

Hierarchical Zinc Oxide Nanostructures for the Photochemical Reduction of Bicarbonate to Solar Fuels

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Abstract

Zinc oxide (ZnO) is an earth abundant, non-toxic, and low-cost material that has been used widely for photocatalytic water splitting, gas sensing, and dye degradation. In this study, several ZnO structures were synthesized, characterized, and tested for the photocatalytic reduction of bicarbonate to formic acid, an intermediate to methanol, a high-octane number fuel. The different ZnO morphologies studied included micron- and nano-particulate ZnO, rods, wires, belts, and flowers. ZnO was also synthesized from the direct calcination of zinc acetate, which provided a cheap and large-scale synthesis method to produce ZnO. The photocatalytic efficiency of the synthesized ZnO was compared to commercial micron- and nano-particulate ZnO, and was proven to be just as efficient. ZnO flowers, possessing the largest surface area of 12.9 m²/g, were found to be the most efficient reaching an apparent quantum efficiency (AQE) of 10.04±0.09%, with a superior performance over commercial TiO₂ (P25), a benchmark photocatalyst. Green chemistry solvent, glycerol, proved to be a far superior hole scavenger in comparison to 2-propanol, which is derived from petroleum sources. This is the first study to compare different shapes and sizes of ZnO for bicarbonate reduction in an aqueous system with excellent photocatalytic performance.

A Charge-Separated Diamondoid Metal-Organic Framework for Selective Gas Separation

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Abstract

Metal-Organic Frameworks (MOFs) are porous coordination polymers formed by linking metal ions to a variety of ligands. These materials have applications in many fields, including gas storage, gas separation, catalysis, and sensors, due to their unique properties, such as porosity, high surface area, low density, stability and rigidity. Most reported MOFs contain neutral clusters with limited local electric fields, resulting weak interactions with the incoming guest molecules. However, some MOFs are ionic with isolated charges, either positive or negative, containing pore clogging counter ions that result in limited pore availability. Charge separated, or zwitterionic, MOFs are ionic MOFs containing positive and negative charges, separated at fixed distances, that possess favorable electrostatic interactions with the guest molecules. Herein, we report the synthesis, characterization and gas adsorption analysis of a zwitterionic diamondoid MOF prepared by coordinating an anionic borate ligand to a cationic Cu(I) metal. The resulting MOF was four-fold interpenetrated with a significantly larger BET surface area of 621 m²/g and high environmental stability due to the absence of free ions. At 313 K and under 1 bar pressure, the CO₂ adsorption isotherm of this MOF displayed a temperature dependent adsorption/desorption hysteresis and CO₂/N₂ ideal selectivity of up to 99. The isosteric heat of CO₂ adsorption at zero coverage was 15.85 KJ/mol, confirming the pure physical interaction of MOF during adsorption. The high CO₂ uptake at 313 K, excellent environmental stability, and reasonable heat of adsorption makes this MOF a potential adsorbent for flue gas treatment in the future.

Controlled Nanomorphology of Hybrid Organic/Inorganic Multi-Component Composites through Cooperative Non-Covalent Interactions

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Abstract

Hybrid organic–inorganic nanocomposite polymers, with inorganic nanoparticles embedded in organic matrix have emerged as a special category of multifunctional materials. With rational materials design, these hybrids can show the synergistic effect of the properties from both phases. Homogenous dispersion and orderly arrangement of the organic and inorganic components are key in their functionalities. By controlling the interface and corresponding interfacial interactions between the organic and inorganic entities, we have developed a logical approach to form stable and controlled hybrid nanofiber structures. We demonstrate the formation of hybrid polymer/quantum dots (or iron oxide nanoparticles) nanocomposites through non-covalent interactions (hydrogen bonding, ionic interactions, etc.). We show that by synthesizing conjugated polymers with specific functionalities, capping nanoparticles with different ligands, we can specifically assemble them into a well-ordered core/shell structure. Besides possessing the excellent conducting properties of the polymer, the resulting nanocomposites also show some added value, such as broader light absorption range when combined with PbS quantum dots, magnetic properties when combined with iron oxide nanoparticles. Further characterization under solar cell operation condition demonstrates their potential application for solar energy harvesting. We believe that this composite nanofiber strategy could be used to generate a wide variety of polymer/nanoparticle hybrid nanocomposites. Also, the achievement of homogeneous dispersion of inorganic species into a polymer matrix may offer opportunities to build a unified hybrid nanocomposite platform for different technical applications.

Keywords: organic photovoltaic, conjugated polymer, quantum dot, magnetic nanoparticles, self-assembly