Charge modulation and structural distortion in decorated sea-urchin-like microspheres TiO_2 by X-ray absorption spectroscopy

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Abstract: TiO_2 mesoporous sea-urchin-like microspheres and porous Ag metal nanoparticles-decorated microspheres were successfully synthesized by a hydrothermal method. Controlling the spines length with different concentrations of $NaBH_4$ precursor and the Ag particle size on TiO_2 microspheres are expected to improve the photocatalytic ability. Our results of X-ray absorption spectroscopy (XAS) indicated that the spines of urchin has the oxygen defect and shows trivalent states for the Ti ions. The decorated Ag ions revealed a lattice distortion as well as a variation in Ti 3*d* orbital orientation. It is also inferred that TiO_6 octoahedral symmetry is significantly affected by the Ag nanoparticles incorporation giving rise to an increase in the Ti 3*d* unoccupied state. An analysis of the results showed a localized surface plasmon resonance (LSPR) effect triggered by the Ag nanoparticles that provided a conductive path to the excited charge carriers resulting in an enhanced photocurrent due to the charge transfer under solar illumination.
Keywords: X-ray absorption spectroscopic, localized surface plasmon resonance, photo catalyst.

1. Introduction

Titania (TiO_2) with different shape, size, and crystal structure and their doping systems show excellent catalytic properties and can be applied for the photo splitting of water to harvest hydrogen gas and in the photoncatalysis of solar cell. The sea-urchin-like microspheres TiO_2 presents attractive features such as size-related optical, and electronic properties, assembly of multiple types, surface functionalization, and applications to catalysis and biology. Recently, people have been trying to fully exploit the complete solar spectrum (UV and visible) by using the porous metal nanoparticles (NPs) like Au, Ag, and Pt, by embedding them on a semiconductor material. The precise control over the shape and size of metal NPs enabled systematic engineering of their LSPR properties. Moreover, the plasmonic metal nanoparticles have been coupled with larger surface area of sea-urchin-like microspheres TiO_2 to form metal-oxide hybrid nanostructures with combined optical, electronic and catalytic properties. In this context, Ag decorated TiO_2 based photocatalysts can be widely used in many industrial processes because of their excellent photocatalytic performances, and owing to the highly surface area and LSPR effect caused by the precursor control and NPs embedding. In addition, NPs entrapped within the sea-urchin-like microsphere architecture can facilitate direct charge transfer from porous metal to TiO_2 and function as traps to minimise electron and energy back flow in the form of surface charge recombination. Further, titania urchin-like microspheres are slightly different from the Ag NPs decorated one in terms of Ti valence state and the light-absorption during photocatalysis. The enhanced photocatalytic efficiency of Ag nanoparticles decorated materials are due to enhanced surface area and the distortion in the TiO_2 local structural symmetry in the sea urchin-like mesoporous spherical structure.

2. Experimental

TiO_2 sea-urchin-like microspheres with varied concentrations of $NaBH_4$ precursor and Ag decorated TiO_2 microspheres were successfully fabricated by one step template-free method under microwave irradiation. The morphology and microstructure of the materials were characterized by Field Emission Scanning Electron Microscope (FESEM), HRTEM, and High-angle annular dark-field (HAADF STEM). The XAS at the Ti L- and K-edges were measured at the BL20A1 and BL17C beamlines, respectively. The

XANES spectra at Ti L-edge were measured in the total-electron-yield (TEY) mode with a pressure ~5x10-^{9} torr in the ultra-high vacuum chamber. All spectra were normalized by following standard procedure. The metal foils and oxide powders, TiO_2 in rutile and anatase phase, were used for energy calibration and also for comparison of spectra.

3. Results and discussion

Figure 1 shows TEM image of sea-urchin-like microspheres (0%Ag) that demonstrates detailed morphologies that is round and spiny. The samples are nearly spherical in shape and the size ranges from 800 nm to 1000nm. The urchin-like microspheres have spines about 100 to 300nm in length, 20 to 30 nm thick, and more or less sharp. The size and the ball shape remain practically unchanged in all the Ag/TiO_2 microspheres samples. X-ray absorption near-edge spectroscopy (XANES) can provide information on the lattice structural symmetry and the unoccupied electronic states. Fig. 2(a) presents Ti L-edge XANES spectra of sea-urchin-like microspheres prepared with different concentrations of $NaBH_4$. The L-edge spectra features are due to the transitions from Ti 2p core level to final empty states above Fermi level, which consist of strongly hybridized Ti 3d orbitals in conduction band. The unoccupied states ratio in Ti 3d t_{2g}/e_g are consistent with the results of photocatalytic degradation of methylene blue as show by a maximum at 0.8g $NaBH_4$.

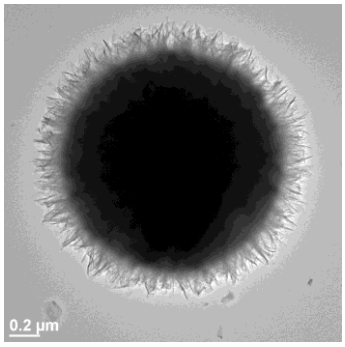

Figure 1. TEM image of sea urchin-like microspheres.

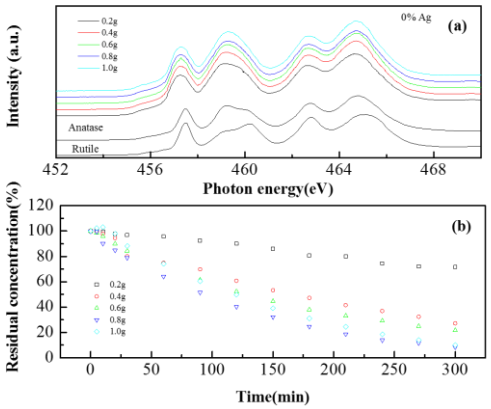

Figure 2. (a) Photocatalytic degradation of methylene blue. (b) Ti $L_{3,2}$-edge XANES spectra of sea-urchin-like microspheres.

4. Conclusions

A study on the sea-urchin-like TiO_2 microspheres and Ag decorated morphology innovative structures were performed and the samples showed an increased surface area for photocatalytic reactions. These materials are chemically stable. XANES measurements are powerful tool to study the local electronic and atomic structure of materials. Our investigations revealed that samples with 0.8g $NaBH_4$ precursor has a significant effect on the electronic structure and showed a strong correlation to the local structural symmetry of TiO_6 octahedra. Further, sea-urchin-like microspheres are also incorporated with different concentration of Ag nanoparticles by a hydrothermal method. The spectra results suggested a model demonstrating the mechanism of plasmonic effect and charge transfer under UV-Visible illumination in Ag/TiO_2 spheres. In brief, our study presents a more detailed knowledge on the LSPR effect in the photocatalytic mechanism.