction.

2. Experimental (or Theoretical)

In a typical synthesis, 0.20 g of CuNW was dispersed under ultrasonication for 30 minutes in 24 mL of $TiCl_3$ aqueous solution of different concentrations to form a red-brown metallic luster suspension. Then the mixture was moved to a 40 ml quartz vessel with a Teflon lid. It was treated at 150 °C for 30 min with a heating rate of 13 °C min-1 and with an initial pressure of 35 bar by nitrogen in a single chamber microwave digestion system (Ethos TC. Milestone), and then cooled down to room temperature by circulation condensate. The reaction chamber was fitted with a temperature probe and a pressure probe to track the real time reaction situation. The desired time, temperature and pressure were programmed by using Milestone's Easy Control Software. After the reaction, the resulting powder was washed with deionized water and absolute ethanol for 3 times, and tried in a vacuum at 80 °C for 4 h.

3. Results and discussion

As shown in Figure 1a-c, both the field emission scanning electron microscopy (FESEM) and the transmission electron microscopy (TEM) images reveal that the CuNWs are uniformly coated by TiO_2 NRs with average diameter and length of 16 ± 5 nm and 120 ± 20 nm, respectively. The HRTEM image (Figure 1d) shows the close contact and obvious interface between TiO_2 and Cu. The lattice fringe spacings of ca.

0.248 and 0.324 nm correspond to (011) and (110) planes of rutile TiO_2 which is agreement with the attached selected area diffraction (SAED) pattern, while the lattice spacing of 0.255 nm matches (011) plane of cubic phase Cu. The lattice between TiO_2 (011) and Cu (011) matches very well, which favored the epitaxial growth of TiO_2 NRs onto the CuNWs. Based on the assembly of TiO_2 NRs on CuNWs, a plausible mechanism was proposed in Figure 2.As well known, the interface between a metal and a semiconductor resulted in the oriented electron flow to the metals, which could effectively inhibit the photoelectron-hole recombination. The direction of electron transfer was mainly determined by their work functions. In the Cu/TiO_2 samples, the high work function of Cu (4.65 eV) than that of TiO_2 (4.13 eV) ensured that the photoelectrons transferred from TiO_2 to CuNWs. Meanwhile, the strong Cu/TiO_2 interaction with large interface and the excellent electric conductivity of Cu created a Schottky barrier, which further facilitated the photoelectron transfers. Moreover, the CuNWs could also work as a co-catalyst for photocatalytic water reduction and the enriched photoelectrons on CuNWs promoted the H^+ reduction to produce H_2. Thus, the light harvesting, the separation of photoelectrons from holes, and the co-catalyst played important roles in determining the H_2 production efficiency.

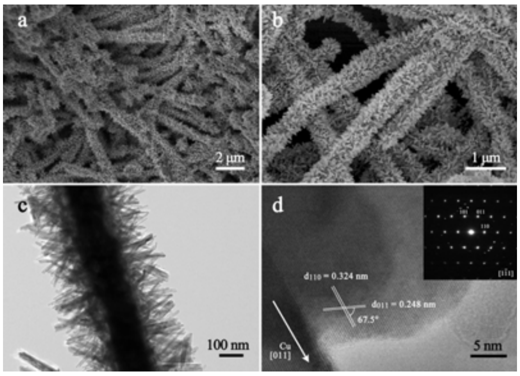

Figure 1. (a, b) FESEM images and (c) TEM image of TiO_2/CuNWs of C3 sample, (d) HRTEM image with the attached SAED pattern of C3 sample.

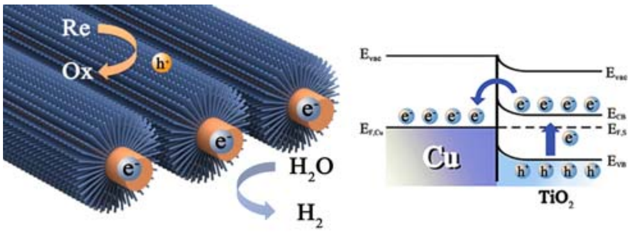

Figure 2. Plausible photocatalytic reaction mechanism of CuNWs/TiO_2.

4. Conclusions

In conclusion, we developed a general microwave-assisted hydrothermal strategy for decorating CuNWs with highly crystalline NRs or NPs of TiO_2, ZnS, MOF-5, and ZIF-8. Typically, The TiO_2/CuNWs exhibited the excellent activity among all the noble-metal free TiO_2 photocatalysts ever reported for H_2-production via water reduction under UV light irradiation. The direct growth of TiO_2 NRs onto CuNWs may increase the contact interfaces, enhance the light harvesting by multiple reflections and facilitate the photoelectron transfer and enrichment which further reduces photoelectron-hole recombination and promotes H^+ reduction to H_2.

References

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