



# Cost-effective platinum alloy counter electrodes for liquid-junction dye-sensitized solar cells



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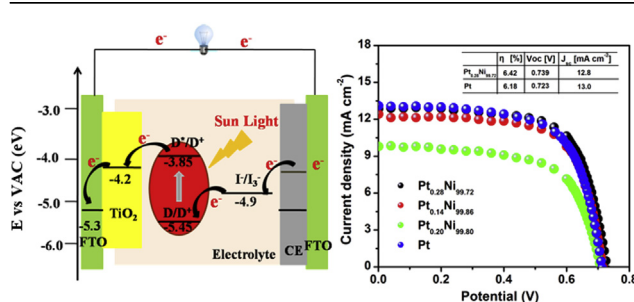
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## HIGHLIGHTS

- $Pt_xM_{100-x}$  ( $M = Ni, Co, Fe$ ) alloy CEs are synthesized by a facile method.
- These alloys CEs with ultra low Pt doages significantly reduce the cost.
- The  $Pt_{0.28}Ni_{99.72}$  alloy CE shows super-catalytic behavior toward  $I_3^-$  reduction.
- The DSSC with  $Pt_{0.28}Ni_{99.72}$  CE yields an efficiency of 6.42%.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 30 July 2015

Received in revised form

28 October 2015

Accepted 17 November 2015

Available online 11 December 2015

### Keywords:

Dye-sensitized solar cell

Electrocatalyst

Platinum alloy

Counter electrode

## ABSTRACT

One of the challenges in developing advanced dye-sensitized solar cells (DSSCs) is the pursuit of cost-effective and robust counter electrodes (CEs). We present here the successful synthesis of binary  $Pt_xM_{100-x}$  ( $M = Ni, Co, Fe$ ) alloy nanostructures on Ti foil by a facile and environmental-friendly strategy for utilization as CEs in liquid-junction DSSCs. Due to the reasonable charge-transfer ability and excellent electrocatalytic activity, the resultant DSSC yields a promising power conversion efficiency (PCE) of 6.42% with binary  $Pt_{0.28}Ni_{99.72}$  CE in comparison with 6.18% for pristine Pt CE based device. The easy synthesis, cost-effectiveness, and good electrocatalytic property may help the  $Pt_{0.28}Ni_{99.72}$  nanostructure stand out as an alternative CE electrocatalyst in a DSSC.

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## 1. Introduction

Dye-sensitized solar cells (DSSCs) have drawn considerable attention as potential candidates for cost-effective and clean energy conversion devices owing to the low cost production, high power

conversion efficiency, easy fabrication process and green environmental protection [1–3]. As one of the components in a typical DSSC device, the counter electrode (CE) plays an important role which facilitates the electron translocation from external circuit back to the redox electrolyte and reduces  $I_3^-$  to  $I^-$ . To fulfill these functions, the CE requires high electrical conductivity, excellent electrocatalytic activity and chemical durability [4,5]. Pt is a preferred CE electrocatalyst, however the high expense of Pt species has been a burden for commercial application [6,7]. Therefore, a prerequisite for DSSC commercialization is to develop cost-effective and efficient CE candidates. Till now, conductive

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polymers [8], carbonaceous materials [9], compounds [10], and hybrids [11–13] have been successfully created to replace noble Pt electrode. Although there are great progresses have been achieved, there still are many unsolved issues. For example, conductive polymers are always organic semiconductor with profounding redox properties, the electron loss when across the conductive layer will reduce the number of electrons involved in  $I_3^-$  reduction reaction. Carbonaceous materials such as graphene have excellent electron-conduction ability, while the unsatisfactory catalytic activity limited the cell performance enhancement. By addressing these issues, we would like to develop a class of alloy CE electrocatalysts by integrating high electron-conduction ability and catalytic activity in a single CE.

Transition metals have aroused great interest due to their good electric conductivity, thermal conductivity, and ductility [14–17]. In the past two decades, alloys from transition metals, especially Fe, Co, Ni, have established themselves as the alternative electrocatalysts practical electrocatalytic applications, such as  $FeSe_2$  for solar cells [18], PtCo [19,20] or PtNi [21] for methanol electrooxide. More recently, advanced alloy electrocatalysts have been utilized in CEs for liquid-junction DSSCs [22–25]. Due to unfilled 3d electron tracks and therefore extraordinary electronic structure, Fe, Co and Ni are intensively studied as preferred alloy species [18,20,22,24]. Additionally, alloying of Pt with Fe, Co, or Ni could be a promising avenue to enhance electrocatalytic activity and to reduce the fabrication cost of preferred Pt catalysts [16,24].

In the current work, cost-effective binary  $Pt_xM_{100-x}$  ( $M = Ni, Co, Fe$ ) alloys having nanoporous structures are obtained by a simple method. When used as CEs in DSSCs, the optimal  $Pt_{0.28}M_{99.72}$  alloy CE shows superior electrocatalytic behavior toward  $I^-/I_3^-$  redox couples owing to the enhanced electron conduction and charge-transfer ability. The power conversion efficiency of DSSC is elevated to 6.42% in comparison with 6.18% of pristine Pt electrode. Although there is only 3.9% enhancement in cell efficiency, the fabrication cost has been markedly reduced.

## 2. Experimental

### 2.1. Synthesis of $Pt_xM_{100-x}$ CEs

The details of synthesizing  $Pt_xM_{100-x}$  ( $M = Ni, Co, Fe$ ) alloys on Ti substrate were as follows. Take  $Pt_xNi_{100-x}$  as example, 1.66 mmol of  $Ni(NO_3)_2$  and 8.33 mmol of  $CO(NH_2)_2$  (molar ratio of Ni to C was controlled at 1:5) were dissolved into 42 mL of deionized water under stirring. After 10 min, the mixture was transferred into a Teflon-lined stainless steel autoclave. Before sealing the autoclave and hydrothermally reacting at 95 °C, three pieces of freshly cleaned Ti foils ( $20 \times 12 \times 0.3$  mm) were immersed into the above solution. After reaction for 8 h, the Ti foils were thoroughly rinsed with deionized water and vacuum dried. Subsequently, the as-synthesized precursors were heat-treated under Ar atmosphere at 450 °C for 1.5 h and  $Ar/H_2$  for 2.5 h (with a rate of 5 °C  $min^{-1}$ ). Finally, the Ti foils were immersed in 2 mM  $H_2PtCl_6$  aqueous solution for 10 min, and then rinsed with deionized water and dried.

For  $Pt_xCo_{100-x}$  and  $Pt_xFe_{100-x}$ , the molar ratio of Co/C and Fe/C were 5 and 1.5, respectively. Due to the different reduction temperature for pure Co and Fe metal, the heat-treatment temperatures were adjusted to 450 and 600 °C, respectively. As references, the pristine Ni, Fe, and Co CEs were also prepared according to the above mentioned method.

### 2.2. Assembly of DSSCs

$TiO_2$  films coated on FTO glass substrate with an average thickness of 10  $\mu m$  were prepared by coating  $TiO_2$  colloid obtained

from a doctor-blade method [20]. The photoanode with  $TiO_2$  films were soaked into ethanol solution of N719 dye (0.25 mM). The sandwiched DSSC was fabricated by injecting redox electrolyte into intermediate between dye-sensitized  $TiO_2$  anode and CE.

### 2.3. Electrochemical measurements

The electrochemical properties were characterized on a traditional electrochemical workstation (CHI 660E). The cyclic voltammetry (CV) profile was measured in a standard three-electrode system with a scan rate of 50  $mV s^{-1}$ . A large-area Pt foil with an area of 1  $cm^2$  and Ag/AgCl electrode were served as the counter and the reference electrode, respectively. The electrolyte contained an acetonitrile solution of LiI (50 mM),  $I_2$  (10 mM), and  $LiClO_4$  (500 mM). Electrochemical impedance spectroscopy (EIS) was performed in a frequency range of 0.01 Hz–100 kHz at 0 V bias and an ac amplitude of 10 mV. The Tafel polarization measurements were recorded by the symmetrical dummy cells assembled with two identical CEs and filling with electrolyte, at a scan rate of 10  $mV s^{-1}$ . The characteristic photocurrent density–voltage (J–V) curves were carried out under simulated solar light irradiation from Xenon arc lamp (XQ–500 W) with a light intensity of 100  $mW cm^{-2}$  in ambient atmosphere.

### 2.4. Characterizations

X-ray diffraction (XRD) characterization was performed on a D8 Tools X-ray diffractometer at 40 utilizing Cu  $K\alpha_1$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The morphologies and components of  $Pt_xFe_{100-x}$  alloys were observed by emission scanning electron (SEM, S–4800, Hitachi) equipped with energy dispersive spectroscopy (EDS). Work functions were measured on SKP RCH020 Kelvin probe with an area of 1.44  $mm^2$  ( $1.2 \times 1.2$  mm). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) analyses were performed on a Tecnai G2 F20. Nitrogen adsorption isotherms were determined on a Quantachrome Autosorb 1 sorption analyzer at the temperature of liquid nitrogen. The pore size distribution of the mesoporous materials was analyzed using BJH method.

## 3. Results and discussion

Crystallographic structures of the binary  $Pt_xM_{100-x}$  ( $M = Ni, Co, Fe$ ) alloy CEs synthesized by a mild method are examined by XRD technique. From the XRD patterns, only strong peaks corresponding to Ni, Co, and Fe with cubic [Fm–3m (225)], cubic [Fm3m (225)], and cubic [Im–3m (229)] structures are detected in the resultant alloy CEs, respectively. No diffraction peaks for Pt species are detected, which may be attributed to low Pt dosage in the alloys and accuracy limit of the XRD equipment. In order to confirm the components of  $Pt_xM_{100-x}$ , the CEs are detected by EDS. As shown in Fig. 1B–D, the alloys can be determined as  $Pt_{0.28}Ni_{99.72}$ ,  $Pt_{0.14}Co_{99.86}$  and  $Pt_{0.20}Fe_{99.80}$ . In this fashion, the low Pt dosages in alloys might be the main possibility for undetected Pt peaks. The result also reconfirms the alloying of M atoms with Pt species.

The SEM images of as-prepared Ni, Co, Fe, and  $Pt_xM_{100-x}$  are represented as Fig. 2a<sub>1</sub>–b<sub>3</sub>. Apparently, the single metal shows network structures comprising of one-dimensional nanowires. After being heat-treated and displaced by  $H_2PtCl_6$ , the morphologies have deviations because of structure damage and reorganization. Notably, the products have nanoporous structure, which can be supported by the specific surface areas of the resultant  $Pt_{0.28}Ni_{99.72}$ ,  $Pt_{0.14}Co_{99.86}$  and  $Pt_{0.20}Fe_{99.80}$  according to  $N_2$ -adsorption isotherms (Fig. S1). The corresponding specific surface areas are summarized in Table S1, yielding 45.231, 116.257 and 19.117  $m^2/$

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