



Cost-effective counter electrode electrocatalysts from iron@palladium and iron@platinum alloy nanospheres for dye-sensitized solar cells



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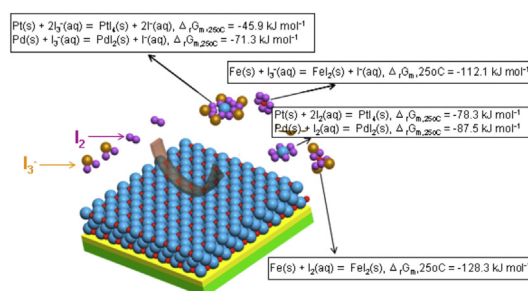
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HIGHLIGHTS

- Fe@M alloy nanospheres catalysts are synthesized by galvanic displacement.
- Fe@M alloy catalysts are employed as CEs for DSSCs.
- The catalytic activity is markedly enhanced by alloying Fe with Pt or Pd.
- The DSSCs with Fe@Pt and Fe@Pd yield efficiencies of 8.74%, and 7.22%, respectively.

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 dye-sensitized solar cells (DSSCs). Here we demonstrate the galvanic replacement realization of cost-effective CEs from Fe@M (M = Pd, Pt) nanospheres for DSSCs. Due to the enhanced catalytic activity originated from compressive strain and extended surface in tuning the electronic structure of Pd (or Pt) shell along with competitive dissolution reaction of Fe with electrolyte, the cells with high durability display efficiencies of 8.74% and 7.22%. The impressive results along with simple synthesis highlight the potential application of Fe@M nanospheres in robust DSSCs.

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1. Introduction

Dye-sensitized solar cells (DSSCs) are determined as electrochemical devices directly converting solar energy into electricity,

and they attract growing scientific and industrial attention owing to their easy fabrication, high conversion efficiency in theory, and environmental friendliness [1–4]. Since the successful development of perovskite solar cells originated from DSSCs [5–7], the DSSCs having mesoscopic thin films are forward missing their previous highlights. One of the main justifications is the relatively higher cost-performance ratio due to the utilization of precious platinum counter electrode (Pt CE) electrocatalyst [8,9]. In the classical DSSCs, Pt nanostructures are preferred CE catalysts for I_3^- reduction reaction attributing to their superior conductivity,

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electrocatalytic activity, and stability. In this fashion, pursuit of Pt-free or low-Pt CE catalysts with high electron-conducting ability and catalysis have been a persistent objective for realizing DSSC industrialization.

In the search for new class of cost-effective CE electrocatalysts without reducing photovoltaic performances of DSSCs, we have recently investigated the pertinent properties of Pt-free alloys and metal selenides [10–12]. Early work in this area was mainly focused on using either conductive polymers decorated with Pt [13], or hybrids from carbonaceous materials [14–17], or transition metal compounds [18,19], etc for application as CE catalysts in DSSCs. However, one of the associated problems is that the long-term stabilities of these catalysts are still unsatisfactory because they are more susceptible to electrolyte attack (partially soluble in redox electrolyte) and electrochemical collapse.

Here we report for the first time the experimental realization of a new category of CE catalysts consisting of Fe@M (M = Pd, Pt) alloy nanospheres by a versatile galvanic displacement strategy. The core@shell structure with precious metal (such as Pd, Pt) “shell” around transition metal “core” not only maximizes the precious metal exposure to redox electrolyte and minimizes the precious metal utilization, but also offers the desired core–shell interactions to tune both electronic and surface strain effects for optimal catalysis [20,21]. The electronic effects of Pt@M result in electron redistribution on the surface of the CE catalysts, making the catalytic sites “hotter” in comparison with planar Pt [22,23], while geometric effects often put shape and atom distance in consideration to tune binding strength between Pt and I [24]. Moreover, the unconstrained zero-dimensional (0D) nanospheres having large specific surface in CE catalysts can directly conduct electrons from fluorine-doped tin oxide (FTO) layer to alloy layer. The core@shell structure is normally sufficient to interface with redox electrolyte. This control over rapid electron transport recommends 0D core@shell nanospheres as ideal CE catalysts to manufacture advanced DSSCs. In the current work, we present our study on tuning Fe@M (M = Pd, Pt) nanospheres into active CE catalysts for I_3^- reduction. Due to the much lower reduction potential of Fe^{2+}/Fe (−0.44 V vs. SHE) pair than $PdCl_4^{2-}/Pd$ (−0.13 V vs. SHE) and $PtCl_6^{2-}/Pt$ (+0.735 V vs. SHE), it is thermodynamically favorable for displacing the superficial atoms in Fe nanospheres by $PtCl_6^{2-}$ or $PdCl_4^{2-}$ ions when exposed to H_2PdCl_4 or H_2PtCl_6 aqueous solution, realizing the core@shell structure of Fe@Pd and Fe@Pt nanospheres. The alloying effect and compressed Pd (or Pt) lattice offer Fe@M nanospheres enhanced electrocatalytic activity toward I_3^- reduction reaction and charge-transfer ability in comparison with corresponding single metals, while the DSSC from Fe@Pt catalyst yields a promising power conversion efficiency of 8.74%.

2. Experimental

2.1. Synthesis of Fe@Pt and Fe@Pd nanospheres

Prior to core@shell fabrication, pristine Fe nanospheres were synthesized by reducing 4 mL of 90 mM $FeSO_4$ aqueous solution by 12 mL of 60 mM $NaBH_4$ aqueous solution. The resultant Fe nanospheres were thoroughly rinsed by deionized water and vacuum dried, and subsequently added in 36 mL of 1 mM H_2PtCl_6 or H_2PdCl_4 aqueous solution at ambient atmosphere. After reaction for 5 h, the hollow Fe@Pt and Fe@Pd nanospheres were collected, rinsed by deionized water and ethanol, and vacuum dried at 50 °C. Similarly, hollow Pt or Pd nanospheres were synthesized by reacting Fe nanospheres in 180 mL of 1 mM H_2PtCl_6 or H_2PdCl_4 aqueous solution for 5 h at room temperature.

2.2. Preparation of Fe@Pt and Fe@Pd CEs

A homogeneous paint having 85 wt% Fe@Pt, Fe@Pd, Fe, Pt, or Pd nanospheres, 10 wt% carbon black, and 5 wt% poly(vinylidene fluoride) (PVDF) in 1-methyl-2-ethylpyrrolidone was prepared by dissolving 85 mg of 0D catalysts, 10 mg of carbon black in 5 mg mL^{−1} of PVDF 1-methyl-2-ethylpyrrolidone solution. The CEs were fabricated by coating the paint onto freshly cleaned FTO glass substrate (sheet resistance: 12 Ω sq^{−1}, purchased from Hartford Glass Co., USA). The thickness and active area were ~5 μm and ~0.5 cm², respectively. Finally, the CEs were vacuum dried at 60 °C for 24 h.

2.3. Assembly of DSSCs

By following the procedures in our previous reports [25,26], a layer of TiO_2 colloid synthesized by a sol-hydrothermal method with a thickness of 10 μm was coated by a doctor-blade technique and subsequently calcined at 450 °C for 30 min. The resultant anodes with an average TiO_2 nanoparticle size of 20 nm (Supporting Information Fig. S1) were sensitized by a 0.50 mM ethanol solution of N719 dye for at least 24 h, acting as light scattering layer for dye excitation. Each DSSC device was fabricated by sandwiching a I^-/I_3^- redox electrolyte between a dye-sensitized TiO_2 anode and a CE.

2.4. Electrochemical characterizations

The electrochemical performances were recorded on a conventional CHI660E workstation. Before measuring cyclic voltammetry (CV) curves, the supporting electrolyte consisting of 50 mM M LiI, 10 mM I_2 , and 500 mM $LiClO_4$ in acetonitrile was degassed using nitrogen for 10 min. Electrochemical impedance spectroscopy (EIS) plots were recorded in a frequency range of 0.1 Hz ~ 10⁵ kHz and an ac amplitude of 10 mV at room temperature. Tafel polarization curves were recorded on the symmetric dummy cell consisting of CE|redox electrolyte|CE structure.

2.5. Photovoltaic measurements

The photovoltaic test of the DSSC with an active area of 0.25 cm² was carried out by measuring the photocurrent-voltage (J – V) characteristic curves using the same CHI660E Electrochemical Workstation under irradiation of a simulated solar light from a 100 W Xenon arc lamp (XQ-500 W) in ambient atmosphere. The incident light intensity was controlled at 100 mW cm^{−2} by calibrating with a standard silicon solar cell. Each sample was measured at least ten times.

2.6. Other characterizations

The morphologies of the CE catalysts were observed on a JEM2010 transmission electron microscopy (TEM). XPS experiment was carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg $K\alpha$ radiation ($h\nu = 1253.6$ eV). X-ray diffraction (XRD) patterns of the resultant alloys were recorded on an X-ray powder diffractometer (X'pert MPD Pro, Philips, Netherlands) with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) in the 2θ range from 20 to 90°. The work functions were achieved by a SKP RCH020 K probe, which featured a gold tip as a reference electrode. The contact potential difference was defined as the work function of the tip minus the work function of the sample.

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