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# Generation of quantum dots at the semiconductor surface for photoreforming of biomass to CO

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In a recent issue of Chem Catalysis, Wang et al proposed a new approach by incorporating CdO quantum dots to CdS surface by partial oxidation of CdS surface. The catalyst demonstrates efficient biomass reforming to CO by the promotion of separation of electrons and holes at CdO-QDs/CdS intimate heterojunction.

Carbon monoxide (CO) is one of the key building blocks in the chemical industry that finds many different applications. For example, it is used for the synthesis of aldehydes by hydroformylation of olefins by CO. Phosgene produced by the reaction of CO with Cl<sub>2</sub> is used for the synthesis of polymers such as polycarbonates and polyurethanes. Simple hydrogenation of CO, for example, over Cu catalysts leads to the synthesis of methanol widely used for the synthesis of fuels, light olefins, acetic acid etc. Hydrogenation of CO combined with C-C coupling over Co, Ru or Fe catalysts by Fischer-Tropsch process is used for the synthesis of hydrocarbons. Another important field is the traditional use of CO as a reducing agent in metallurgy for the conversion of metal oxide to pure metal forming carbon dioxide as a by-product.

These processes require a significant amount of CO, which is produced nowadays in the mixture with H<sub>2</sub> called syngas (CO + H<sub>2</sub>) by steam methane (CH<sub>4</sub>) reforming: CH<sub>4</sub> + H<sub>2</sub>O = CO + 3H<sub>2</sub> or dry methane reforming: CH<sub>4</sub> + CO<sub>2</sub> = 2CO + 2H<sub>2</sub>. The use of renewable resources such as biomass would be highly desirable for the synthesis of CO, however, the traditional route requires gasification at high temperatures (>700 °C) with the formation of CO<sub>2</sub> as a product of deeper oxidation: C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> + O<sub>2</sub> + H<sub>2</sub>O → CO + CO<sub>2</sub> + H<sub>2</sub>. It would be highly desirable to find a route to produce CO from biomass at high selectivity and mild reaction conditions.

Photocatalysis provides an opportunity to lower the reaction temperature of the reaction by generating electrons and holes able to activate the chemical bonds. Photocatalytic reforming (photoreforming) of biomass usually results in its partial decomposition with the generation of acids, aldehydes, etc. or full decomposition to hydrogen and CO<sub>2</sub><sup>1</sup>. This is the result of non-selective transformations over conventional photocatalysts containing metal sites (Pt, Ru, Au...) over semiconductors such as TiO<sub>2</sub>. Strong adsorption of CO over the metal sites usually results in dissociation to C and O with further hydrogenation or water gas shift (WGS) reaction with the production of CO<sub>2</sub> and H<sub>2</sub>. Thus, it is necessary to provide the catalyst able to dissociate C-C bonds and O-H bonds in biomass to CO without metals being able to convert it further.

Recently, Wang et al.<sup>2</sup> reported the design of the photocatalyst containing CdO quantum dots (QDs) over CdS nanorods for the generation of CO with selectivity up to 74 % with the highest productivity of 2.37 mmol·g<sup>-1</sup>·h<sup>-1</sup> (**Figure**). The reaction has been performed at room temperature

in an oxygen atmosphere using blue LED light as an energy source. Semiconductor quantum dots (QDs) such as CdS, CdSe, PbS and InAs are widely used in photocatalysis for oxidative and redox reactions<sup>3</sup>. The advantage of quantum dots is the ability to vary their solar spectrum absorption by tuning the particle size and the optical band gap. Traditionally quantum dots can be prepared by bottom-up approach by self-assembly of QDs from the solutions containing precursors<sup>4</sup>. The top-down approach involves different ways for deposition of QDs over the surface by molecular beam epitaxy, lithography, ion implantation, etc<sup>4</sup>. This is especially important for the design of QDs semiconductors over the surface of another semiconductor with the generation of Z-scheme with the transfer of electrons from one semiconductor to another for efficient charge separation<sup>5</sup>.

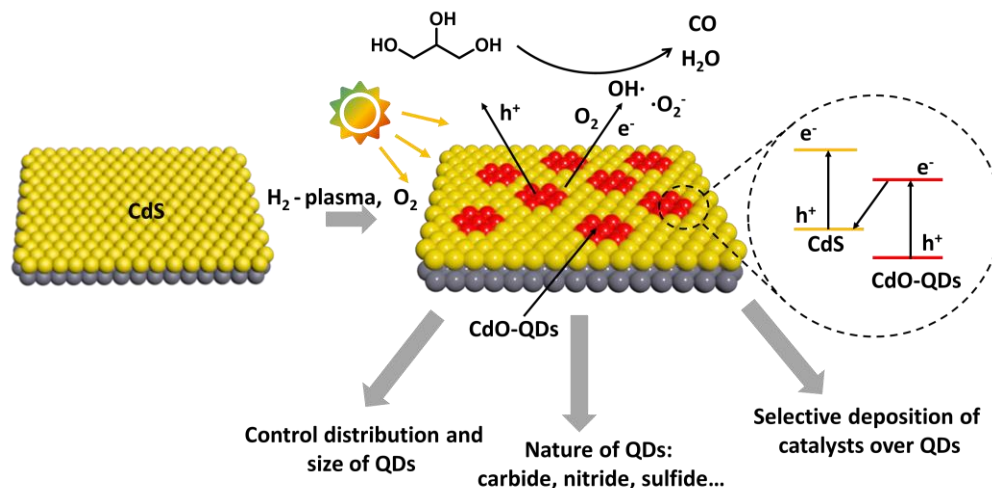
The question here is how to provide efficient contact between QDs and surface semiconductors? Wang et al.<sup>2</sup> proposed an elegant approach to incorporate CdO-QDs to CdS surface first by plasma-assisted hydrogenation of CdS to partially remove sulfur with subsequent oxidation. It results in the generation of QDs directly in the structure CdS providing high intimacy for the interaction between semiconductors reinforcing Z-effect. This approach can find a lot of interesting applications in catalysis and solar cells applications; however, there are several challenges (**Figure**). First of all, it is not clear how to control the density and size of generated quantum dots. The proposed method by plasma treatment results in the generation of QDs most probably at the defects of CdS, which is hard to control. The possible solution could be the partial surface masking to protect the semiconductor surface from conversion to QDs or deposition of reagents for the generation of QDs. Secondly, it would be interesting to use this concept for the preparation of different types of QDs by reaction using NH<sub>3</sub>, H<sub>2</sub>S... Finally, the spatial separation of electrons and holes on the surface could be used for the selective deposition of catalytic sites for more efficient oxidation and reduction reactions.

The CdO-QDs catalyst prepared by this new approach demonstrates the generation of superoxide radical ( $\cdot\text{O}_2^-$ ) and hydroxyl radical ( $\cdot\text{OH}$ ) from oxygen under irradiation promoting CO evolution (**Figure**). The low CB potential of CdO (0.1 V vs RHE) in comparison with the potential of reduction of O<sub>2</sub> to  $\cdot\text{O}_2^-$  (-0.33 V vs RHE) indicates on Z-scheme in CdO-QDs/CdS in which electrons in CB of CdO-QDs transfer to the VB of CdS (**Figure**). The catalyst demonstrates 4 times higher activity in comparison with pure CdS.

However, the photoreforming of biomass to CO requires further improvement in terms of substitution of organic solvent (CH<sub>3</sub>CN) with an aqueous phase and increasing the selectivity to CO, especially for complex biomass molecules. It is similar to the situation with aqueous phase reforming (APR), which can be used for selective conversion of simple polyols like glycerol and ethylene glycol to H<sub>2</sub> and CO<sub>2</sub>, however, has lower efficiency for complex biomass-based molecules due to side reactions<sup>6</sup>.

## Declaration of interests

The authors declare no competing interests.



**Figure 1.** Generation of QDs for photoreforming

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