Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supporting Information

Outstanding activity of sub-nm Pt clusters on CdS for photocatalytic hydrogen production: A combined of experimental and first-principles study

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Preparation of photocatalyst

The synthetic methods of Pt synthesis employed in this work were based on the recently reported procedures by Cuenya et al.,[1, 2] which were subsequently modified in our lab. The CdS sample was synthesized by using a standard method reported in literature[3]. More specifically, the sub-nm Pt clusters were synthesized by a method[4] based on the inverse micelle encapsulation approach.[1, 2] In this methodpoly(styrene)-block-poly(2vinylpyridine) was firstly dissolved in toluene to form the reverse micelles. In order to achieve sub-nm Pt cluster size, the ratio of $H_2PtCl_6 \cdot 6H_2O$ to polymer-head (P2VP) was selected to be 0.1. Subsequently Pt nano clusters were deposited on CdS achieving0.5, 0.7, 1, 2, and 5wt. % loadings of Pt. The deposition procedure was then followed by stir-drying overnight followed by removal of encapsulating polymer in *vacuo* (400℃, 24 h). The reduction of samples was achieved in H_2 atmosphere at 400℃ for 2h. For comparison, CdS samples loaded with regular size Pt NPs were also prepared by a modified photodeposition method.[5] Subsequently the samples were characterized by transmission electron microscopy (TEM, JEOL2100F, 200 kV).Given the fact that imaging of Pt on CdS present significant challenges in terms of poor contrast, the sub-nm Pt clusters were also loaded on Al_2O_3 substrate to get better resolved images. X-ray photoelectron spectroscopy (XPS) characterization was also carried out for the as prepared sample.

Photocatalytic activity testing

Photocatalytic water splitting was carried out in a customized Pyrex reactor loaded with 100mg of catalyst and 200 ml of aqueous solution containing 0.25 M Na_2S and 0.35 M Na_2SO_3.The continuously stirred suspension was irradiated by a 300W Xe lamp (Newport, model 66984) equipped with a cut-off optical filter (λ> 420 nm, L42, Hoya) and a 10 cm water filter (λ> 800 nm). The evolved gas was directly transferred to a gas chromatography instrument (Agilent, 7890A) through a gas circulation and evacuation system.

DFT calculation

Spin-polarized density functional theory (DFT) calculations were carried out with the Vienna *Ab initio* Simulation Package,[6, 7] using the PBE exchange-correlation functional[8] and the projected augmented wave potentials[9] with a plane-wave energy cutoff of 400 eV. The geometries were optimized without symmetry constraint until the forces on atoms were less than 10 meV/Å. We first examined the size and shape effects on the energetic and electronic properties of unsupported Pt clusters. A series of Pt_N (N=13, 38 and 55) clusters with closed shell truncated octahedral structures were chosen as they fall within the same size range of the observed TEM results. These 3D clusters were further truncated layer by layer along (111) facets to obtain the corresponding bilayer 2D-like Pt_N clusters with N=10, 19 and 38. Interface properties of Pt on CdS was then investigated by studying the adsorption characteristics of supported Pt_{38} cluster on the nonpolar $CdS(10\bar{1}0)$ surface, which was modeled using a periodic slab of 8 atomic layers with a (5x3) surface unit cell.

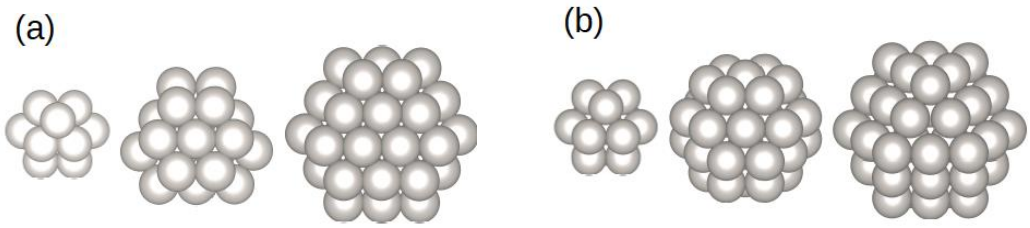

Fig. S1. Top view of DFT-optimized geometries of Pt_N clusters of (a) 2D bilayer structures (N=10, 19, 31) and (b) 3D structures with O_h symmetry (N=13, 38, 55).

Pt Clusters		***D* (nm)**	***E*$_B$ (eV)**	**IP (eV)**	**EA (eV)**
2D	Pt_{10}	0.7	3.6	6.9	3.1
	Pt_{19}	1.0	4.0	6.8	3.7
	Pt_{31}	1.2	4.3	6.6	3.9
3D	Pt_{13}	0.7	3.7	7.0	3.4
	Pt_{38}	1.0	4.4	6.8	4.2
	Pt_{55}	1.3	4.5	6.3	4.1

Table S1: Computed binding energy per atom (E_B), ionization potential (IP) and electron affinity (EA) of Pt clusters shown in Fig. S1.

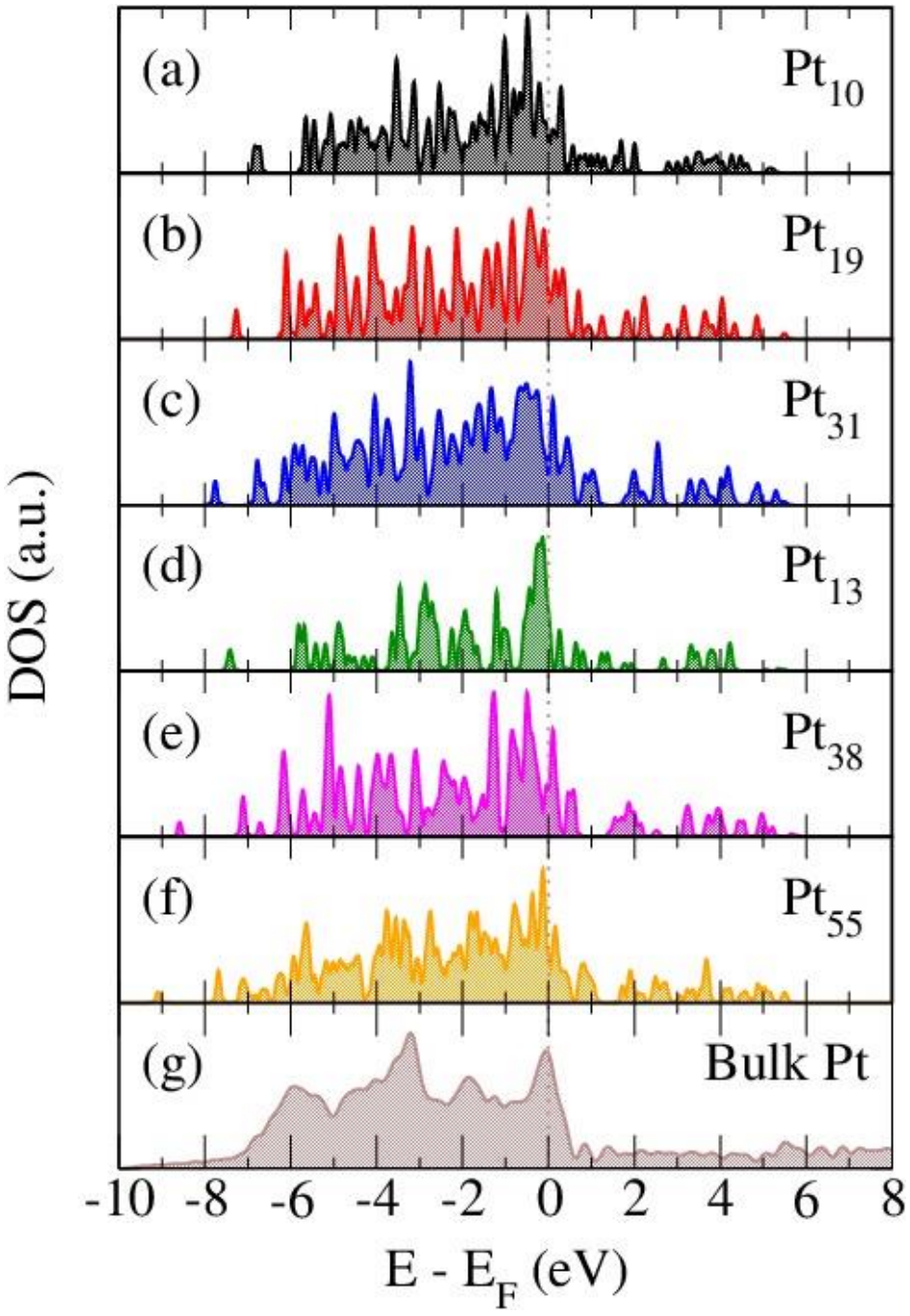

Fig. S2. Total density of states (DOS) of bilayer (a-c) and 3D (d-g) structures of Pt clusters in comparison with that of bulk Pt (g). A broadening of 0.2 eV is applied.

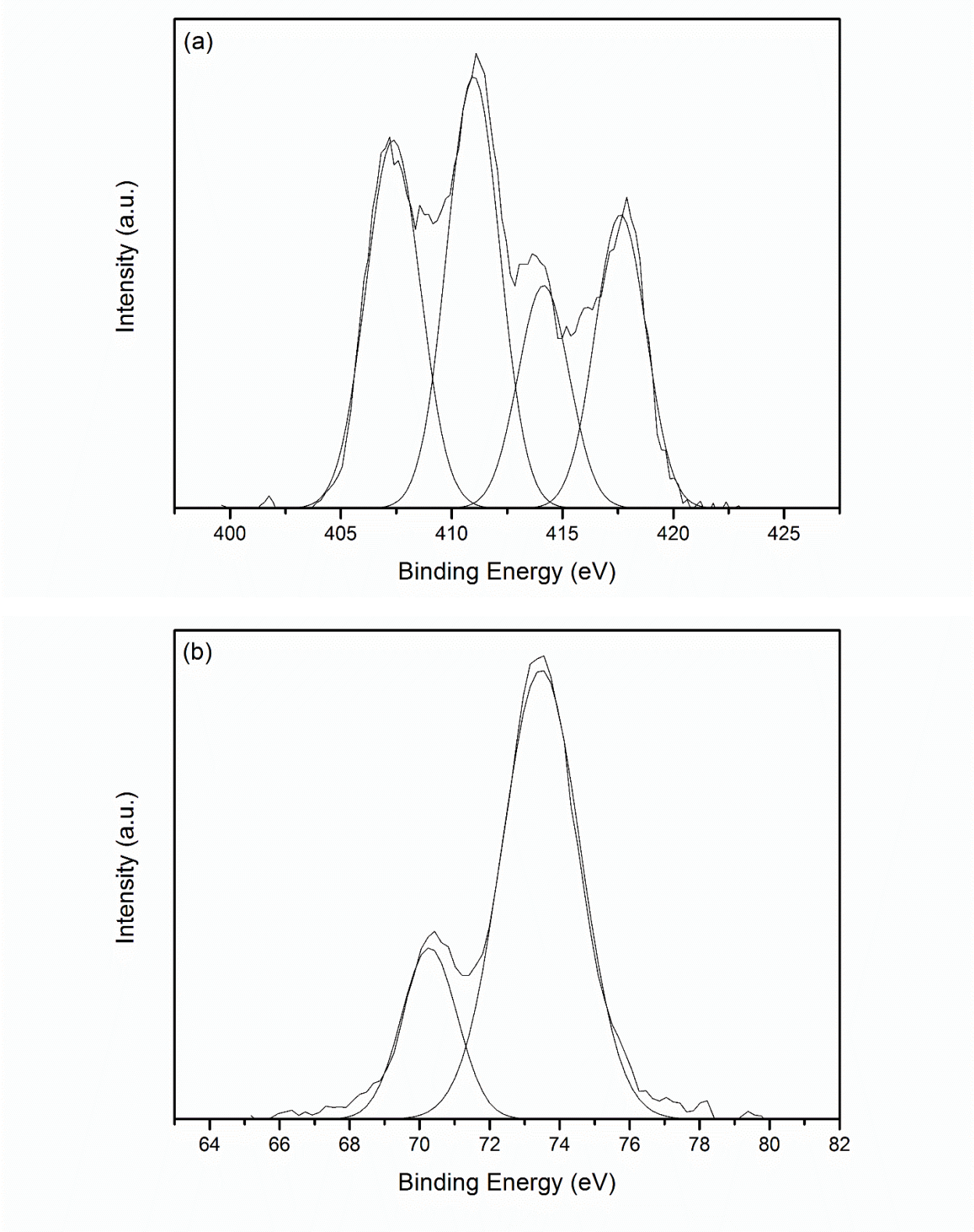

Fig. S3. XPS results of as-prepared 1 wt.% sub-nm Pt loaded CdS sample. (a) Cd 3d peaks: there were two CdS species, indicating some CdO formation as described in the text; (b) Pt 4f peaks The atomic ration between Pt and Cd is 1: 7.60.

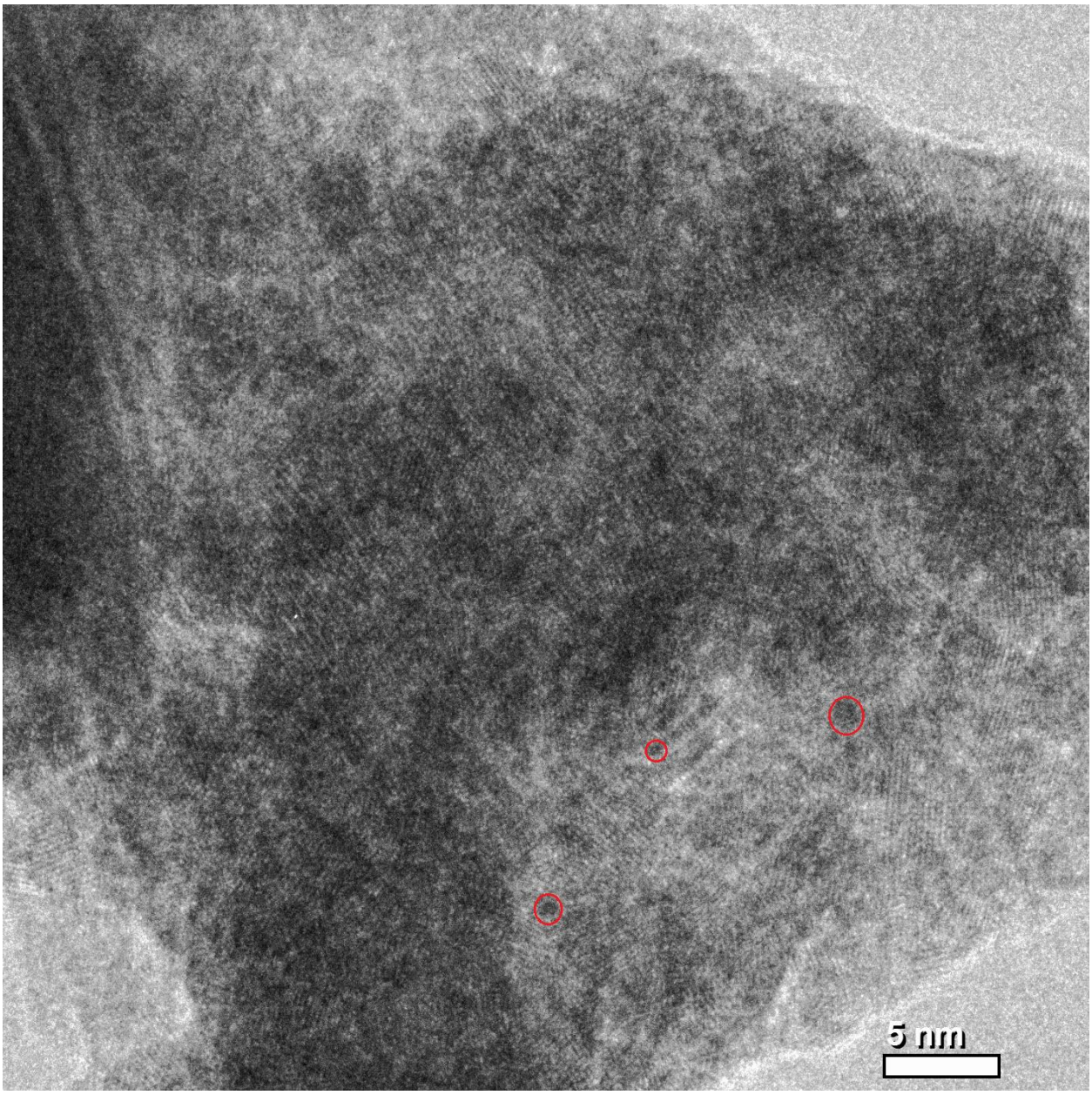

Fig. S4. TEM image of 1wt.% Pt loaded CdS sample before activity testing reaction. Red circle shows the Pt cluster. The contrast is poor as mentioned above.

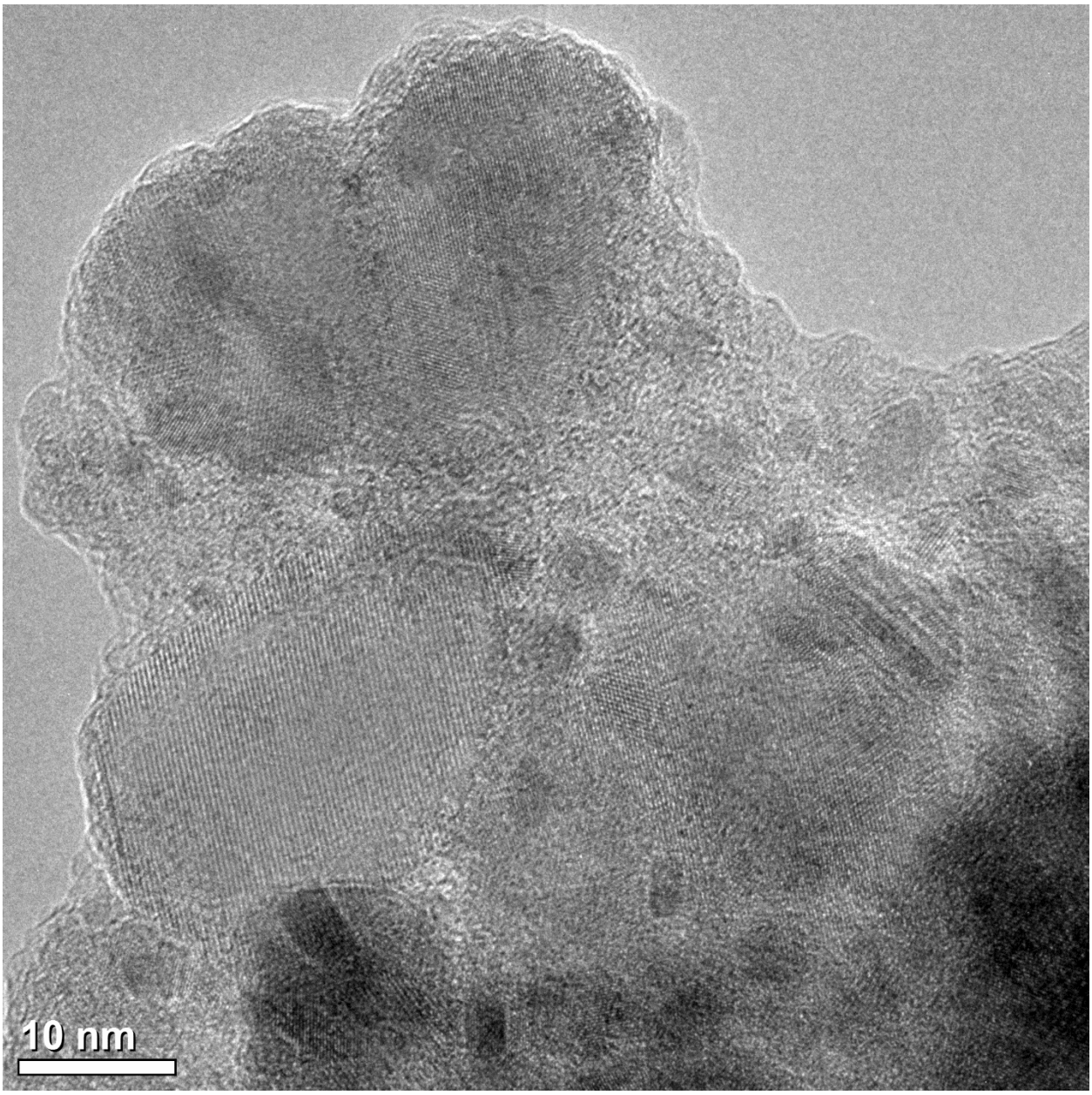

Fig. S5. TEM image of 1 wt.% Pt loaded CdS sample after activity testing reaction. The size of Pt cluster is larger compared to that pictured in Fig. S4.

Reference

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