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Enhanced photocatalytic properties of core@shell SiO_2@TiO_2 nanoparticles

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ABSTRACT

SiO_2@TiO_2 core@shell nanoparticles (CSNs) have recently attracted great attention due to their unique and tunable optical and photocatalytic properties and higher dispersion of the supported TiO_2. Thus, development of facile, reproducible and effective methods for the synthesis of SiO_2@TiO_2 CSNs and a fundamental understanding of their improved properties, derived from combination of different core and shell materials, is of great importance. Here we report a very facile and reproducible method for the synthesis of CSNs with a control of particle morphology, crystallinity and phase selectivity, and provide important insight into the effect of core@shell configuration on the photocatalytic and optical properties of SiO_2@TiO_2 CSNs. For this purpose, synthesis of highly dispersed anatase nanocrystals (~5 nm) of high surface area was carried out by supporting these nanocrystals on silica sub-micron spheres in the form of a porous shell of controlled thickness (10–30 nm). The amorphous TiO_2 shell was crystallized into anatase using a low temperature (105 °C) hydrothermal treatment. The resulting CSNs were characterized by scanning electron microscopy, transmission electron microscopy, energy dispersive spectroscopy, x-ray photoelectron spectroscopy, X-ray diffraction, vibrational spectroscopy, zeta-potential measurements, BET surface area and electron paramagnetic resonance measurements. Both experimental data and theoretical simulations showed that due to the size of the complete particle (SiO_2@TiO_2), the general optical response of the system is regulated by Rayleigh scattering, exhibiting a red-shift of the extinction spectra as shell-thickness increases. The SiO_2@TiO_2 configuration leads to efficient light harvesting by increasing the optical path inside the core@shell particles. An enhanced photoactivity and good recyclability of SiO_2@TiO_2 CSNs was demonstrated compared to unsupported TiO_2. Together with BET surface area measurements, direct assessment of the density of photocatalytic sites probed by electron paramagnetic resonance measurements was used to provide insight into the enhanced photocatalytic activity of CSNs, which is also understood as a consequence of Rayleigh scattering, relative enhancement of the adsorption of organic molecules on the core@shell photocatalyst surface and increased optical path inside the SiO_2@TiO_2 particles. All these aspects are directly influenced by the core@shell configuration of SiO_2@TiO_2 samples.

1. Introduction

TiO_2 is still the most used among the photocatalysts based on benefit-cost ratio, as well as due to its suitable electronic and optical properties and good chemical stability. TiO_2 is widely used in photocatalysis [1,2], self-cleaning coatings [3], dye-sensitized solar

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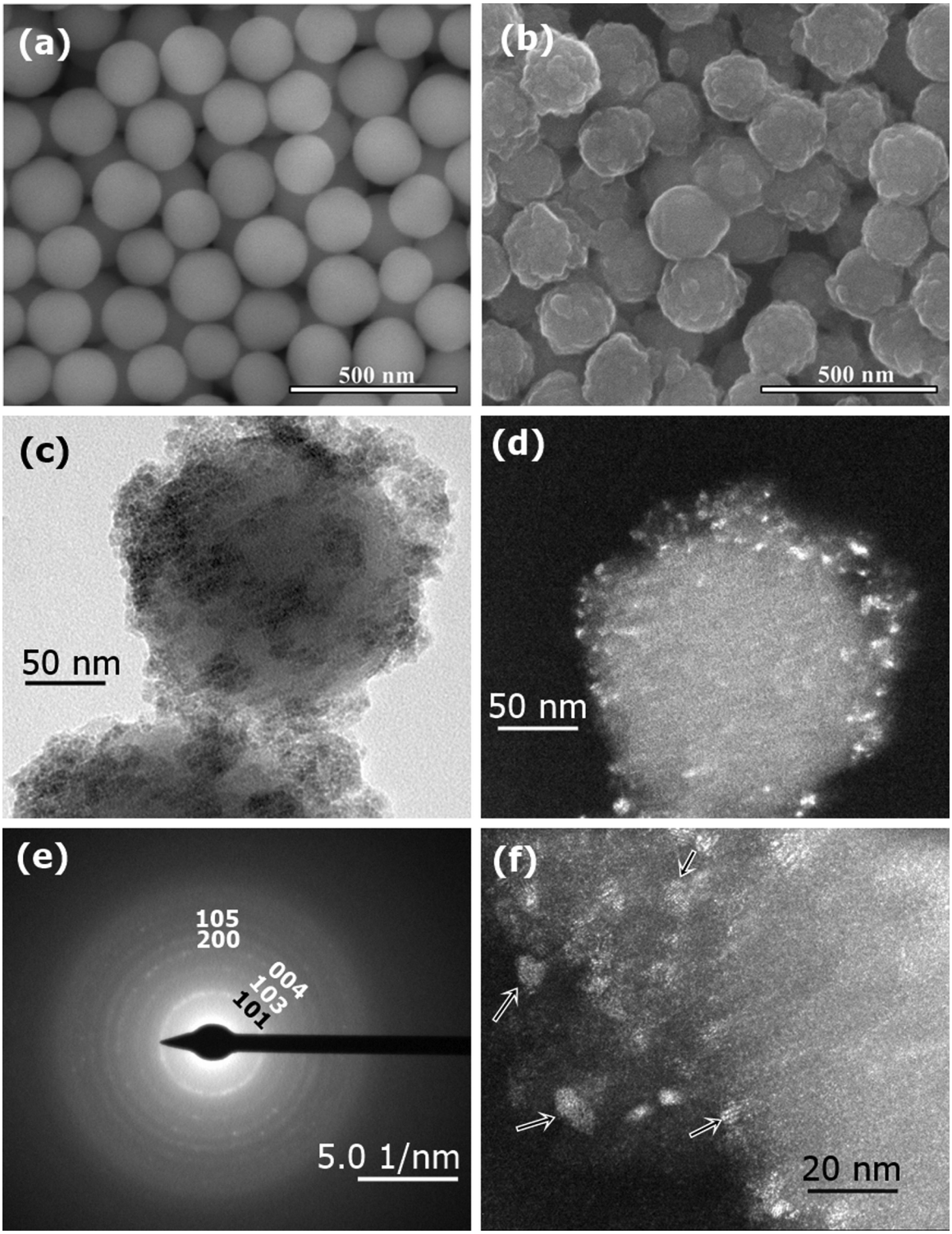

Fig. 1. FEG-SEM images of (a) unmodified silica and (b) CS-10; (c) bright field and (d) dark field TEM images of sample CS-20; (e) the SAED pattern and (f) the corresponding dark field image of CSNs obtained by collecting the electron diffracted from (1 0 1) and (1 0 3) planes of the SAED pattern.

cells [4], nanoparticles-coated facemasks [5], antibacterial coatings on medical devices [6] and optoelectronic and energy storage devices [7]. However, these applications, especially photocatalysis by TiO_2, closely depend on physical properties such as surface area, crystallinity, morphology, particle size and crystalline phase of titania, with anatase being the most active photocatalytic form of TiO_2 [8,9]. Despite such excellent properties of TiO_2, there are certain problems associated with nanometric TiO_2, which make practical applications difficult and costly. Such problems include nanoparticles' agglomeration [10], phase transformation [11,12], decrease in surface area upon thermal treatment [12,13], recombination of photogenerated electron–hole pair [14], lack of visible light photoactivity due to its wide band gap (E_g = 3.2 eV) [14] and the difficulty in recovery of the nanocatalyst from aqueous suspension.

To solve most of these problems, titania [15–20] and other functional metals/metal oxides [21,22] nanoparticles can be coated in