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Supplementary Information for

**Pt₃Co-Loaded CdS and TiO₂ for Photocatalytic Hydrogen Evolution
 from Water**

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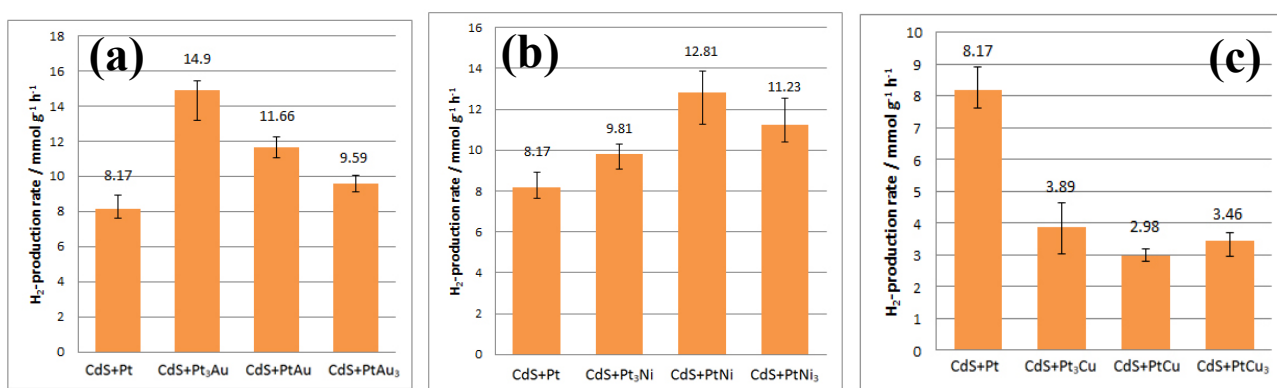


Fig. S1 Comparison of the photocatalytic activities of CdS loaded with different (a) Platinum-gold alloys, (b) Platinum-nickel alloys and (c) Platinum-copper alloys under visible light irradiation (a 300 W xenon lamp with a 420 nm filter). Reaction conditions: 10 mg of photocatalysts, 45 mL of water, 5 mL of lactic acid

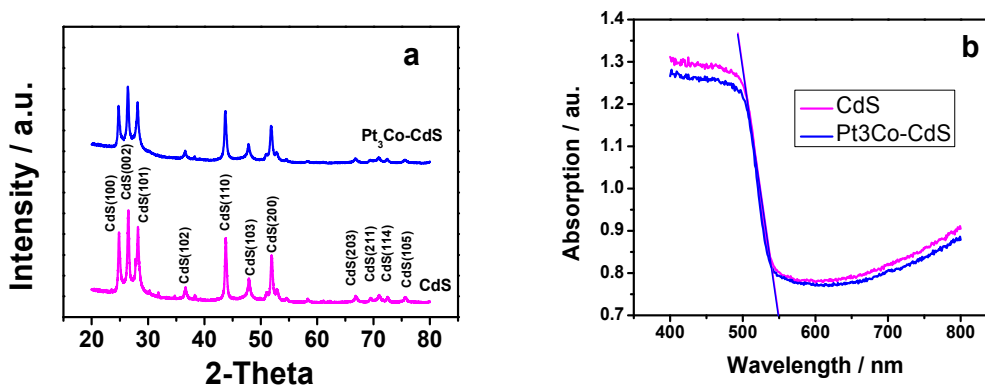


Fig. S2 (a) XRD patterns of CdS and Pt₃Co-CdS, (b) UV-visible diffuse reflectance spectra of CdS and Pt₃Co-CdS.

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Table S1 Photocatalytic hydrogen evolution rates of some CdS loaded with Pt

Photocatalyst	Synthetic method	Cocatalyst	Gas production rate (mmol h ⁻¹ g ⁻¹)	Reference
CdS	photoreduction	Pt	4.5 ¹	1
CdS	Ball-milling	Pt	0.5 ²	2
CdS	chemical precipitation method	Pt	0.26 ³	3
CdS	hydrothermal	Pt	4.0 ⁴	4
CdS	photoreduction	Pt	4.4 ⁵	5
CdS	Photoetching	Pt	1.1 ⁶	6
CdS	thermal treatment	Pt	0.6 ⁷	7

Table S2 Photocatalytic hydrogen evolution rates of some CdS or TiO₂ loaded with different cocatalyst

Photocatalyst	Cocatalyst	Gas production rate (mmol h ⁻¹ g ⁻¹)	Reference
CdS	MoS ₂	5.0 ¹	1
CdS	MoS ₂	13.0 ²	2
CdS	MoS ₂	5.5 ⁸	8
CdS	graphene oxide	5.6 ⁹	9
CdS	N-graphene	1.0 ¹⁰	10
TiO ₂	MoS ₂	1.6 ¹¹	11
TiO ₂	MoS ₂ and graphene	2.1 ¹²	12
TiO ₂	Graphene	0.1 ¹³	13
TiO ₂	Graphene	0.75 ¹⁴	14

Table S3 Photocatalytic hydrogen evolution rates of some heterostructure composites.

Photocatalyst	Cocatalyst	Gas production rate (mmol h ⁻¹ g ⁻¹)	Reference
CdS/TiO ₂	Pt	6.4 ¹⁵	15
CdS-TiON	graphene	3.0 ¹⁶	16
CdS-ZnS	-	4.2 ¹⁷	17
CdS-ZnS- graphene oxide	-	3.75 ¹⁸	18

Table S4 Photocatalytic hydrogen evolution rates of some ternary or multi-component semiconductors.

Photocatalyst	Cocatalyst	Gas production rate (mmol h ⁻¹ g ⁻¹)	Reference
CuGa ₂ In ₃ S ₈	Rh	10.7 ¹⁹	19
CdIn ₂ S ₄	-	6.96 ²⁰	20
CuFeO ₂ /SnO ₂	-	11.6 ²¹	21
TiO ₂ /Pt-RuO ₂ /8-hydroxyquinoline	-	8.92 ²²	22
SiO ₂ -HfO ₂ -Nb ₂ O ₅	Pt	10.8 ²³	23
Cd _{0.1} Cu _{0.01} Zn _{0.89} S	-	1.16 ²⁴	24
(Zn _{0.95} Cu _{0.05}) _{0.67} Cd _{0.33} S	-	3.63 ²⁵	25

Table S5. BET Surface Areas of CdS, Pt-CdS and Pt₃Co-CdS.

Photocatalyst	BET Surface Area (m ² /g)
CdS	16.23
Pt-CdS	16.41
Pt ₃ Co-CdS	16.51

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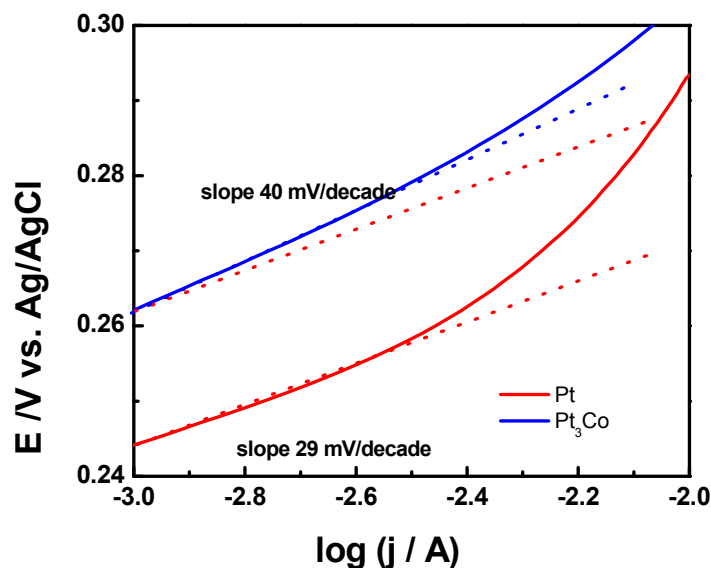


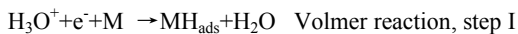
Fig. S3 Tafel plots of Pt nanoparticles and Pt₃Co nanoparticles recorded on glassy carbon electrodes with a catalyst loading of 0.12 mg/cm².

Electrons transfer between photoexcited semiconductors and metals has been widely studied.²⁶ In general, if semiconductors and metals are in contact, electrons will transfer between them until the system reaches equilibrium. When n-type semiconductors (such as CdS) and metals (such as Pt, Co) are in contact, electrons move from semiconductors to metals, because the Fermi level of the former is higher than that of the latter. If the n-type semiconductor-metals system (such as CdS-Pt) is illuminated, many photoexcited electrons will be created in CdS, and further transfer to Pt. Such phenomenon is very similar to the transfer of electrons in the process of charging a Pt electrode by applying cathodic bias, because electrons are injected into Pt in the both processes. From this viewpoint, the semiconductor under illumination is just like an “external power supply” for Pt.

For hydrogen evolution reaction at a Pt electrode under negative potential, electrons transfer from external circuits to Pt electrodes, and then combine with the hydrogen ion near the surface of Pt to form H₂. Similarly, in case of photocatalytic hydrogen evolution, electrons transfer from illuminated semiconductors to Pt, and react with hydrogen ion to form H₂. As is discussed by Fujishima,²⁷ the hydrogen evolution sites for photocatalytic decomposition of water are mainly assigned to the loaded metals. Therefore, the final steps of hydrogen evolution on the two occasions are the combination of electrons and hydrogen ion on the surface of metals. Consequently, the surface structure of metals is crucial for hydrogen evolution.

In this work, we attempt to use electrochemical measurements to investigate the mechanism of hydrogen evolution at Pt or Pt₃Co alloys. Specifically, we study the kinetics of them in 0.5 M H₂SO₄ solution by using a typical three-electrode system (see the experiment section). Tafel plots of Pt and Pt₃Co are given in Fig. S1. The linear portions of them were fitted by the Tafel equation $\eta = b \log j + a$, where b is the Tafel slope and j is the current density.

H₂ evolution on a metal surface involve the following steps:²⁸ First, an adsorbed H intermediate (H_{ads}) is formed on Metals (M)



Followed either by an electrochemical desorption step:



Or a recombination step



In hydrogen evolution reaction (HER), Tafel slope is determined by the rate-controlling steps. The Tafel slope will be about 120, 40

and 30 mV/decade when the rate-controlling step is Volmer step, Heyrovsky step or Tafel step, respectively.²⁹

It has been reported that rate-controlling steps of hydrogen evolution on different metals are not the same. HER on the surface of Pt has been proved to undergo the Volmer-Tafel pathway. The Tafel step is the rate-controlling step in both electrochemical²⁹ and photocatalytic²⁷ hydrogen evolution, as can be confirmed by the Tafel slope of Pt electrode in our experiment (30 mV/decade). However, the observed Tafel slope of Pt₃Co (40 mV/decade) suggests that HER on the surface of Pt₃Co proceeds different mechanism when compared to that of Pt. As is mentioned by Dai et al.,²⁹ the 40 mV/decade Tafel slope suggests that Volmer-Heyrovsky mechanism may operate on the surface of Pt₃Co for hydrogen evolution reaction.

Obviously, alloying Pt with Co results in the change of rate-controlling steps from recombination step to electrochemical desorption step. We assume that Co in the lattice of Pt₃Co alloy inhibits the recombination of H_{ads} adsorbed on the adjacent Pt atoms. Hence, H_{ads} are more likely to combine H₃O⁺ in the solution to form H₂ on the surface of Pt₃Co.

Besides, for other photocatalytic cocatalysts, Volmer-Heyrovsky mechanism was also observed in hydrogen evolution reaction. One typical example is MoS₂, which has been accepted as an efficient cocatalyst for photocatalytic hydrogen evolution. The working mechanism on MoS₂ is Volmer-Heyrovsky mechanism, as is discussed by Dai's group.²⁹ Therefore, we propose that Volmer-Heyrovsky mechanism may favor photocatalytic hydrogen evolution reaction. However, due to insufficient data about the Tafel slope of different cocatalysts, further experiments are still required.

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