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Carbon dioxide reduction under visible light: a comparison of cadmium sulfide and titania photocatalysts

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Synthesis details

The following chemicals were used as supplied: $CdCl_2 \cdot 2.5H_2O$ (Vekton, Russia, 98%), $Zn(NO_3)_2 \cdot 6H_2O$ (Acros Organics, 98%), $Na_2S \cdot H_2O$ (Acros Organics, 60–63%), H_2PtCl_6 (Reakhim, Russia, 98%), $NaBH_4$ (Acros Organics, 98%), $AgNO_3$ (Reakhim, Russia, 98%).

TiO_2-based photocatalysts

To prepare the photocatalysts, we used Evonik Aeroxide P25 (formerly Degussa P25) titanium dioxide.

In the case of chemical reduction of platinum, titania was impregnated with an H_2PtCl_6 solution and then a $NaBH_4$ solution was added for reducing Pt^{4+}. This sample was referred as to **1% Pt/P25 $NaBH_4$**.[1]

The other method was photodeposition of platinum. A deaerated suspension, which consisted of TiO_2 P25, H_2PtCl_6 in a proper amount, an excess of isopropanol and water, was illuminated with the radiation of a 367-nm LED (China, 30 W). During the illumination, electron and hole pairs are generated on the surface of titania; photogenerated electrons are able to reduce Pt^{4+} to Pt^0, whereas the holes oxidize isopropanol. This sample was referred as to **1% Pt/P25 photo**.[1]

In the case of the sample **1% Ag/P25 $NaBH_4$** the deposition of silver on the surface of titania was carried out by the same methodology as in the case of the sample **1% Pt/P25 $NaBH_4$**; silver precursor was $AgNO_3$.

The **1% Ag/P25 $AgNO_3$** sample was prepared by impregnation of titania with $AgNO_3$ solution with subsequent ultrasonic treatment and drying at 120 °C within 3 h.

CZS sample

The synthesis technique included the formation of the mixture of cadmium and zinc hydroxides from a mixture of soluble metal salts.[2,3]

$0.8\ CdCl_2 + 0.2\ Zn(NO_3)_2 + 2NaOH \leftrightarrow 0.8\ Cd(OH)_2 + 0.2\ Zn(OH)_2 + 1.6\ NaCl + 0.4\ NaNO_3$,

with the further addition of sodium sulfide

$0.8\ Cd(OH)_2 + 0.2\ Zn(OH)_2 + Na_2S \leftrightarrow Cd_{0.8}Zn_{0.2}S + 2NaOH$.

This sample was denoted as **CZS**.

Also, platinum and silver were deposited on the surface of **CZS** by chemical reduction technique described above, the samples were denoted as **1% Pt/CZS NaBH$_4$** and **1% Ag/CZS NaBH$_4$**.

The theoretical silver and platinum content in all samples was 1 wt. %. Elemental analysis showed that the deviation from this value did not exceed 10%.

Photocatalyst characterization

The phase composition of the samples was studied by the XRD technique. The XRD patterns were recorded on a D8 Advance diffractometer (Bruker, Germany) using the CuKα radiation. The scanning was performed in the 2Θ range from 20^o to 65^o with a step of 0.05^o and an acquisition time of 10 s at each point.

The UV–Vis diffuse reflectance spectra were recorded at room temperature in the range of 400–800 nm with a resolution of 1 nm using a Cary 300 UV–Vis spectrophotometer from Agilent (USA) equipped with a DRA-30I diffuse reflectance accessory.

The XPS measurements were performed on the photoelectron spectrometer build by SPECS equipped with hemispherical electron energy analyser PHOIBOS 100 and X-Ray source XR-50 with double Al/Mg anode. In a present work AlK$_\alpha$ irradiation (hν = 1486.6 eV, 150 W) was used. The binding energy (BE) scale was pre-calibrated using the positions of the photoelectron of Au$4f_{7/2}$ (BE=84.0 eV) and Cu$2p_{3/2}$ (BE=932.67 eV) core level peaks. The binding energy of measured spectra was calibrated by the position of the C*1s* peak (BE = 284.8 eV) corresponding to the hydrocarbons presented on the sample surface.

Elemental analysis was conducted by means of mass spectrometry with inductively coupled plasma (ICP-MS) using 7700 series mass-spectrometer (Agilent, USA).

Photocatalytic carbon dioxide reduction

The photocatalytic experiments were carried out in a 130 cm^3 batch glass reactor with a quartz window.[2,3] The catalyst was uniformly deposited on a round glass plate with 9.1 cm^2 area and placed on a Teflon support in the reactor. This construction of the reactor allowed us to perform the experiments with a constant amount of gas phase and to avoid the leakage of components and inleakage of outside air. To remove oxygen, the reactor was purged with argon for 1 h. After that, 2 ml of deionized water was injected, and the reactor was purged with ultra-pure CO_2 (PTK Kriogen, Russia, >99.999% purity) for 30 min. The total pressure of gas mixture in the reactor was 1 atm. LED plate with the irradiance in the range 400–510 nm equal to 285 mW/cm^2 was used as a light source. The kinetics of product formation was investigated by the gas chromatography analysis (Khromos, Russia).

References

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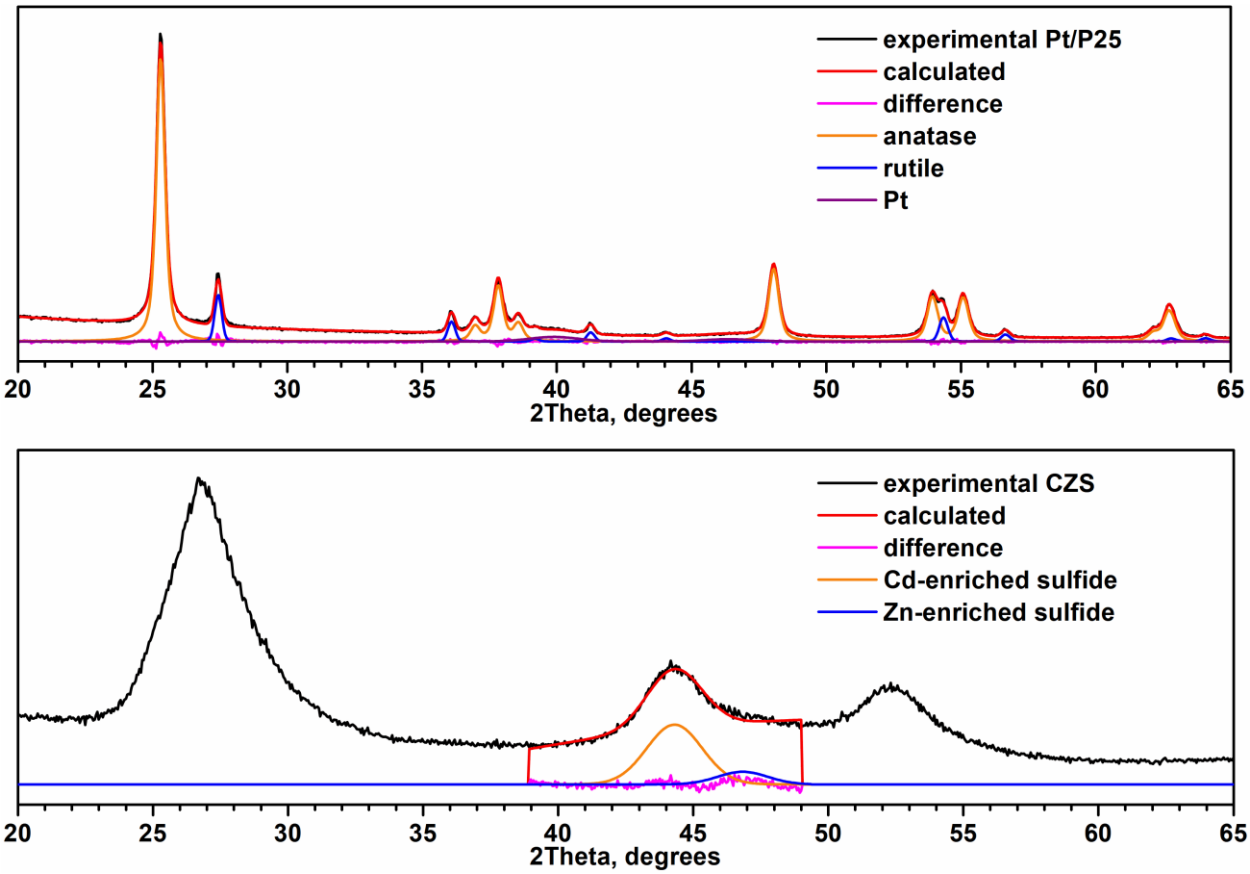

Figure S1 XRD patterns of the samples **1% Pt/P25 SCR** and **CZS.**

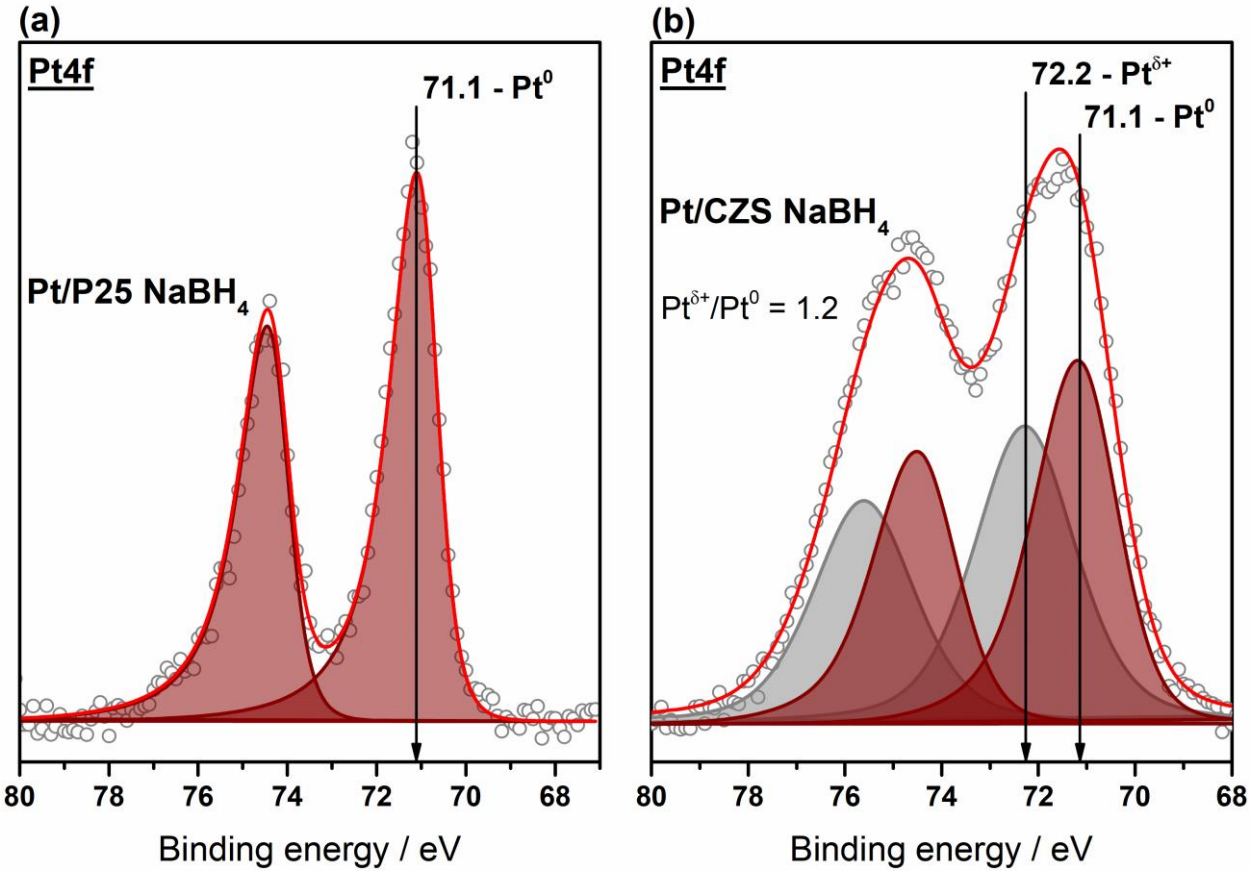

Figure S2 Pt4*f* spectra of the **1% Pt/P25 NaBH4** and **1% Pt/CZS NaBH4** samples.