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Sol-gel synthesis of mesoporous hollow titania microspheres for photodegradation of 4-chlorophenol

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Mesoporous titania (TiO_2) hollow microspheres have been prepared by sol-gel method and characterized by XRD, Raman, FTIR, N_2 adsorption-desorption study, FESEM, TEM and UV-DRS. The FESEM images reveal hollow spherical shaped particles of size 2–4 µm. The BET surface area, total pore volume and average pore diameter of 400 °C-treated sample are found to be 74.52 m^2 g^{-1}, 0.23 cm^3 g^{-1} and 12.37 nm, respectively. The band gap energy of the product is calculated as 3.06 eV. The prepared TiO_2 hollow spheres show ~90% photodegradation of the water pollutant, 4-chlorophenol, within 1 h. The photocatalytic reaction shows pseudo-first order reaction with a rate constant of 0.027 min^{-1}. The photocatalytic experiments repeated for another three cycles showed no significant changes in the k (min^{-1}) values, indicating the potential reusability of the material.

Keywords: Mesoporous materials, Sol-gel method, Microspheres, Microstructures, Photocatalysis, Titania

Over the past several years, inorganic hollow spheres of different dimensions have attracted extensive attention due to their low density, large specific area, mechanical and thermal stability and surface permeability.[1–6] Hollow spheres could open up possibility for various new application fields, such as in catalysis, controlled delivery, photonic crystals etc.[7-11] For the formation of hollow structures, different synthetic approaches such as chemical etching, galvanic replacement, template-mediated, and chemically induced self-assembly are followed.[8] Among these, the template-mediated method is a more effective and versatile approach for the formation of hollow structures. Templating method is performed by hard templating materials such as silica, polymer spheres, carbon, $CaCO_3$ spheres, etc., and soft templating process using microemulsion droplets, ionic liquids, bubbles, etc.[9–15] Jiang *et al.*[16] prepared hollow titania by freezing assisted reverse-microemulsion templated sol-gel method. Wang *et al.*[17] have synthesized hollow TiO_2 microspheres using polystyrene spheres as hard templates. Titania is considered as a promising material with excellent properties, like photocatalytic, electrochromic, and hydrogen storage properties, which are always influenced by the nanostructure. TiO_2/natural hematite-supported bentonite was used for photocatalytic degradation of 4-nitrophenol.[18] Ksibi *et al.*[19] synthesized phosphorus modified TiO_2 for photocatalytic degradation of 4-chlorophenol.

In this study, we have synthesized mesoporous titania (TiO_2) hollow microspheres by sol-gel process using copper hydroxycarbonate as the templating agent. Photocatalytic activity of TiO_2 hollow microspheres for the degradation of a phenol derivative (4-chlorophenol (4-CP)) is also studied. The product shows ~90% photodegradation of 4-CP under UV light within 60 min.

Experimental

The precursor, $Cu_2(OH)_2CO_3$ microsphere, was prepared first according to our previous report (see Supplementary data).[20] In a typical experiment, 0.5 g of $Cu_2(OH)_2CO_3$ microspheres was ultrasonically dispersed in 30 mL of ethanol to form a suspension. A solution of titanium isopropoxide (2 mmol) in ethanol (5 mL) was added to the above suspension with continuous stirring. After 15 minutes of stirring, a solution of water (3 mL) and ethanol (3 mL) was added dropwise to make a sol. It was further stirred for 2 h to form a greenish white mass. Then, 10 mL HCl (1 M) was added into it and stirred for 5 min to obtain a white product. It was then collected by centrifugation and washed, followed by drying at 60 ºC for 4 h. The as-prepared product was calcined at 400 ºC at a heating rate of 1 ºC min^{-1} and a dwell time of 2 h to obtain TiO_2 hollow microspheres.

The sample was characterized by XRD (Philips X'Pert Pro PW 3050/60, Ni-filtered Cu-Kα radiation, λ = 0.15418 nm), FTIR (Spectrum two, Perkin Elmer), Raman (RENISHAW spectrometer with 514 nm radiation), nitrogen adsorption-desorption (Quantachrome ASIQ MP), FESEM (Zeiss, Supra™ 35VP, Oberkochen, Germany), TEM (Tecnai G2 30ST, FEI) and UV-vis spectrophotometer (Jasco V-730).

The photocatalytic degradation of 4-chlorophenol (4-CP) was studied with the synthesized product. In this study, 5 mg of the TiO_2 sample was mixed with 10 mL of 1.5×10^{-4} M 4-CP solution. After stirring the dispersion for 60 min in dark, the adsorption equilibrium was achieved. Then the aliquot was taken out followed by filtration with millipore filter paper (pore dia. 0.22 mm). The filtrates were analyzed using a UV-visible spectrophotometer. The remaining solution was placed in a rectangular box (36 cm × 30 cm × 44 cm), fitted with eight tubes with a power source of 6 W each placed at the inside top of the box. After a certain interval of irradiation (λ = 365 nm), aliquots were collected, filtered and monitored by UV-visible spectrophotometer. The depletion of absorption intensity at λ_{max} = 225 nm signifies the degradation of 4-CP.

Results and discussion

Figure 1(a) shows the XRD patterns of synthesized TiO_2 hollow spheres. The presence of diffraction peaks at around 25.09^o, 37.65^o, 48.02^o, 53.89^o, 55.07^o, 62.38^o, 68.7^o, 70.07^o and 75^o related to the crystal planes of (101), (004), (200), (105), (211), (204), (116), (220), and (215), respectively confirm the formation of anatase TiO_2 (JCPDS No. 21-1272). No characteristic peaks of impurities were observed signifying the formation of a highly pure product. The crystallite size (*D*) of the particles obtained from Scherrer formula was found to be 19.04 nm. Raman spectrum of the sample is shown in Fig. 1(b). For the sample, the presence of sharp intense peak at 144 cm^{-1} and a weak peak at around 196 cm^{-1} representing E_g mode of vibration is attributed to anatase TiO_2. The peaks at higher frequency region, around 400, 516 and 639 cm^{-1} corresponding to B_{1g}, A_{1g} and E_g modes also confirm the presence of phase pure anatase TiO_2.[21] The FTIR spectrum of the mesoporous TiO_2 hollow spheres is shown in Fig. 1(c). The transmittance at around 513 cm^{-1} is due to TiO_2. The appearance of peaks at around 1634 cm^{-1} and 3443 cm^{-1} is due to the bending and stretching modes of -OH from water, respectively.

Figure 2(a) demonstrates the optical absorption spectra of TiO_2 hollow microspheres. The optical band gap energy (E_g) of the sample was calculated using the Tauc equation, $(\alpha hv)^{1/n} = A(hv\text{-}E_g)$, where α, hv, A and n are the absorption coefficient, photon energy, proportionality constant depending on the transition probability, and n is a constant depending on the nature of transition, i.e., direct allowed

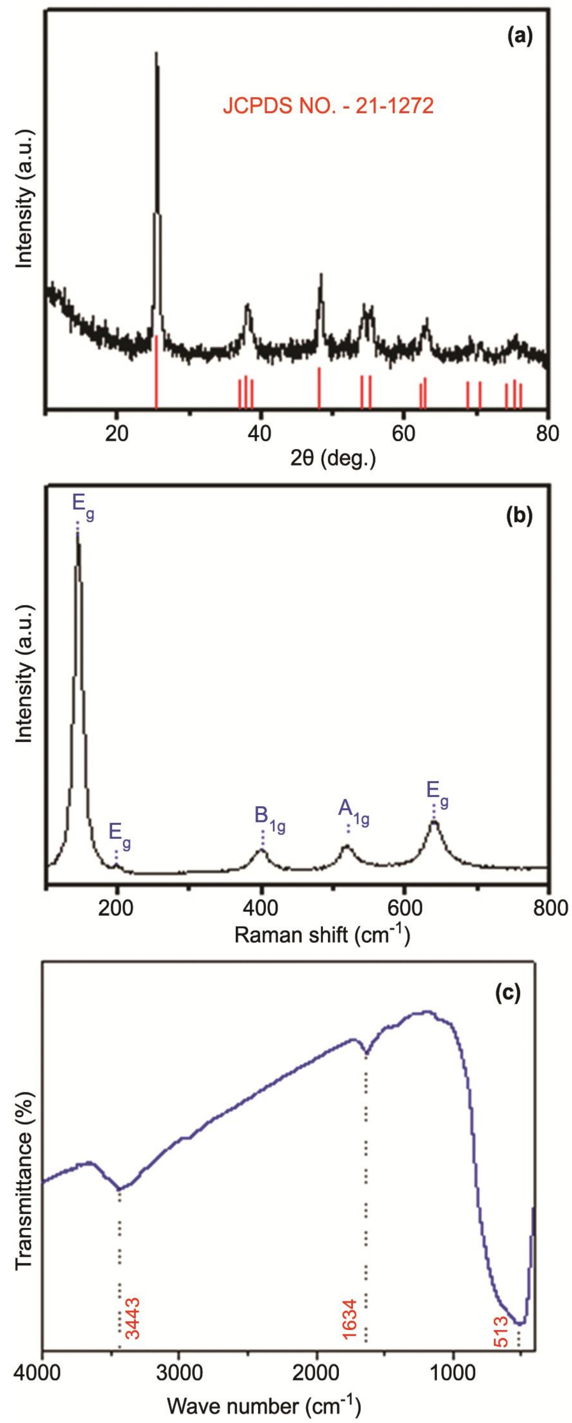


Fig. 1 — (a) XRD pattern, (b) Raman spectra and (c) FTIR spectra of TiO_2 hollow microspheres.

(n = 1/2), indirect allowed (n = 2), direct forbidden (n = 3/2) and indirect forbidden (n = 3). In this case, n = 2 for indirect allowed band gap.[22,23] Figure 2(b) shows the plots of $(\alpha hv)^{1/2}$ versus hv for the TiO_2 hollow sphere. The band gap energy was calculated

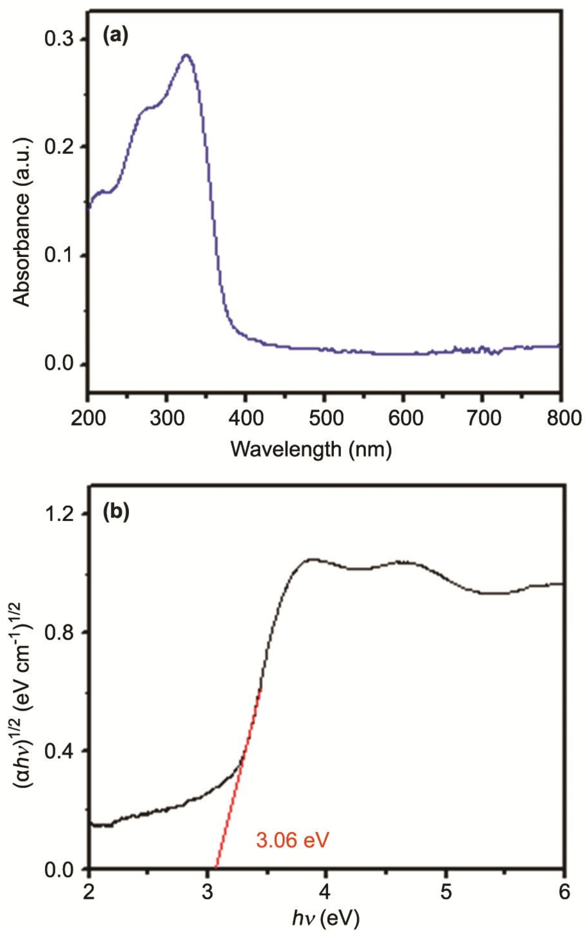


Fig. 2 — (a) Diffused reflectance spectra and (b) variation of $(\alpha h\nu)^{1/2}$ versus photon energy of TiO_2 hollow microspheres.

By extrapolating a tangent to the *x*-axis. The calculated band gap for TiO_2 hollow sphere was found to be 3.06 eV.

The N_2 adsorption-desorption isotherms of TiO_2 hollow spheres are presented in Fig. 3, which shows type IV isotherm with H3 hysteresis loop. This type of hysteresis is due to the presence of slit-like pores with non-uniform size and/or shape[24]. The BJH pore size distribution resulting from adsorption data of the isotherm is revealed in the inset of Fig. 3, which also suggests the absence of regular shape and size of the pores in the sample. The BET surface area, total pore volume and average pore diameter of the 400 °C treated particles were found to be 74.52 m^2 g^{-1}, 0.23 cm^3 g^{-1} and 12.37 nm, respectively.

The morphological feature of the sample studied by FESEM analysis (Fig. 4), indicated the formation of TiO_2 microspheres. The broken sphere in Fig. 4b shows the hollowness of the microsphere. Scheme 1

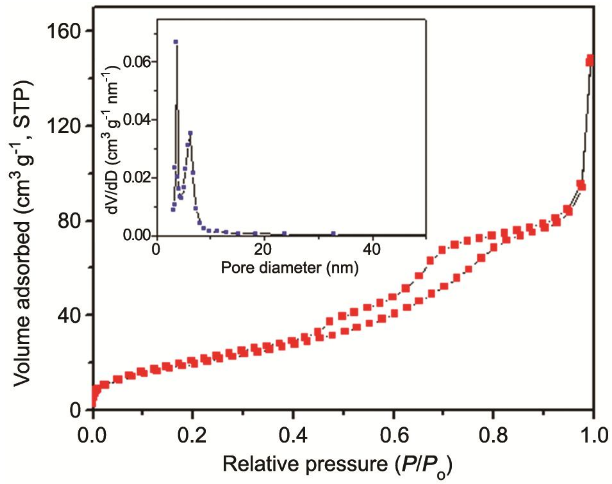


Fig. 3 — N_2 adsorption-desorption isotherm of TiO_2 hollow microspheres. [Inset: pore size distribution curve].

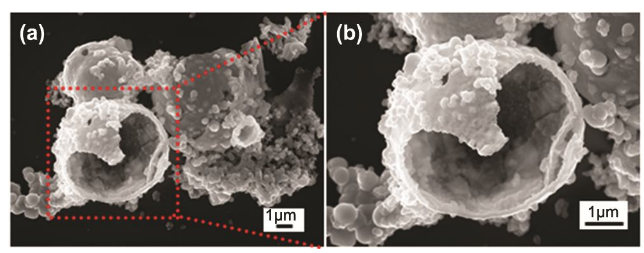
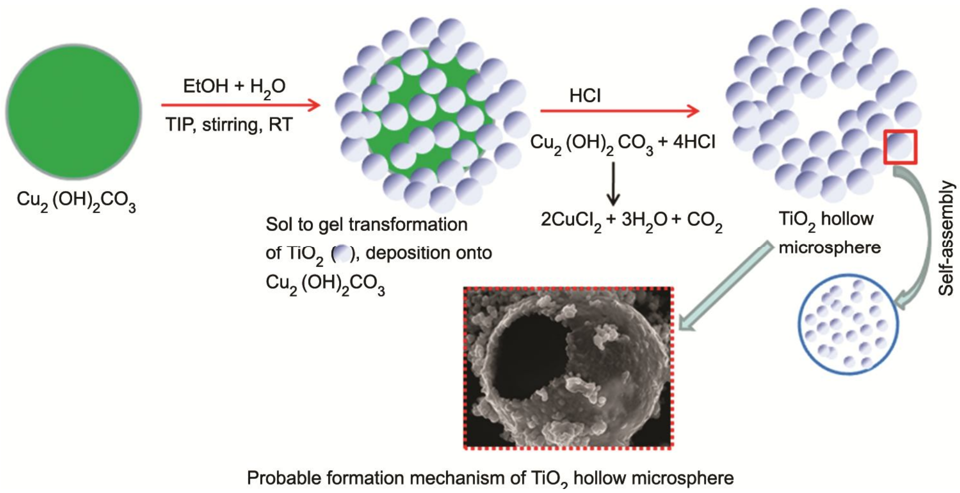


Fig. 4 — FESEM images of TiO_2 hollow microspheres at (a) low and (b) high magnifications.

Illustrates the probable formation mechanism of titania hollow sphere. In the reaction medium, the titania nanoparticles are deposited onto the $Cu_2(OH)_2CO_3$ spheres. In the presence of HCl, $Cu_2(OH)_2CO_3$ are etched out as soluble $CuCl_2$ (green) in aqueous medium, rendering white hollow microspheres of TiO_2 in which TiO_2 are self-assembled. Pure anatase TiO_2 hollow microsphere was obtained upon 912alcinations at 400 °C. The microspheres were also studied by TEM (Fig. 5a and 5b), HRTEM (Fig. 5c) and SAED (Inset of Fig. 5c). The lattice spacing of 0.35 nm corresponds to the (101) plane of anatase TiO_2. The SAED image shows the polycrystalline nature of the particles. The TEM-EDS analysis (Fig. 5d) reveals the presence of Ti and O in the particles with their atomic ratio of 0.78.

Before irradiation with UV light, adsorption capacity of the product was studied. The photocatalytic degradation of 4-CP was examined under UV light irradiation (365 nm). Figure 6 shows the UV-visible absorption spectra for the degradation of 4-CP as a function of irradiation time. A steady



Scheme 1

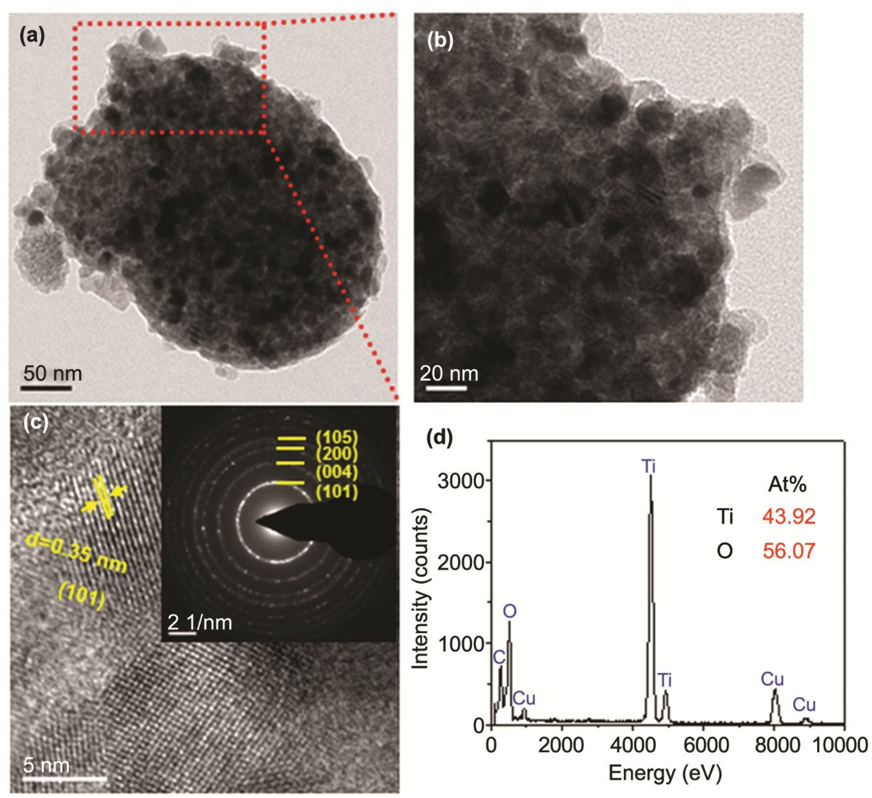


Fig. 5 — TEM images of TiO_2 sphere [(a) low and (b) high magnifications], (c) HRTEM images [Inset: SAED pattern], and, (d) energy dispersive X-ray spectroscopy.

depletion of the absorbance peak at 225 nm with time is observed. The amount of 4-CP photodegradation with time is shown in Fig. S1 (Supplementary data). It reveals about 90% photodegradation of 4-CP within 1 h. The logarithm plot of the absorbance ($-\ln A/A_o$) with reaction time for 4-CP, exhibits pseudo-first order reaction with rate constant of 0.027 min^{-1} (Supplementary data, Fig. S2). To identify the potential reusability of the synthesized photocatalyst of TiO_2 hollow microsphere, the photocatalytic experiments were performed for another three cycles and showed no significant changes in the k (min^{-1}) values (Supplementary data, Fig. S3).

In summary, mesoporous TiO_2 hollow microspheres were synthesized by a simple sol-gel method. Formation of anatase TiO_2 was confirmed by XRD

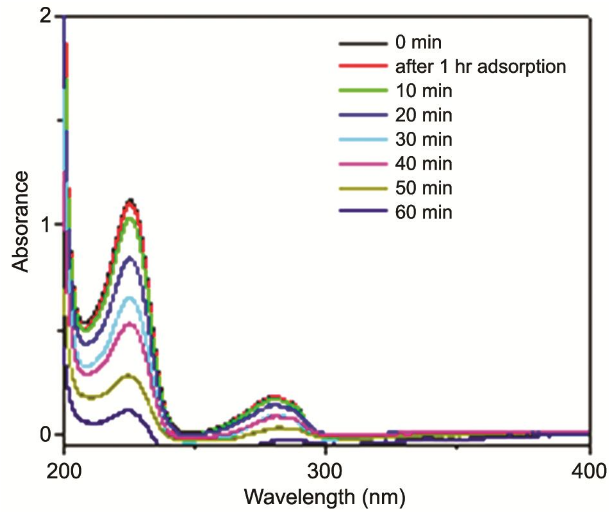


Fig. 6 — UV-visible absorption spectra of the sample for the degradation of 4-CP.

and Raman spectroscopy. N_2 adsorption-desorption isotherms indicated slit-like non-uniform pore geometry. FESEM and TEM studies revealed the hollow microstructure of TiO_2. The prepared TiO_2 hollow microspheres showed 90% photodegradation of 4-chlorophenol within 1 h with potential reusability. The process is useful to design shape controlled synthesis of TiO_2 and other oxide particles which could have potential applications for the removal of other organic pollutants from contaminated water in textile and pharmaceutical industries.

Supplementary data

Supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_57A(07)910-914_SupplData.pdf.

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