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Fractal to monolayer growth of AgCl and Ag/AgCl nanoparticles on vanadium oxides (VO_x) for visible-light photocatalysis†

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A facile and simple methodology was adopted for the trapping of highly crystalline AgCl and Ag/AgCl nanoparticles (NPs) into the interlayer spacings of vanadium oxides (VO_x). Self-organization of AgCl and Ag/AgCl-NPs on VO_x was found to be governed by the nature of the dicarboxylic acids used during the synthesis of the nanocomposites. A "fractal-like" morphology of the AgCl@VO_x nanocomposite was achieved in the presence of *cis*-1,2 cyclohexanedicarboxylic acid. Heating of the AgCl@VO_x nanocomposite above 68 °C resulted in the growth of polydispersed and ultrafine (3–4 nm) Ag/AgCl-NPs and its self-organization into monolayer formation on a partly crystalline VO_x matrix. Change in the conformation of the dicarboxylic acid to the *trans*-isomer resulted in the formation of a 'rod-like' structure of Ag/AgCl-NPs on a highly crystalline VO_x matrix. The band gaps of the nanocomposites were within the range of 1.8 to 2.9 eV. Because of such a low band gap, the synthesized nanocomposites were found to be highly active toward the photooxidation of methylene (MB) and methyl orange (MO) under sunlight.

Introduction

Semiconductors and nanomaterials with a suitable band gap that can trap solar energy have emerged as a fascinating class of materials due to their multiple applications in solar cells, photovoltaics, optoelectronics and Li-batteries, for example.[1–6] Apart from their application in energy storage devices, such materials are also very useful as photocatalysts in water treatment and water splitting reactions.[7–10] Photocatalysts have the ability to absorb solar light of different wavelengths based on the band gap.[7–9] Semiconductors with a small band gap, such as CdS and $BiVO_4$, respond well to visible light and act as a photocatalyst;[11–13] although not all semiconducting materials with small energy barriers act in this way. For example, TiO_2, a well-known photocatalyst, does not use visible light during photocatalysis.[9] Furthermore, materials with a larger band gap can sometimes also act as a photocatalyst and promote reactions.[14] Nanoparticles with surface plasmon resonance (SPR) also appear to be potential candidates for visible-light photocatalysis,[15,16] although single plasmon nanoparticles show poor stability which limits their application.[17] Materials with the ability to absorb visible light are, however, considerably less common compared with those that can use UV-light. Therefore, a substantial amount of research has been devoted toward the development of materials to act as visible-light carriers.[7–13] Furthermore, reacting molecules do not usually absorb visible light directly to drive a reaction. Visible-light photocatalysts can thus act as a bridge to promote energy transfer between visible light and the reacting substrates.[18–22]

Removal of organic contaminants such as colored dye (*e.g.* methylene blue [MB] or methyl orange [MO]) from water using a visible-light photocatalyst has become a major area of research due to the increase in environmental pollution from industrial waste[23] and stringent regulations imposed by environmental laws.[24] Among the different processes adopted by researchers,[13] photocatalytic oxidation or degradation of such organic dye contents from water is considered to be the greener approach.[9–11] Hence, in recent progress a large number of catalysts have been designed for the photocatalytic decomposition of these organic pollutants.[7–13] Very recently, Zhang *et al.*[25] found ultradispersed amorphous silver silicates/ultrathin g-C_3N_4 nanosheet heterojunction composites (a-AgSiO/CNNS) to be effective photocatalysts for dye degradation.[26,27] Silver doped in vanadium oxides ($AgVO_x$) also shows good photo-redox

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