Cu₂ZnSnS₄–PtM (M = Co, Ni) Nanoheterostructures for Photocatalytic Hydrogen Evolution

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Supporting Information

ABSTRACT: We report the synthesis and photocatalytic and magnetic characterization of colloidal nanoheterostructures formed by combining a Pt-based magnetic metal alloy (PtCo, PtNi) with Cu₂ZnSnS₄ (CZTS). While CZTS is one of the main candidate materials for solar energy conversion, the introduction of a Pt-based alloy on its surface strongly influences its chemical and electronic properties, ultimately determining its functionality. In this regard, up to a 15-fold increase of the photocatalytic hydrogen evolution activity was obtained with CZTS–PtCo when compared with CZTS. Furthermore, two times higher hydrogen evolution rates were obtained for CZTS–PtCo when compared with CZTS–Pt, in spite of the lower precious metal loading of the former. Besides, the magnetic properties of the PtCo nanoparticles attached to the CZTS nanocrystals were retained in the heterostructures, which could facilitate catalyst purification and recovery for its posterior recycling and/or reutilization.

INTRODUCTION

Maximizing material performance in a particular application frequently requires the simultaneous optimization of several functional properties. In the field of photocatalysis, the material needs to be able to absorb the major part of the solar spectra, to adsorb the reactants, and generally to efficiently exchange charge with them. In quasi-homogeneous photocatalytic systems involving colloidal nanoparticles, it is also necessary to ensure the suspension stability and to introduce a mechanism for material recovery. Such multifunctionality is generally incompatible with the limited parameters of a single material, thus the engineering of heterostructures and particularly nanoheterostructures has a remarkable fundamental and technological interest.^{1,2}

Cu₂ZnSnS₄ (CZTS) has been recently proposed as an alternative absorber to more conventional CdTe and Cu(In,Ga)Se₂ semiconductors. Compared with these binary and ternary/quaternary compounds, CZTS is made of more abundant and lower toxicity elements, while conserving an optimal direct band gap of 1.5 eV and a large absorption coefficient.³ CZTS has been shown as an excellent light absorber not only for solar energy conversion through photovoltaics but also for photocatalytic generation of

hydrogen and other value-added chemicals and for photo-degradation of pollutants.^{4,5}

On the other hand, platinum is the most used catalyst for hydrogen evolution due to its excellent catalytic activity.⁶ However, Pt is a rare and thus expensive element, whose usage needs to be minimized in practical applications. One way to reduce the amount of Pt used is by increasing its activity and maximizing the ratio of atoms exposed to the media.^{7,8} A second strategy to minimize the amount of Pt is to alloy it with lower cost transition metals.^{9,10} In this direction, bimetallic catalysts not only have made it possible to reduce the amount of expensive noble metals used but also have further allowed us to modify the electronic and chemical properties of the noble metal, enabling the engineering of catalysts with improved activities, selectivities, and stabilities. In particular, bimetallic Pt–Co and Pt–Ni alloys are well-known oxygen reduction electrocatalysts.^{11–13} They have been also proposed for hydrogenation reactions,¹⁴ for hydrogen generation,¹⁵ and recently even as counter electrodes in dye-sensitized solar cells when supported on Cu₂ZnGeS₄.¹⁶

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Herein, monodisperse CZTS nanocrystals were synthesized and used as support to produce CZTS–PtCo and CZTS–PtNi nanoheterostructures. CZTS–PtCo metal–semiconductor nanoheterostructures were characterized by higher photocatalytic activities toward hydrogen generation from water when compared not only with the bare CZTS semiconductor but also with CZTS–Pt. They also show a potentially convenient magnetic moment.

■ EXPERIMENTAL SECTION

Chemicals and Solvents. *tert*-Dodecylmercaptan, dodecanethiol, tin(IV) chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$), zinc oxide (ZnO), copper(II) chloride dehydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), platinum(II) acetylacetonate, nickel(II) acetate, cobalt(II) acetate, 1-octadene (ODE), oleylamine (OLA, 70%), and oleic acid (OA, 90%) were purchased from Aldrich. Chloroform, isopropanol, tetrahydrofuran, toluene, and methanol were of analytical grade and obtained from various sources.

Synthesis of CZTS–Metal Alloy Heterostructures. Quasispherical CZTS nanoparticles with wurtzite structure were prepared by the reaction of copper, tin, and zinc salts with a mixture of the *tert*-dodecylmercaptan and dodecanethiol in the presence of oleylamine (OLA) as we previously described.⁵ CZTS–Pt, CZTS–PtCo, and CZTS–PtNi nanoheterostructures were prepared from the nucleation of Pt, PtCo, or PtNi on the surface of the quasi-spherical CZTS nanoparticles. In a typical synthesis, oleic acid (0.20 mL), oleylamine (0.20 mL), 1,2-hexadecanediol (43 mg), and phenyl ether (10 mL) were loaded into a reaction flask and kept at 120 °C for 30 min. Then, the mixture was purged with nitrogen and heated to 200 °C. In another flask, CZTS nanocrystals were mixed with platinum(II) acetylacetonate (40 mg) and different amounts of cobalt acetate or nickel acetate, and the mixture was heated at 80 °C for 10 min. Then, the metal precursor solution containing the CZTS nanoparticles was injected into the surfactant solution maintained at 200 °C. After 10 min, the reaction was quenched in a water bath. The final product was washed by multiple precipitation/dispersion cycles with toluene and ethanol, and it was finally dispersed in toluene.

Characterization Techniques. The morphological, chemical, and structural characterizations of the nanoparticles were carried out by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). Carbon-coated TEM grids from Ted-Pella were used as substrates. HRTEM images were obtained using an FEI Tecnai F20 field-emission gun microscope with a 0.19 nm point-to-point resolution at 200 keV with an embedded Gatan image filter for EELS analyses. Images were analyzed by means of Gatan Digital micrograph software.

Scanning electron microscopy (SEM) was performed using a ZEISS Auriga SEM with an energy-dispersive X-ray spectroscopy (EDS) detector to study composition. Powder X-ray diffraction (XRD) patterns were obtained with Cu $K\alpha 1$ ($\lambda = 1.5406 \text{ \AA}$) radiation in a reflection geometry on a Bruker D8 operating at 40 kV and 40 mA. Ultraviolet–visible–near-infrared spectroscopy (UV–vis–NIR) spectra were recorded on a LAMBDA 950 UV–vis spectrophotometer from PerkinElmer. X-ray photoelectron spectroscopic (XPS) measurements were performed on a Thermo Scientific XPS spectrometer. Field-dependent magnetization measurements (M–H) were conducted with a SQUID magnetometer (Quantum Design MPMS XL) at 5 K.

Photocatalytic Hydrogen Generation Experiments.

Nanocrystals were rendered water-soluble by replacing the initial surfactants with $[\text{NH}_4]_2\text{S}$. For the photocatalytic H_2 generation experiments, 10 mg of nanoparticles was dispersed in 50 mL of deionized water, containing 0.1 M Na_2S and Na_2SO_3 as hole scavengers. Before irradiating the solution, the reactor was thoroughly purged with argon to remove all oxygen in the headspace of the reactor and dissolved in water. A baseline was taken to ensure that there was no detectable oxygen in the system. A 300 W Xe lamp (Newport) was used to irradiate the sample after a suitable baseline was obtained. The reaction product was monitored by periodically sampling the gas phase from the glass chamber using a gastight syringe and analyzing it by a gas chromatograph (Varian GC-450). Argon was used as the gas chromatograph (GC) carrier gas.

Fabrication of Thin-Film Electrodes and Electrochemical Measurements. Amounts of 5 mg of photocatalysts and 10 μL of Nafion solution (5 wt %) were dispersed using sonication in 1 mL of water/isopropanol mixed solvent (3:1 v/v) until forming a homogeneous catalyst ink. An amount of 100 μL of this ink was deposited onto 1 cm^2 FTO-coated glass to fabricate the working electrode. A platinum wire was used as a counter electrode, and a Ag/AgCl reference electrode completed the three-electrode electrochemical system. Electrochemical impedance spectrometry (EIS) experiments in the frequency range 0.1 Hz to 100 kHz were carried out on a Zahner Zennium electrochemical workstation (Zahner Instrument Inc., Germany) in the presence of a 1 mM $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ (1:1) mixture as a redox probe in 0.1 M KCl aqueous solution. The signal amplitude was set to 5 mV.

■ RESULTS AND DISCUSSION

Representative TEM micrographs of the CZTS nanoparticles used to support the bimetallic nanocrystals are shown in Figure 1a. CZTS nanoparticles were characterized by a quasi-spherical morphology and an average size of 12 nm. XRD analysis (Figure S11) showed their crystal structure to be that of

Figure 1. Representative TEM images of CZTS nanoparticles (a) and CZTS–PtCo nanoheterostructures with different nominal Co/Pt ratios: Co/Pt = 0.5 (b); Co/Pt = 1 (c); Co/Pt = 2 (d).

Figure 2. Top row: TEM (a), STEM-HAADF (b), and HRTEM (c,d) micrographs of CZTS–PtCo nanoheterostructures with $[\text{Co}]/[\text{Pt}] = 0.5$. Micrographs show the ~ 12 nm faceted CZTS nanoparticles decorated with ~ 1 – 2 nm PtCo nanocrystals as pointed with arrows in (c) and circled in (d). Bottom row: TEM (e) and HRTEM (f,g) micrograph of CZTS–PtCo nanoheterostructures with $[\text{Co}]/[\text{Pt}] = 2$. Micrographs show the ~ 12 nm faceted CZTS nanoparticles decorated with ~ 3 nm PtCo nanocrystals. A structural model of a faceted wurtzite CZTS nanocrystal randomly decorated with ~ 2 nm fcc PtCo NPs is shown in (h). Color code: Cu, Zn, and Sn atoms in red; S atoms in yellow; and Pt and Co in green.

Figure 3. (a) XPS Pt 4f spectra for CZTS–Pt. (b) XPS Pt 4f spectra for CZTS–PtCo ($\text{Co}/\text{Pt} = 1$). (c) Comparison of the fitted Pt^0 subpeaks of $\text{Pt } 4f_{7/2}$ for CZTS–Pt and CZTS–PtCo. (d) XPS Co 2p spectra for CZTS–PtCo ($\text{Co}/\text{Pt} = 1$).

wurtzite. This crystal phase was confirmed by HRTEM analysis (Figure 2).

CZTS–PtCo nanoheterostructures obtained with different nominal Co/Pt ratios (0, 0.5, 1, 2) were produced as detailed in the Experimental Section. After metal deposition, no significant change in the size and shape of the CZTS nanocrystals was observed by TEM analysis. However, TEM micrographs clearly displayed small higher-contrast spots homogeneously distributed over the CZTS nanocrystal surface (Figure 1b–d). These

higher contrast spots had average sizes between 1 and 2 nm for the CZTS–PtCo nanoheterostructures with the lowest nominal Co/Pt molar ratios tested ($\text{Co}/\text{Pt} = 0.5$) and of around 3 nm for the highest ($\text{Co}/\text{Pt} = 2$). EDS analysis revealed that both Pt and Co were present on the final material (Figure S12). The metal ratios increased with the increase of the ratio of cobalt and platinum acetates introduced in the precursor mixture, although slight deviations from the nominal values were obtained (Table S11).¹⁷

Figure 4. (a) TEM micrograph of CZTS–PtNi nanoheterostructures. (b) STEM-HAADF micrographs showing PtNi nanoparticles in brighter contrast and EDX line scan through the arrow in the STEM-HAADF micrograph. Intensity scale between the elemental counts and STEM intensity is not proportional. (c) HRTEM micrograph showing two PtNi nanoparticles attached to a CZTS nanoparticle and power spectra obtained from the CZTS and the upper PtNi nanoparticle. (d) Color structural map of the CZTS (in red) and PtNi (in green). (e) Different epitaxial relations between the CZTS and PtNi nanoparticles.

Figures 2a and 2b show higher magnification TEM and STEM-HAADF micrographs of the CZTS–PtCo (Co/Pt = 0.5) sample. STEM-HAADF micrograph shows the CZTS surfaces to be randomly decorated with multiple 1–2 nm metal (brighter contrast) nanocrystals. Figure 2c and 2d show two HRTEM micrographs obtained with certain defocus in order to reveal the presence of the metal nanocrystals. Figure 2h displays a 3D structural model of a faceted CZTS nanoparticle decorated with several ~ 2 nm fcc PtCo NPs.¹⁸

CZTS–PtCo nanoheterostructures obtained with higher Co/Pt ratios displayed slightly larger PtCo nanocrystals (Figure 2e). HRTEM characterization of CZTS–PtCo (Co/Pt = 2) showed the metal nanocrystals to be crystalline and tightly anchored to CZTS, although no epitaxial relation could be identified (Figure 2f). In Figure 2g a HRTEM micrograph of a single CZTS nanoheterostructure is displayed. The lower contrast lattice of the support nanoparticle has an interplanar distance of 0.32 nm, which corresponds to the (0002) plane of CZTS. The interplanar distance of the higher contrast nanocrystal was 0.22 nm, which is slightly smaller than the (111) interplanar distance of Pt (0.23 nm). This slight difference is most probably related to a decrease of the lattice parameter when replacing part of the Pt by Co to form the PtCo alloy.

Figure 3 shows the Pt 4f and Co 2p XPS spectra obtained from CZTS–Pt and CZTS–PtCo nanoheterostructures. As for monometallic CZTS–Pt (Figure 3a),¹⁹ the Pt 4f spectrum of CZTS–PtCo (Figure 3b) presented relatively broad bands, which pointed to the presence of at least two pairs of doublets and thus two Pt chemical states, Pt⁰ and Pt²⁺. From the fitting of the spectra it became clear that in both samples the metallic Pt⁰ state is the main component. It is also evident that the Pt⁰ peak in the CZTS–PtCo samples is slightly shifted to higher binding energies than that of CZTS–Pt (Figure 3c). This positive shift is attributed to a slight Pt electron loss and is a hallmark of the Pt–Co alloying.²⁰ Similarly, two pairs of doublets were also fitted to the Co 2p binding energy region (Figure 3d), the stronger peaks being associated with Co⁰ and the weaker to Co²⁺. The presence of Co²⁺ in PtCo alloys is a common observation due to the easy oxidation of Co when exposed to air.^{21,22}

CZTS–PtNi (Ni/Pt = 1) nanoheterostructures were prepared following the same synthesis procedure. As described for PtCo, multiple PtNi nanoparticles with an average size of ~ 2 nm were randomly grown on the surface of the CZTS nanocrystals by adding nickel acetate to the growth solution (Figure 4a). EDS (Figure SI3), XPS (Figure SI4), and ICP (Table SI1) analysis showed the presence of both Pt and Ni

with a ratio Ni/Pt = 0.64. The XPS binding energies of the Ni $2p_{3/2}$ and $2p_{1/2}$ states were located at 856.0 and 873.4 eV, respectively, which agreed with the literature values for metallic Ni.²³

Figure 4b displays a STEM-HAADF micrograph of the CZTS–PtNi nanoheterostructures showing several CZTS nanoparticles decorated by numerous PtNi nanocrystals in brighter contrast. An EDX line scan was obtained through the arrow displayed in the STEM-HAADF micrograph. While the intensity scale between the elemental counts and STEM intensity is not proportional, it is clear that the brighter metal spots are composed by both Pt and Ni.

Figure 4c shows a HRTEM micrograph of a CZTS–PtNi nanoheterostructure where the CZTS nanoparticle and two attached ~2–3 nm PtNi nanoparticles are in fairly good zone axes and clearly visible. In the middle, FFTs from the CZTS and upper PtNi are shown. A power spectrum (FFT) obtained from the CZTS nanoparticle reveals its wurtzite phase with lattice parameters of $a = b = 0.3839$ nm and $c = 0.6339$ nm (space group = $P6_3mc$) and visualized along the $[10\bar{3}1]$ zone axis. The power spectrum of the green squared region reveals that the surface nanocrystal comprises a face centered cubic PtNi phase (space group = $Fm\bar{3}m$) with a lattice parameter of $a = 0.387$ nm and visualized along its $[011]$ zone axis. On the right (Figure 4d), a color structural map showing the wurtzite CZTS phase in red and fcc PtNi phase in green is shown, where it is clear that there is an epitaxy between the base CZTS and attached PtNi nanoparticles. In the lower row, several epitaxial relations between the CZTS and PtNi nanoparticles from the areas indicated with red and green squares are shown. The first series on the right shows the epitaxial relation between $\{1\bar{1}0\}$ and $\{01\bar{1}\}$ planes of CZTS (blue circles) and $\{111\}$ planes of PtNi (yellow circles), where there are five PtNi planes for every four CZTS planes (indicated with black parentheses) with a total lattice mismatch of ~7%. The same epitaxial relation is observed between the CZTS and the lower PtNi nanocrystal (shown on the far right). Another possible epitaxy is shown (in the middle) between the $\{10\bar{1}2\}$ planes of CZTS and $\{200\}$ planes of PtNi where there is 1 PtNi plane for every 1 CZTS planes but the lattice mismatch for this epitaxial relation is quite high (~17%).

To illustrate the influence of inexpensive Co alloying on the CZTS photocatalytic properties, CZTS–PtCo nanoheterostructures were transferred from toluene to water by means of a ligand exchange with $(\text{NH}_4)_2\text{S}$. Figure 5 shows the activities of CZTS, CZTS–Pt, and CZTS–PtCo metal alloy heterostructures with different nominal Co/Pt ratios. The photocatalytic H_2 evolution activity of CZTS (0.13 mmol/g·h) was relatively low due to a rapid recombination of photogenerated charge carriers. The activity was greatly enhanced to 1.02 mmol/g·h in the presence of Pt, as Pt reduces the overpotential in the production of H_2 from water.²⁴ CZTS–PtCo nanoheterostructures, with H_2 evolution rates up to 1.85 mmol/g·h, were even more active than CZTS–Pt. H_2 evolution rates up to 15-fold higher than pure CZTS nanocrystals and almost 2-fold higher than CZTS–Pt were measured. The superior performance of CZTS–PtCo indicated these heterostructures could not only reduce the high price of noble metals but also enhance their catalytic activity. The highest H_2 production rates were obtained for a nominal molar ratio Co/Pt = 1. Further increasing the amount of Co caused a drop in the activity to 0.74 mmol/g·h. The decrease of photocatalytic activity with the higher Co content might be induced by the increase of the

Figure 5. Comparison of photocatalytic H_2 evolution activity of CZTS, CZTS–Pt, CZTS–Pt₂Co, CZTS–PtCo, and CZTS–PtCo₂ under full-arc light irradiation.

nanocrystal size, thus reducing the total metal surface area, but also by a reduced number of active Pt sites on the particle surface, which would decrease adsorption of hydrogen ions that preferentially takes place on Pt instead of Co.

The main key parameters determining the photocatalytic hydrogen production rate are charge carrier photogeneration, separation, and transport efficiencies.²⁵ As no significant difference in the absorption spectra of CZTS nanocrystals was obtained when introducing Pt and PtCo (Figure S15), we assume that the presence of neither the noble metal or the metal alloy increased the charge carrier photogeneration. To better understand the role of cobalt in the photocatalytic H_2 generation, the carrier dynamics in the photocatalysts were analyzed by electrochemical impedance spectra (EIS). As shown in Figure 6, the radius of the semicircle in the Nyquist

Figure 6. Electrochemical impedance spectra of CZTS, CZTS–Pt, and CZTS–PtCo (Co/Pt = 1) nanocrystals modified electrodes.

plots, which is proportional to charge transfer resistance, of CZTS was much larger than that of CZTS–Pt and CZTS–PtCo nanocrystals. These differences indicated that the transport of charge carriers was indeed significantly influenced by the formation of the semiconductor–metal nanoheterostructures. Furthermore, the radius of the semicircle obtained with the CZTS–PtCo electrode was even smaller than that of CZTS–Pt, indicating a lower interface and thus charge transfer resistance from the material surface to the solution.²⁶

Figure 7. (a) Magnetization vs applied field hysteresis loops measured at 5 K for CZTS and CZTS-PtCo (Co/Pt = 1) nanoparticles. (b) Enlarged part for CZTS-PtCo nanoparticles.

Besides, alloying Pt with Co may facilitate the accumulation of photoexcited electrons as pointed out by Z. Hu and C. Y. Jimmy.¹⁵ Thus, more photogenerated charge carriers have the chance to participate in the hydrogen generation, leading to an improvement of the photocatalytic activity. Therefore, the incorporation of an optimal amount of transition metal allows increasing both the separation of photogenerated charge carriers and their transfer to surface-adsorbed species, enhancing in this way the material photocatalytic activity.

The incorporation of a Co-based metal alloy should also provide the final nanoheterostructures with a magnetic moment which can be used for material purification during its production and for material recovery for recycling and reuse during its active lifetime. Figure 7 displays the magnetic hysteresis loops of CZTS and CZTS-PtCo nanoparticles measured at 5 K. As expected, CZTS-PtCo nanoheterostructures showed a soft ferromagnetic character with a coercive field (H_c) $\approx$ 65 Oe (Figure 7b). Such hybrid nanoheterostructures, with the ferromagnetic component grown directly onto the semiconductor, could be also useful for studying nanoscale spin injection into semiconductor nanostructures.^{27,28}

CONCLUSION

In summary, monodisperse CZTS nanocrystals were synthesized via a hot-injection method and further used as support to produce CZTS-PtCo and CZTS-PtNi nanoheterostructures. CZTS-PtCo materials showed much higher photocatalytic hydrogen generation activity than CZTS and even CZTS-Pt nanoparticles. The higher activity was ascribed to the enhanced charge carrier separation and transport efficiency. The presence of Co enhanced the accumulation of photoexcited electrons in the alloy and facilitated the charge transfer to the surface-adsorbed species. Furthermore, the magnetic properties of the metal alloy PtCo attached to the CZTS nanocrystals were preserved, providing the final CZTS-PtCo catalyst with a magnetic moment potentially useful for material purification and recovery.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b06199.

XRD pattern of CZTS nanocrystals, EDS analysis of CZTS-metal alloy nanocrystals, XPS spectra of CZTS-

PtNi nanocrystals, and UV-vis-NIR spectra of CZTS-PtCo materials (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Mokari, T.; Rothenberg, E.; Popov, I.; Costi, R.; Banin, U. Selective Growth of Metal Tips onto Semiconductor Quantum Rods and Tetrapods. *Science* **2004**, *304*, 1787–1790.
- (2) Zhao, Q.; Ji, M.; Qian, H.; Dai, B.; Weng, L.; Gui, J.; Zhang, J.; Ouyang, M.; Zhu, H. Controlling Structural Symmetry of a Hybrid Nanostructure and its Effect on Efficient Photocatalytic Hydrogen Evolution. *Adv. Mater.* **2014**, *26*, 1387–1392.
- (3) Katagiri, H.; Saitoh, K.; Washio, T.; Shinohara, H.; Kurumadani, T.; Miyajima, S. Development of Thin Film Solar Cell Based on $\text{Cu}_2\text{ZnSnS}_4$ Thin Films. *Sol. Energy Mater. Sol. Cells* **2001**, *65*, 141–148.
- (4) Carrete, A.; Shavel, A.; Fontané, X.; Montserrat, J.; Fan, J.; Ibáñez, M.; Saucedo, E.; Pérez-Rodríguez, A.; Cabot, A. Antimony-Based Ligand Exchange to Promote Crystallization in Spray-Deposited $\text{Cu}_2\text{ZnSnSe}_4$ Solar Cells. *J. Am. Chem. Soc.* **2013**, *135*, 15982–15985.
- (5) Yu, X.; Shavel, A.; An, X.; Luo, Z.; Ibáñez, M.; Cabot, A. $\text{Cu}_2\text{ZnSnS}_4$ -Pt and $\text{Cu}_2\text{ZnSnS}_4$ -Au Heterostructured Nanoparticles for Photocatalytic Water Splitting and Pollutant Degradation. *J. Am. Chem. Soc.* **2014**, *136*, 9236–9239.
- (6) Amirav, L.; Alivisatos, A. P. Photocatalytic Hydrogen Production with Tunable Nanorod Heterostructures. *J. Phys. Chem. Lett.* **2010**, *1*, 1051–1054.
- (7) Sau, T. K.; Rogach, A. L. Nonspherical Noble Metal Nanoparticles: Colloid Chemical Synthesis and Morphology Control. *Adv. Mater.* **2010**, *22*, 1781–1804.
- (8) Ataee-Esfahani, H.; Nemoto, Y.; Wang, L.; Yamauchi, Y. Rational Synthesis of Pt Spheres with Hollow Interior and Nanospunge Shell

Using Silica Particles as Template. *Chem. Commun.* **2011**, 47, 3885–3887.

(9) Strasser, P.; Koh, S.; Anniyev, T.; Greeley, J.; More, K.; Yu, C.; Liu, Z.; Kaya, S.; Nordlund, D.; Ogasawara, H.; et al. Lattice-Strain Control of the Activity in Dealloyed Core–Shell Fuel Cell Catalysts. *Nat. Chem.* **2010**, 2, 454–460.

(10) Yu, W.; Porosoff, M.; Chen, J. Review of Pt-Based Bimetallic Catalysis: From Model Surfaces to Supported Catalysts. *Chem. Rev.* **2012**, 112, 5780–5817.

(11) Stamenkovic, V.; Mun, B. S.; Mayrhofer, K. J.; Ross, P. N.; Markovic, N. M.; Rossmeisl, J.; Greeley, J.; Nørskov, J. K. Changing the Activity of Electrocatalysts for Oxygen Reduction by Tuning the Surface Electronic Structure. *Angew. Chem.* **2006**, 118, 2963–2967.

(12) Antolini, E.; Salgado, J.; Gonzalez, E. The Stability of Pt–M (M = First Row Transition Metal) Alloy Catalysts and its Effect on the Activity in Low Temperature Fuel Cells: A Literature Review and Tests on a Pt–Co Catalyst. *J. Power Sources* **2006**, 160, 957–968.

(13) Yang, H.; Vogel, W.; Lamy, C.; Alonso-Vante, N. Structure and Electrocatalytic Activity of Carbon-Supported Pt–Ni Alloy Nanoparticles Toward the Oxygen Reduction Reaction. *J. Phys. Chem. B* **2004**, 108, 11024–11034.

(14) Wu, Y.; Cai, S.; Wang, D.; He, W.; Li, Y. Syntheses of Water-Soluble Octahedral, Truncated Octahedral, and Cubic Pt–Ni Nanocrystals and Their Structure–Activity Study in Model Hydrogenation Reactions. *J. Am. Chem. Soc.* **2012**, 134, 8975–8981.

(15) Hu, Z.; Yu, J. C. Pt₃Co-Loaded CdS and TiO₂ for Photocatalytic Hydrogen Evolution from Water. *J. Mater. Chem. A* **2013**, 1, 12221–12228.

(16) Huang, S.; He, Q.; Zai, J.; Wang, M.; Li, X.; Li, B.; Qian, X. The Role of Mott–Schottky Heterojunctions in PtCo–Cu₂ZnGeS₄ as Counter Electrodes in Dye-Sensitized Solar Cells. *Chem. Commun.* **2015**, 51, 8950–8953.

(17) Yu, Y.; Yang, W.; Sun, X.; Zhu, W.; Li, X.-Z.; Sellmyer, D.; Sun, S. Monodisperse MPt (M = Fe, Co, Ni, Cu, Zn) Nanoparticles Prepared from a Facile Oleylamine Reduction of Metal Salts. *Nano Lett.* **2014**, 14, 2778–2782.

(18) Bernal, S.; Botana, F. J.; Calvino, J. J.; López-Cartes, C.; Pérez-Omil, J. A.; Rodríguez-Izquierdo, J. M. The Interpretation of HREM Images of Supported Metal Catalysts Using Image Simulation: Profile View Images. *Ultramicroscopy* **1998**, 72, 135–164.

(19) Hull, R. V.; Li, L.; Xing, Y.; Chusuei, C. C. Pt Nanoparticle Binding on Functionalized Multiwalled Carbon Nanotubes. *Chem. Mater.* **2006**, 18, 1780–1788.

(20) Jiang, S.; Ma, Y.; Jian, G.; Tao, H.; Wang, X.; Fan, Y.; Lu, Y.; Hu, Z.; Chen, Y. Facile Construction of Pt-Co/CN_x Nanotube Electrocatalysts and Their Application to the Oxygen Reduction Reaction. *Adv. Mater.* **2009**, 21, 4953.

(21) Duong, H. T.; Rigsby, M. A.; Zhou, W.-P.; Wieckowski, A. Oxygen Reduction Catalysis of the Pt₃Co Alloy in Alkaline and Acidic Media Studied by X-Ray Photoelectron Spectroscopy and Electrochemical Methods. *J. Phys. Chem. C* **2007**, 111, 13460–13465.

(22) Zheng, J. N.; He, L. L.; Chen, C.; Wang, A. J.; Ma, K. F.; Feng, J. J. One-Pot Synthesis of Platinum Cobalt Nanoflowers with Enhanced Oxygen Reduction and Methanol Oxidation. *J. Power Sources* **2014**, 268, 744–751.

(23) Lang, L.; Shi, Y.; Wang, J.; Wang, F.-B.; Xia, X.-H. Hollow Core–Shell Structured Ni–Sn@C Nanoparticles: A Novel Electrocatalyst for the Hydrogen Evolution Reaction. *ACS Appl. Mater. Interfaces* **2015**, 7, 9098–9102.

(24) Gao, P.; Liu, J.; Lee, S.; Zhang, T.; Sun, D. D. High Quality Graphene Oxide–CdS–Pt Nanocomposites for Efficient Photocatalytic Hydrogen Evolution. *J. Mater. Chem.* **2012**, 22, 2292–2298.

(25) Liu, J.; Yu, X.; Liu, Q.; Liu, R.; Shang, X.; Zhang, S.; Li, W.; Zheng, W.; Zhang, G.; Cao, H. Surface-Phase Junctions of Branched TiO₂ Nanorod Arrays for Efficient Photoelectrochemical Water Splitting. *Appl. Catal., B* **2014**, 158, 296–300.

(26) Zhang, H.; Lv, X.; Li, Y.; Wang, Y.; Li, J. P25-Graphene Composite as a High Performance Photocatalyst. *ACS Nano* **2009**, 4, 380–386.

(27) Yuhas, B. D.; Habas, S. E.; Fakra, S. C.; Mokari, T. Probing Compositional Variation within Hybrid Nanostructures. *ACS Nano* **2009**, 3, 3369–3376.

(28) Lee, J. S.; Bodnarchuk, M. I.; Shevchenko, E. V.; Talapin, D. V. Magnet-in-the-Semiconductor” FePt–PbS and FePt–PbSe Nanostructures: Magnetic Properties, Charge Transport, and Magnetoresistance. *J. Am. Chem. Soc.* **2010**, 132, 6382–6391.