



Evaluation of Pt-based alloy/graphene nanohybrid electrocatalysts for triiodide reduction in photovoltaics



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ABSTRACT

This work focuses on systematic studies of dissolution engineering for Pt_{0.9}M_{0.1}/graphene (M = Au, Co, Cu, Fe, Mo, Ni, Pd, Ru, and Sn) counter electrodes (CEs). The developed nanohybrid materials exhibit higher catalytic activity and electrical conductivity compared with those of Pt/graphene CEs. The results also indicate the improved stability of the developed CEs in iodide electrolyte. Furthermore, the trend in the variation of the reactivity of the PtM alloys agrees well with the concept of density functional theory (one-electron description). An enhancement in the catalytic activity of the developed nanohybrids results from the electronic effect that originates from an upward shift of the platinum *d*-band to the Fermi energy level upon alloying. Thus, the Pt_{0.9}M_{0.1}/graphene nanohybrids are cost-effective alternative CE materials to the expensive Pt. The obtained results provide a foundation for enhancing the catalytic activities of CEs for dye-sensitized solar cells (DSCs). The implementation of the Pt_{0.9}M_{0.1}/graphene nanohybrids offers significant potential for increasing the efficiency of DSCs.

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1. Introduction

Dye-sensitized solar cells (DSCs) are remarkable devices because they are potentially cost-effective alternatives to commercial silicon solar cells [1]. The regeneration of iodide ions from triiodide ions is critical in state-of-the-art photoelectrochemical DSCs. The precious platinum (Pt) is regarded as the best counter electrode (CE) material due to its high electrical conductivity and good electrochemical stability, as well as its excellent catalytic activity for the regeneration of iodide ions from triiodide ions at the CE/electrolyte interface [2].

In general, a high Pt loading is required in order to improve the

CE properties, which results in increases in the cost of solar cells. Thus, the development of efficient Pt-free CEs or CEs with a low Pt catalyst loading is crucial for large-scale application of DSCs. Furthermore, improvement of the long-term stability of Pt electrocatalysts under corrosion in the electrolyte remains a significant obstacle.

Over the past decade, Pt-based alloys have attracted increasing interest as alternative materials for DSCs. The conventional method for varying the reactivity of pure metal catalysts is alloying with another transition metal [3]. In this regard, many efforts have focused on understanding how these modifications in the electronic structure of pure metals induced by the formation of heteronuclear metal-metal bonds can affect its catalytic activity. It has been established that the reactivity of the metal surface depends on the electronic and geometric structures of the surface. The alloying of the metallic surface increases the bonding geometries of the adsorbents and changes the electronic structure of the pure

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metallic surface [4]. However, given that the surface composition of the alloy is controlled by the tendency of one metal to segregate and move to the surface of the other, the impact of the segregation energies should also be considered.

Recently, PtM alloys ($M = \text{Ni, Co, Pd, Fe, Mo, Cu, Cr, Sn, and Ru}$) have been developed and used as CEs due to their high electrical conductivity, superior electrochemical catalytic activity, and low cost [5–14]. Thus far, the PtM alloys have been deposited using conventional methods such as sputtering and electrodeposition. Despite the abundance of PtM alloy studies, problems remain in the processing and material costs due to the requirement of expensive vacuum conditions and high Pt loadings. In addition, for ecologically sustainable development of energy systems, toxic reagents should be removed from the process. Therefore, the large-scale application of Pt-based alloys requires facile and ecologically sustainable processing techniques that are compatible with solution dispersible materials and printing technologies. In order to solve these problems, the synthesis of Pt-based alloys on fluorine doped tin oxide (FTO) glass and reduced graphene oxide (RGO) substrates [15,16] using dry plasma reduction (DPR) has been developed recently. The synthesis proceeds under atmospheric pressure and low temperature, and without using toxic chemical agents [17].

The current study focuses on the synthesis and systematic screening of alloyed $\text{Pt}_{0.9}\text{M}_{0.1}/\text{RGO}$ ($M = \text{Au, Co, Cu, Fe, Mo, Ni, Pd, Ru, and Sn}$) nanohybrid materials and their applications as efficient low-cost CEs for DSCs. Note that the abbreviation $\text{Pt}_{0.9}\text{M}_{0.1}/\text{RGO}$ are used for nanohybrid alloys synthesized using the precursor solutions with the same volume percentage of Pt to metal. For this purpose, a versatile and reproducible experimental approach was established using DPR to synthesize a series of alloys with well-defined compositions. Finally, the catalyst-related properties of the Pt-based alloy/graphene nanohybrids were critically examined for the regeneration of iodide ions from triiodide ions in the DSCs. The findings in this work contribute to the basic understanding of catalysts and provide a foundation for further development of alloy/graphene nanohybrid CEs for large-scale applications.

2. Results and discussion

2.1. Synthesis and characterization of the Pt-based alloys/RGO nanohybrid materials

The syntheses of alloyed $\text{Pt}_{0.9}\text{M}_{0.1}/\text{RGO}$ nanohybrid materials are presented in the experimental section (Supporting Information). The CE morphologies are depicted in Fig. 1. As seen in the figure, the alloy nanoparticles (NPs) are immobilized on the surface of the RGO flakes for all CEs except that in Fig. 1(a). The NPs are randomly aggregated, crumpled, and closely associated with each other, as well as perpendicularly stacked. This morphology indicates the existence of numerous channels for the triiodide ions to move across the nanohybrid films, and this is a primary requirement for the high electrochemical catalytic activity in the CEs. It should be noted that the formation of RGO from graphene oxide (GO) under plasma reduction has been demonstrated previously using X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy [18]. The formation of Pt-based alloys/graphene nanohybrid were also further confirmed by transmission electron microscopy (TEM), and X-ray diffraction (XRD) measurements in previous studies [9,10,15,16,26].

In this study, the systematic screening of Pt alloyed with Au, Co, Cu, Fe, Mo, Ni, Pd, Ru, and Sn metals was conducted. It is well known that the electronegativity and lattice constants of Au, Co, Cu, Fe, Mo, Ni, Pd, Ru, and Sn are 2.54/4.07, 1.88/2.51, 1.90/3.61, 1.83/2.87, 2.16/3.15, 1.92/3.53, 2.20/3.89, 2.20/2.70, and 1.96/3.18 Å, respectively. These values are lower than those of 2.28/3.92 Å for Pt;

the only exception to this trend was gold. The difference in the electronegativity between M and Pt induces a charge transfer from M to Pt, which produces an increase in the electron–electron repulsion on the Pt atoms upon alloying. A consequence of the formation of the surface heteronuclear metal–metal bonds is a change in the electronic structure of the $\text{Pt}_{0.9}\text{M}_{0.1}$ alloys in comparison with pristine Pt [19].

In order to clarify the modifications in the electronic state of Pt that were induced by the alloying, XPS analyses were conducted. First, the surface compositions of the Pt-based alloy/RGO were derived from the XPS characterizations. The chemical formulae of the developed materials were determined as follows: $\text{Pt}_{0.91}\text{Au}_{0.09}/\text{RGO}$, $\text{Pt}_{0.72}\text{Co}_{0.28}/\text{RGO}$, $\text{Pt}_{0.87}\text{Cu}_{0.13}/\text{RGO}$, $\text{Pt}_{0.76}\text{Fe}_{0.24}/\text{RGO}$, $\text{Pt}_{0.64}\text{Mo}_{0.36}/\text{RGO}$, $\text{Pt}_{0.89}\text{Ni}_{0.11}/\text{RGO}$, $\text{Pt}_{0.92}\text{Pd}_{0.08}/\text{RGO}$, and $\text{Pt}_{0.91}\text{Sn}_{0.09}/\text{RGO}$. It should be noted that the chemical formulae of PtRu/RGO cannot be derived from the XPS measurements because the Ru3d subshell emission (290–279 eV) from Ru was masked by the C1s core-level emission (283–285 eV) from the RGO substrate. The difference in the binding energy of the Ru3d and C1s peak positions was too small to be determined. It was found that the same ratio as the precursor volume ratio used in the synthesis of the nanohybrids was not reflected in the chemical formulas, which were determined for the surface. This discrepancy has two potential explanations: the first is the metal missing occurring differently in Pt and M during the plasma reduction process and the second is the impact of the segregation energies of the metals. It is well known that the surface composition of an alloy is controlled by the tendency of one metal to segregate to the surface of the other.

In order to identify the difference in the chemical state of the Pt in the PtM alloys and pure Pt, the Pt4f core level emissions were recorded for all samples under investigation. All spectra exhibited well separated spin-orbit splitting of $\text{Pt}4f_{7/2}$ – $\text{Pt}4f_{5/2}$. These results are presented in Table S1. The shifts of the $\text{Pt}4f_{7/2}$ peaks were found toward the Fermi energy level (the binding energy scale is referred to as the Fermi level) upon alloying for the PtAu/RGO, PtCo/RGO, PtNi/RGO, PtPd/RGO, and PtRu/RGO nanohybrids. The obtained results agree well with the trend of the electronegativity of the transition metals used. It was proven for the transition metal series that the shift in the surface core-level for the host metal was accompanied by a similar shift of its valence *d*-band center. Thus, it is expected that the centers of the *d*-bands of the PtM alloys shifted toward the Fermi energy, which leads to the depopulation of the antibonding states [20]. Therefore, an enhancement in the catalytic activity of the PtM electrodes can be expected due to the electronic effect that originates from an upshift of the platinum *d*-band upon alloying [21,22]. The XPS results indicate that the PtM alloys bind adsorbents more strongly and have lower transition state energies compared with pure Pt. Thus, the increased *d*-vacancies at the Pt surface due to the formation of the bimetallic PtM NPs should result in a strong metal–triiodide interaction, which indicates an increase of triiodide ion adsorption on the metal surface, a weakening of the I–I bond in the triiodide, and, consequently, an increase in the bond lengths. The results imply fast bond scission to the formation of iodide in the electrolyte.

The change in the geometric structure of the host Pt with metal alloying also affects the surface reactivity. Due to the low lattice constants of the M atoms compared with the Pt atom, the M atoms may enter the face-center cubic Pt lattice, which leads to the formation of a binding strength between Pt and I, and, as a result, the creation of additional active sites for electrolyte adsorption [5,23]. Thus, it can be expected that the geometric factor positively affects the catalytic activities of the synthesized PtM alloys. However, an important yet unexplored issue in alloy/graphene nanohybrids is the understanding of the effect of the graphene substrate on the reactivity of the catalyst surface: what is the impact of the graphene

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