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Size Effect of $(CuO)_n$ ($n = 1$–6) Clusters on the Modification of Rutile–TiO_2 Photocatalysts

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The size-dependent properties of metal/metal oxide clusters have received increasing interest due to their significant role in promoting heterogeneous catalysis. Herein, an ab initio method is used to investigate the photocatalytic properties of TiO_2-supported $(CuO)_n$ nanoclusters ($n = 1-6$). The molecular configuration and energetic evolution of gas-phase $(CuO)_n$ clusters are first investigated using a combined simulated annealing–density functional theory (DFT) method, and the quantum size effect is found in planar cluster structures due to the scarcity of electron levels. Subsequently, by supporting the $(CuO)_n$ clusters on rutile–TiO_2 (110) facets, the stability, the light-absorption ability, the charge separation efficiency, and the reactivity of excited electrons for different $(CuO)_n-TiO_2$ heterojunctions are analyzed. It is noted that $(CuO)_3$ and $(CuO)_4$ clusters have the best antiaggregation property, and the small clusters usually possess higher charge separation efficiency, whereas large clusters show better light-absorption performance. Photocatalytic hydrogen evolution reaction is favored on middle-sized CuO clusters-modified TiO_2, e.g., $(CuO)_3-TiO_2$, due to its proper band alignment, high photoelectron reactivity, good light-absorption ability, and structural stability.

1. Introduction

Recently, the scientific community witnessed an actual explosion of works in nanoscience, particularly in preparation, characterization, and application of nanomaterials for heterogeneous catalysis.[1–3] Indeed, supported nanosized and subnanosized cluster catalysts are receiving enormous interest, thanks to the burgeoning nanoscale characterization and simulation techniques.[4–7] As a consequence, it is possible to rationalize the influence of cluster size on catalytic reactivity.

Among the applications of cluster-sized catalysts, photocatalysis for hydrogen production, as a state-of-the-art approach for solar energy harvesting and utilization, has received extensive attention.[8–11] One particular research topic is the modification of titanium dioxide (TiO_2), which has been applied in many photocatalytic scenarios due to its favorable positions of band edge, chemical stability, nontoxicity, and low cost.[12–18] However, the photocatalytic efficiency of TiO_2 is limited by its inherent high charge recombination rate and weak photoabsorption ability in the visible range.[19,20] So far, numerous investigations have been done to enhance the H_2 production efficiency of TiO_2 mixed-phase nanomaterials.[21–25] Photonic crystal structures and carbon-coated nanolayers of three-dimensional ordered macroporous carbon-coated (3DOM-TiO_2@C) support enhance visible light-harvesting efficiency.[26]

Generally, modification through copper (Cu) is considered very promising, taking the advantage of the narrow bandgap of its oxides, which can increase photoabsorption and charge separation. The Cu species and its oxides exist as high-dispersion clusters on the surface of supports due to the strong metal–support interaction (SMSI).[27–29] However, as far as the different forms of copper and the related activities are concerned, varied reaction dynamics of copper species in the hydrogen evolution reaction have been reported, especially for Cu(II) species and CuO.[30–32] There has long been a living debate on the role of Cu(II) species and CuO in the photocatalytic reactions.[33,34] On one side, the negative effect of CuO on photocatalytic activities due to its unfavorable band-edge position are reported,[34] whereas others have highlighted a positive role of Cu(II) species on the activities, due to the enhanced interfacial charge separation.[35] Meanwhile, it appears that the discrepancies in experimental studies are attributed to the size effects of these Cu(II) species clusters on the surface modification of supports.[36]

Given these backgrounds, cluster modification strategies were proposed, aiming at shifting the onset of the response from the UV to the visible-light region and the improvement of its charge separation efficiency (which thus improves the overall quantum efficiency). Chief among them are surface modification of noble metals or transitional metal oxides, which can effectively form interface energy levels as well as promote the formation of surface oxygen vacancy sites or Ti interstitials, leading to an enhanced light-absorption ability and thus, remarkable improvement in photocatalytic activities.[37,38]

Previous experimental results indicate that TiO_2 in the as-prepared samples is determined as the mixture of rutile and anatase, and numerous researchers have conducted numerous researches on the photocatalytic properties of CuO cluster-modified anatase–TiO_2 catalysts.[27,31,39] Cu_4O_4 clusters supported on the anatase–TiO_2 surface can create a type-I

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