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Shape Effects of Pt Nanoparticles on Hydrogen Production via Pt/CdS Photocatalysts Under Visible Light

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Supporting Information

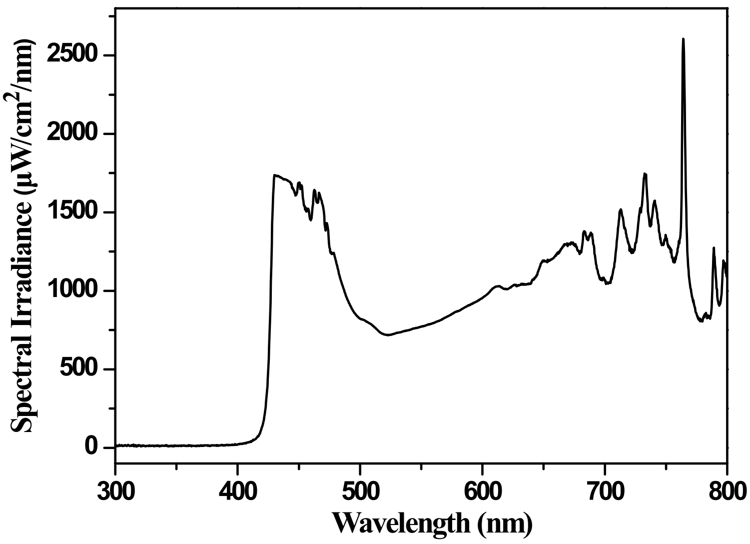

Figure S1. Xe light radiation spectrum after a UV cutoff filter (UVCUT420, λ > 420nm)

The Xe light we used in photocatalytic experiments was a 300W Xe arc lamp (Perfectlight Co., PLS-SXE300) equipped with a UV cutoff filter (UVCUT420, λ > 420nm) to simulate sunlight irradiation (Figure S1). The illumination intensity was 12.1 mW/cm^2 for wavelengths between 410 and 520nm.

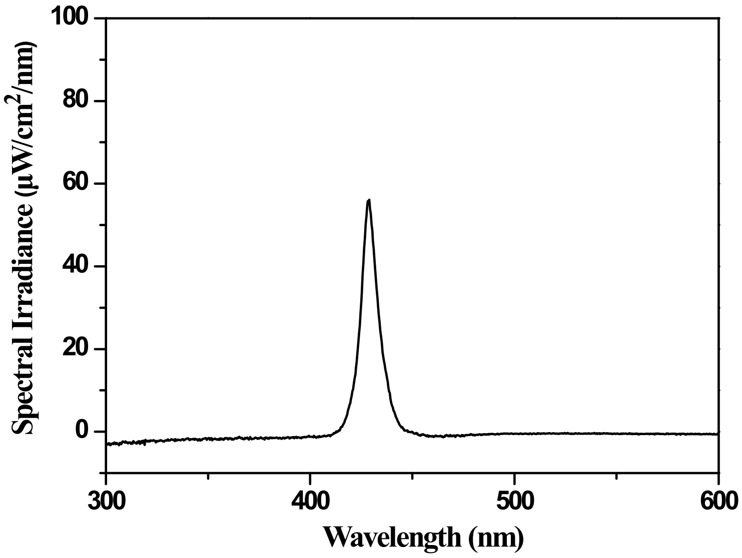

Figure S2. Irradiance of Xe light radiation after an interference filter (λ = 420nm).

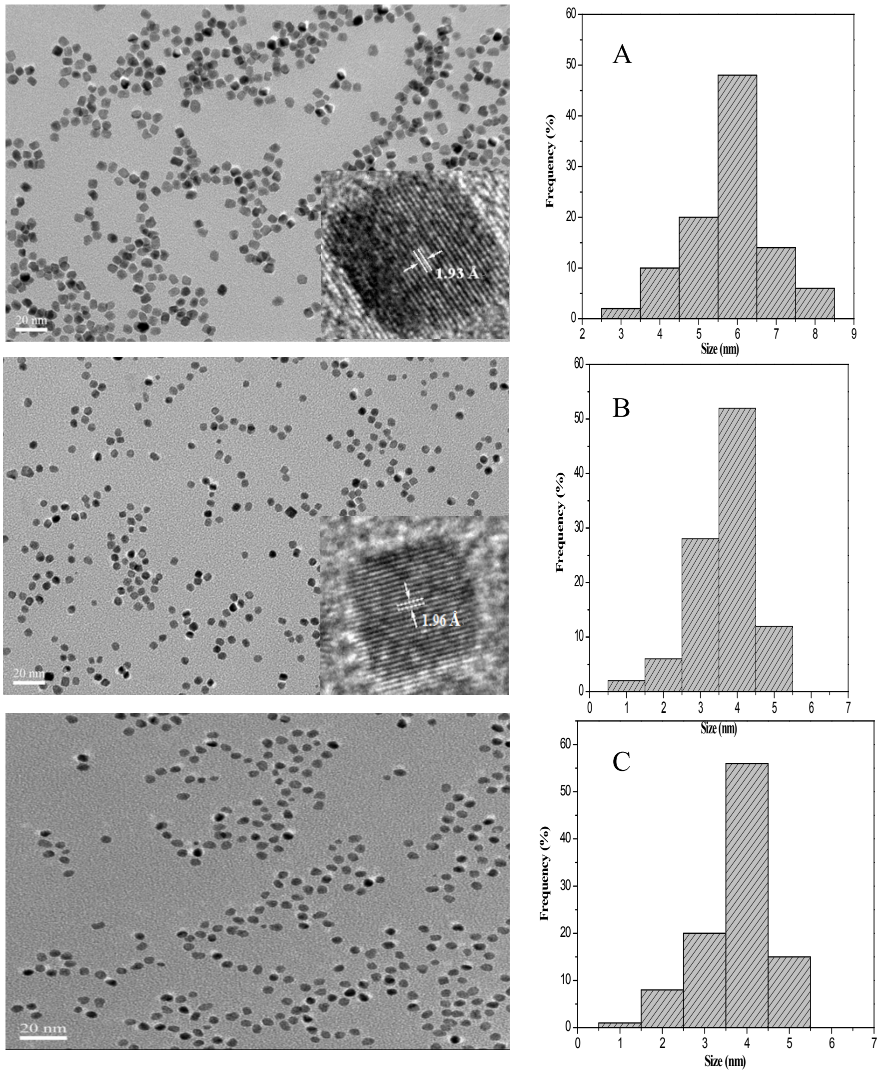

Figure S3. TEM, HRTEM images and Size distributions of single-crystalline Pt nanoparticles: 6nm nanocubes (A), 4nm nanocubes (B) 4nm irregular nanospheres and (C) HRTEM images of single Pt nanocubes (Insets)

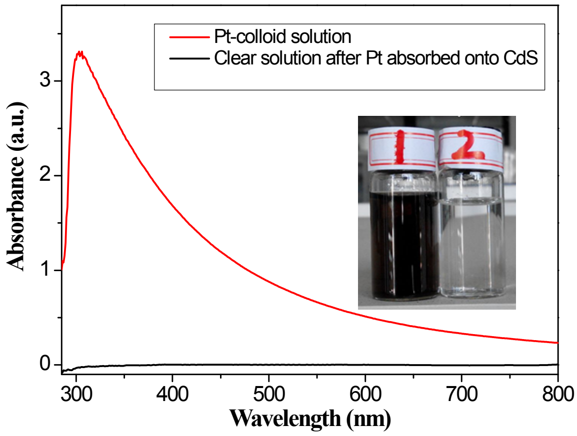

Figure S4. UV-visible absorption spectra of Pt colloidal solution and clear solution after Pt nanoparticles were loaded onto CdS. Insert: Photo of Pt colloidal solution (1) and clear solution after Pt nanoparticles were loaded onto CdS (2).

The amount of Pt loading on CdS is 0.5 wt.%, which is controlled by adding a known amount of CdS into a known amount of a Pt colloidal solution. As shown in Figure S4, the prepared Pt colloidal solution is dark black color, with UV-Vis absorption spectrum peaked at 305 nm. When CdS powder was added to the colloidal solution Pt nanoparticles were absorbed onto CdS surface. After filtration the remaining solution was clear and no featured UV-Vis absorption peak was observed. This result indicates that Pt nanoparticles were completely deposited onto the surface of CdS particles.

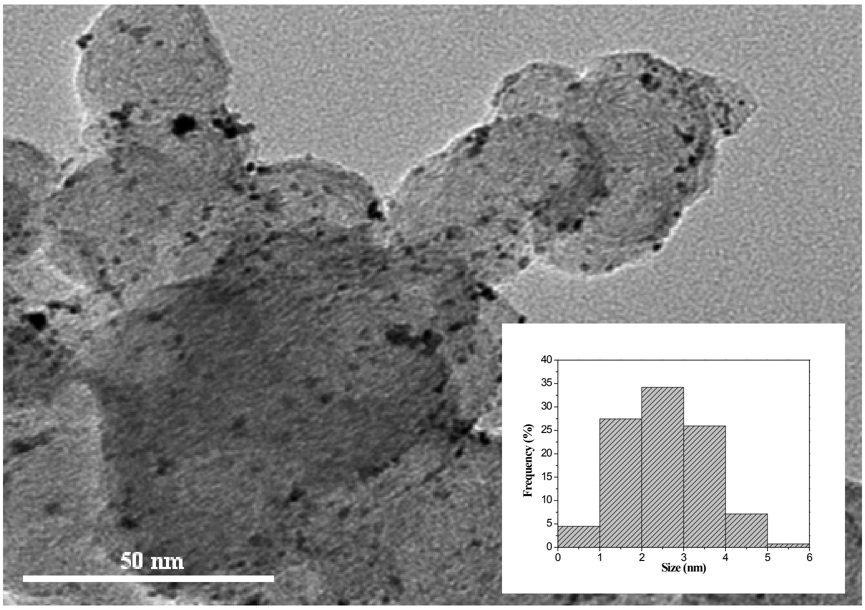

Figure S5. TEM images of photodeposited Pt nanoparticles on CdS and the size distribution of Pt nanoparticles (Inset)

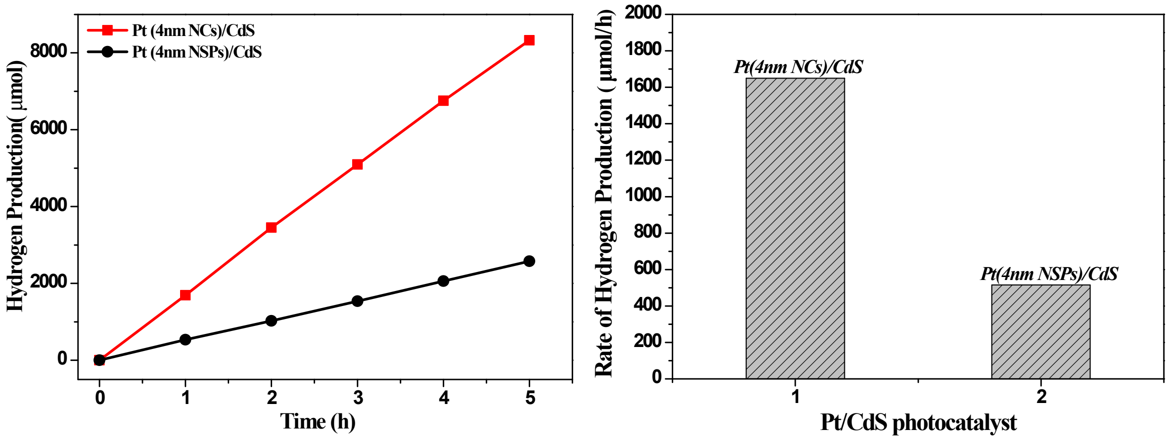

Figure S6. Photocatalytic hydrogen production over Pt(4nm NCs)/CdS and Pt (4nm NSPs)/CdS at the same Pt nanoparticle coverage (198 particles/μm^2 of CdS surface area)

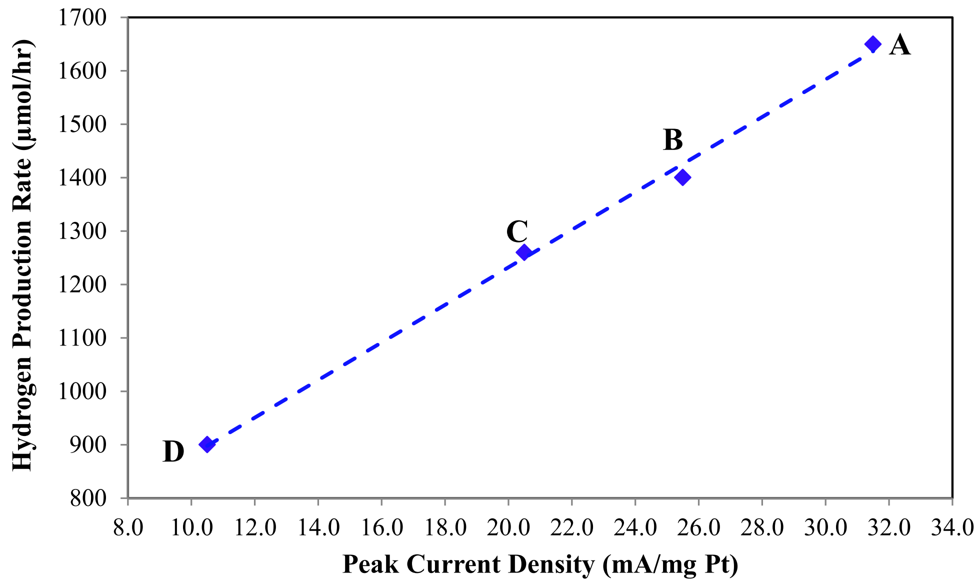

Figure S7. Rate of photocatalytic hydrogen production over Pt/CdS photocatalysts as a function of proton reduction activity for prepared Pt nanoparticles in $HClO_4$ solution: (A) Pt(4nm nanocubes)/CdS, (B) Pt(6nm nanocubes)/CdS, (C) Pt(4nm nanospheres)/CdS and (D) Pt(8nm nanocubes)/CdS.

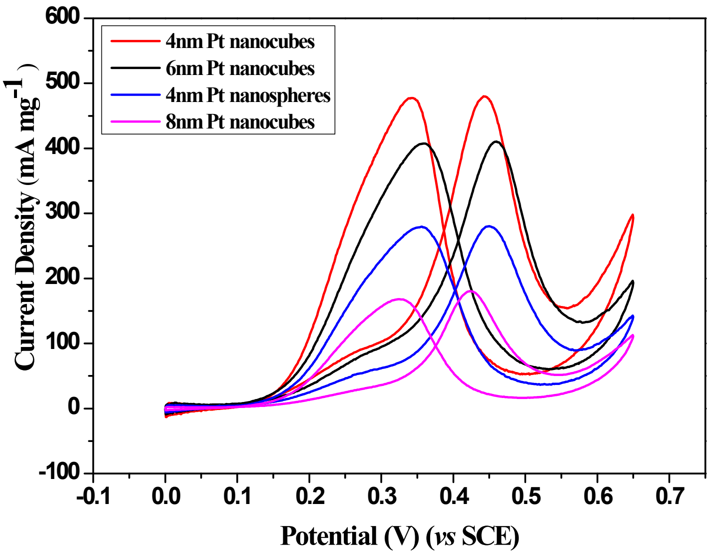

Figure S8. CV curves of the prepared Pt nanocubes and nanospheres obtained in 0.1M $HClO_4$ and 1.0M CH_3OH aqueous solutions at a scan rate of $50mV \cdot s^{-1}$.

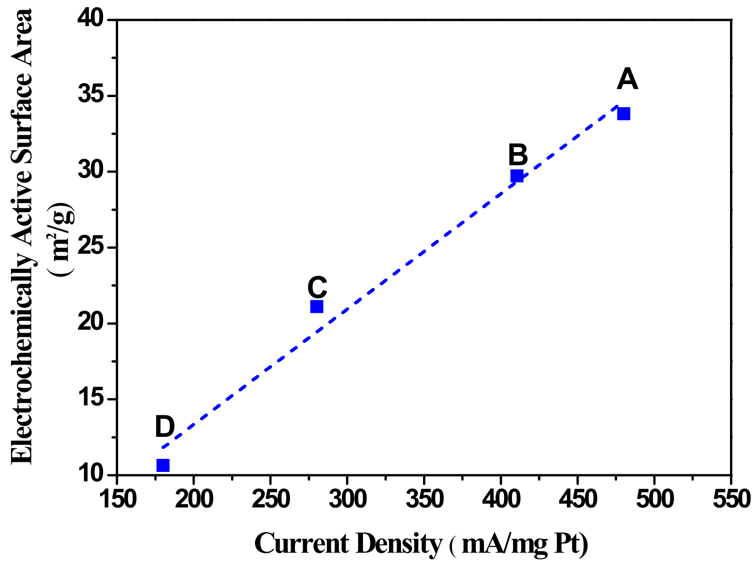

Figure S9. Linearly related electrochemically active surface area (EASA) and electrocatalytic activity for methanol oxidation over prepared (A) 4nm Pt nanocubes, (B) 6nm Pt nanocubes, (C) 4nm Pt nanospheres and (D) 8nm Pt nanocubes.

Table S1. Hydrogen Production Rates and Quantum Efficiencies for Various Pt/CdS Photocatalysts

Pt/CdS Photocatalyst	H_2 Evolution Rate (μmol/h)	Quantum Efficiency (Q.E.) (%)
Pt(4nm NCs)/CdS	1650	56.3
Pt(6nm NCs)/CdS	1400	47.8
Pt(8nm NCs)/CdS	900	30.7
Pt(4nm NSPs)/CdS	1260	43.0
Pt(6nm NSPs)/CdS	957	32.7
Photodeposited Pt/CdS	1330	45.4

Table S2. Geometrical Parameters of Pt Nanoparticles[+]

Shape	Apparent size (nm)	Average size (nm)	Single particle volume (nm^3)	Single particle mass (mg)	Total mass (mg)	Total particles no.	Surface coverage[*]
Nanocube	4.0	4.2	74.0	1.59E-15	0.25	1.575E+14	198
Nanosphere	4.0	4.0	33.5	7.19E-16	0.113	1.572E+14	198

[+]Assuming shape selectivity is 100%; [*]Surface coverage is calculated based on the number of Pt particles per surface area of CdS (NPs/μm^2 of CdS). CdS mass used in this research is 0.05g and CdS specific surface area is 15.9 m^2/g. CdS total surface area can be calculated as 15.9∗0.05 = 0.795m^2 = 7.95E+11μm^2.

Calculation of total surface areas of Pt nanoparticles:

Pt loading in this research is 0.25mg (0.00025g) for all five Pt nanoparticle loaded Pt/CdS photocatalyst samples. The Pt particle volumes and total numbers of Pt nanoparticles can be calculated based on particle shapes and average sizes. As shown in Table S3, when average particle edge length of Pt nanocubes is equal to the average diameter of Pt nanospheres, the total surface areas of two nanoparticles are the same. This can be proved as follows:

Table S3. Total Surface areas of Pt nanoparticles (0.25mg Pt loading on 0.05g of CdS; The density of Pt is 21.45g/cm^3 assuming 100% shape selectivity)

Shape	Apparent size (nm)	Average size (nm)	Volume (nm^3)	Single particle mass (g)	Total number of Pt particles	A single particle surface area (cm^2)	Total surface area (cm^2)
Cube	4.0	4.2	74.1	1.5873E-18	1.5750E+14	1.06E-12	167.0
Cube	6.0	6.1	22.7	4.8692E-18	5.1343E+13	2.23E-12	114.5
Cube	8.0	8.2	55.1	1.1819E-17	2.1152E+13	4.03E-12	85.2
Sphere	4.0	4.0	33.5	7.1858E-19	3.4780E+14	5.03E-13	175.0
sphere	6.0	5.7	97.0	2.0807E-18	1.2015E+14	1.02 E-12	122.6

The volumes and surface areas of a cube and a sphere are:

Cube: volume = $V_C = a^3$ (a is the edge length of a cube)

Sphere: volume = $V_S = 4/3*\pi*(d/2)^3 = 4/3*\pi*(a/2)^3 = \pi/6*a^3$

(d is the diameter of a sphere and "a" is equal to "d")

Surface area of a cube = $S_C = 6*a^2$

Surface area of a sphere = $S_S = 4*\pi*(d/2)^2 = \pi*a^2$

Total number of Pt nanoparticles:

$$\text{Cube: } N_c = M/(V_C * \rho) = M/(\rho * a^3)$$

$$\text{Sphere: } N_S = M/(V_S * \rho) = M/(\rho * \pi * a^3/6) = 6 * M/(\pi * \rho * a^3)$$

M is Pt loading mass and ρ is the density of Pt.

Total surface areas of Pt nanoparticles (S_T):

$$\text{Cube: } S_{CT} = N_c * S_C = (M/(\rho * a^3)) * (6 * a^3) = 6M/(\rho * a)$$

$$\text{Sphere: } S_{ST} = N_S * S_S = ((6 * M/\pi * \rho * a^3) * (\pi * a^2) = 6M/(\rho * a)$$

Therefore, total surface areas (S_T) for both Pt cubic and spherical particles are the same as $6M/\rho * a$.

This calculation also shows that the total surface areas of Pt nanoparticles are proportional to their Pt loading mass (M) and reciprocal to their size (a or d).

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