Counter electrode electrocatalysts from one-dimensional coaxial alloy nanowires for efficient dye-sensitized solar cells

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HIGHLIGHTS

- Cu@M@Pt nanowire electrocatalysts are synthesized by galvanic displacement.
- Cu@M@Pt alloy catalysts are employed as CEs for DSSCs.
- The catalytic activity is markedly enhanced by alloying Cu, M with Pt.
- The DSSCs yield maximum efficiency of 8.21%.

GRAPHICAL ABSTRACT
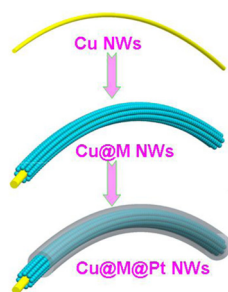
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ABSTRACT

Pursuit of cost-effective counter electrode (CE) electrocatalysts with no sacrifice of photovoltaic performances has been a persistent objective for advanced dye-sensitized solar cell (DSSC) platforms. Here we demonstrate the experimental realization of CE electrocatalysts from Cu@M@Pt (M = Fe, Co, Ni) coaxial alloy nanowires for efficient DSSCs. The reasonable electrocatalytic activity is attributed to work function matching of alloy CEs to potential of I^-/I_3^- and redistribute the electronic structure on the Pt surface. In comparison with 8.48% for the Pt nanotube CE based DSSC, the solar cells yield power conversion efficiencies up to 8.21%, 7.85%, and 7.30% using Cu@Fe@Pt, Cu@Co@Pt, and Cu@Ni@Pt NWs, respectively. This work represents an important step forward, as it demonstrates how to make the CE catalyst active and to accelerate the electron transport from CE to electrolyte for high-efficiency but cost-effective DSSC platforms.

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1. Introduction

Recent advances in energy research call for the rational design and synthesis of catalysts with unprecedented efficiency in catalyzing energy conversion reactions [1—4], especially the reduction reaction of I_3^- ions in liquid-junction dye-sensitized solar cells

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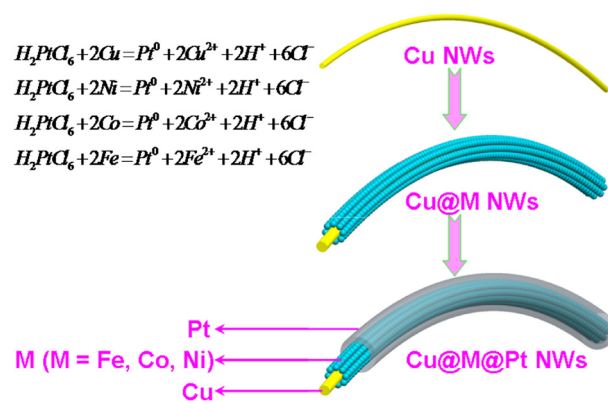
(DSSCs) [5–7]. Numerous studies on counter electrode (CE) electrocatalysts have lied on advanced Pt nanostructures [8,9] or replacement of cost-effective alternatives [10–13], with both electronic and geometric effects being used to explain I_3^- reduction. These CEs show a high electrical conductivity and electrocatalytic activity for I_3^- species, but the charge-transfer ability to liquid electrolyte is limited due to the low surface-to-volume ratio [14]. By controlling morphologies, it is realized to provide higher electrochemical−catalytic activity and charge-transfer capacity by increasing specific surface area [15]. Jung et al. reported periodically arranged catalytic Pt nanocup arrays with a controlled diameter and pitch size by UV-based nanoimprint lithography [9]. In comparison with planar Pt electrode, the CE from Pt nanocups displays more active sites for I_3^- reduction reaction since the electrolyte can contact the inner and outer surfaces of the nanocups. Another interesting work is from our recent report on double-layered polyaniline CE [16], in which a markedly enhanced catalytic activity and therefore conversion efficiency in its DSSC is recorded due to high surface area for I_3^- reduction and porous structure for electrolyte diffusion. Even though the great progresses in advances Pt nanostructures and promising candidates have been achieved, the large consumption of expensive Pt species or unsatisfactory long-term stability of metal-free candidates has made us fall into a dilemma.

Arguably one of the arising routes to reduce the fabrication cost of CE electrocatalysts with no sacrifice of catalytic activity is to alloy Pt with other metals/nonmetals or to replace Pt with Pt-free alloys [17–22]. Notably, the low-Pt alloys have been established as robust CE electrocatalysts for DSSCs [19,21,22], however, the dense Pt-based alloy films with spherical nanoparticles are believed to weaken the electronic effects for charge redistribution [23,24]. Recently, one-dimensional (1D) core/shell nanostructures are found to be more promising as electrocatalysts with much improved activity and durability [25]. The core/shell structure with Pt present around the thin shell not only maximizes the Pt exposure to electrolyte and minimizes the Pt utilization for CE catalysts, but also offers the desired core−shell interactions to tune both electronic and surface strain effects for optimal catalysis [26]. Moreover, the unconstrained 1D nanostructures having large aspect ratio in CE catalysts can direct conduction of electrons from fluorine-doped tin oxide (FTO) layer to alloy layers. The length of 1D Pt alloy nanostructures is normally sufficient to interface with redox electrolyte. This control over rapid electron transport recommends 1D core/shell nanostructures as ideal materials to manufacture advanced DSSCs. Herein, we present our study, for the first time, on tuning Cu@M@Pt (M = Fe, Co, Ni) nanowires (NWs) into the active CE catalysts for I_3^- reduction. The unique aspect of the ternary core/shell Cu@M@Pt NWs is that it allows the dual tuning of both surface strain and work function to achieve more rational control on catalytic activities and to facilitate catalysis optimization. Due to the much lower reduction potential of Cu^{2+}/Cu (+0.34 V vs. SHE) and M^{2+}/M (−0.44 V vs. SHE for Fe^{2+}/Fe, −0.28 V vs. SHE for Co^{2+}/Co, and −0.23 V vs. SHE for Ni^{2+}/Ni) pairs than $PtCl_6^{2-}/Pt$ (+0.735 V vs. SHE) [27], the superficial Cu and M atoms in Cu@M NWs can be displaced by $PtCl_6^{2-}$ ions when exposing to H_2PtCl_6 aqueous solution, as illustrated in Scheme 1, realizing the deposition of Pt layers on Cu@M NWs and core@shell structure of Cu@M@Pt NWs (see the Supporting Information for details).

2. Experimental

2.1. Synthesis of Cu NWs

The feasibility of synthesizing Cu NWs was confirmed by a mild

$$H_2PtCl_6 + 2Cu = Pt^0 + 2Cu^{2+} + 2H^+ + 6Cl^-$$
$$H_2PtCl_6 + 2Ni = Pt^0 + 2Ni^{2+} + 2H^+ + 6Cl^-$$
$$H_2PtCl_6 + 2Co = Pt^0 + 2Co^{2+} + 2H^+ + 6Cl^-$$
$$H_2PtCl_6 + 2Fe = Pt^0 + 2Fe^{2+} + 2H^+ + 6Cl^-$$

Scheme 1. Schematic diagram of designing Cu@M@Pt NWs by the displacement reactions between Cu@M NWs and H_2PtCl_6 aqueous solution.

solution approach: A mixing aqueous solution consisting of 20 mL of 15 M NaOH and 1 mL of 0.1 M $Cu(NO_3)_2$ was made under vigorous agitation. Subsequently, 0.15 mL of ethanediamine and 0.025 mL of hydrazine hydrate aqueous solution (35 wt%) were dropped into the above solution, after vigorous agitating for 5 min, the reactants were sealed and heated to 60 °C. After 1 h, the resultant Cu NWs were thoroughly rinsed by deionized water and anhydrous ethanol, and vacuum dried at 50 °C.

2.2. Synthesis of Cu@M NWs

6.4 mg of Cu NWs were dispersed in 13 mL of 2 wt% polyvinylpyrrolidone ethylene glycol solution, and subsequently 1 mL of 0.1 M $Ni(NO_3)_2$, $Co(NO_3)_2$, or $FeSO_4$ was dropped into the above solution. After forming a homogeneous solution, the reactant was transferred into a 50 mL of Teflon-lined autoclave and 0.85 mL of hydrazine hydrate aqueous solution (35 wt%) was added for reaction at 200 °C for 12 h to synthesize Cu@Ni@Pt, Cu@Co@Pt, or Cu@Fe@Pt NWs. The as-synthesized coaxial NWs were rinsed by deionized water and anhydrous ethanol, and vacuum dried at 50 °C.

2.3. Synthesis of Cu@Pt NWs

15 mL of 1 mM H_2PtCl_6 aqueous solution was dropped into 100 mL of dispersion containing 6.4 mg of Cu NWs. After reaction for 1 h, the resultant nanomaterials were rinsed by deionized water and vacuum dried at 50 °C.

In order to synthesize Pt NTs, the dosage of 1 mM H_2PtCl_6 aqueous solution was tuned to 50 mL. The other synthesis conditions were the same to Cu@Pt NWs. According to ref [27], Cu species could also be identified in the resultant Pt NTs.

2.4. Synthesis of Cu@M@Pt NWs

15 mL of 1 mM H_2PtCl_6 aqueous solution was dropped into 100 mL of dispersion containing 10 mg of Cu@M NWs. After reaction for 1 h, the resultant nanomaterials were rinsed by deionized water and vacuum dried at 50 °C.

2.5. Fabrication of CEs

A homogeneous paint having 90 wt% Pt NTs, Cu@Pt NWs, or Cu@M@Pt NWs and 8 wt% carbon black was prepared by dissolving 1D catalysts and carbon black in 5 mg mL^{-1} of poly(vinylidene fluoride) (PVDF) 1-methyl-2-ethylpyrrolidone. The concentration of PVDF in the coating was controlled at 2 wt%. The CEs were