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Facile Preparation in Synthesizing Nano-size Hollow Silicate Particles by Encapsulating Colloidal-Hydroxyapatite nanoparticles

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Materials. Nano-size colloidal Hydroxyapatite solution (1g/L) with specific gravity of 1.001 (HAp, $Ca_{10}(PO_4)_6(OH)_2$) (provided by Tanaka et al[1]) was used as nano-core particles / template for the formation of hollow nano-size/oblique shape silica particles. Tetraethoxysilane (Wako pure chemical) was used as precursor of silica shell. Ammonia water (28% Wako pure chemical) used as catalyst and Ethanol (Wako pure chemical) used for washing the template reaction.

Preparation. Unique shape / nano-sized hollow silicate particles were synthesized based on the previous principle done by our laboratory (CRL, NIT) [2]. In this case, 50 ml of hydroxyapatite solution (1g/L) ($Ca_{10}(PO_4)_6(OH)_2$) was dispersed by ultra-sonic for 5 min (2 times), and 0.0197 mol of ammonium aqueous solution (H_2O:NH_3) were added to the solution, after then stirred for 30 min. Then 0.00225614 mol (0.5 mL) of tetraethoxysilane (TEOS) was added drop wise to the solution, followed by stirring for at least 2 h, a core-shell HAp / silica particles was prepared. (note: amount of TEOS was varied from 1 mL, 0.5 mL, 0.25 mL and 0.1 mL for optimization). In obtaining hollow silicate particles, after 2 h continuous stirring, the white gel solution were filtered and washed several times (4X or until becomes neutral) by ethanol, then dried in a vacuum oven to 90 ^oC for 5 h. In removing the HAp core, acid treatment (3.0 mol/L, HCl) was done for 8 h stirring. After then, filtered and washed several times (4X or until becomes neutral) with distilled water. Finally, vacuum dried the obtained sample to 90 ^oC for 1 d; oblique nano-size hollow silicate particle was obtained. The principle of hollow silicate template with HAp nanoparticles is shown schematically in Figure 1.

Characterization. The product were characterized by X-ray Diffraction (XRD, Model RINT 1100, Rigaku) with Cu Kα radiation (λ= 1.54056 Å), at a scanning rate of 0.02 °/ s (5 ° to 60 °, 2θ) with an operating voltage of 40 kV and emission current 30 mA. The thermal property of the sample was investigated using the Thermogravimetry (TG, TG-8120, Rigaku, Japan) under oxygen atmosphere. The heating rate of the temperature increase at 10 °C/min with temperature ranged from (22 to 1000) °C. Morphology and microstructure of hollow particles were examined using scanning electron microscopy (SEM; JSM-7000F, JEOL) and transmission electron microscopy (TEM, 2000EXII). The specific surface area of the sample was determine by Brunauer-Emmett-Teller (BET) while the cage (pore) size distribution by Barrett-Joyner-Halenda (BJH) method via the automatic analyzer (BELSORP-max) with Nitrogen gas adsorption and desorption isotherm recorded at 77K.

Results

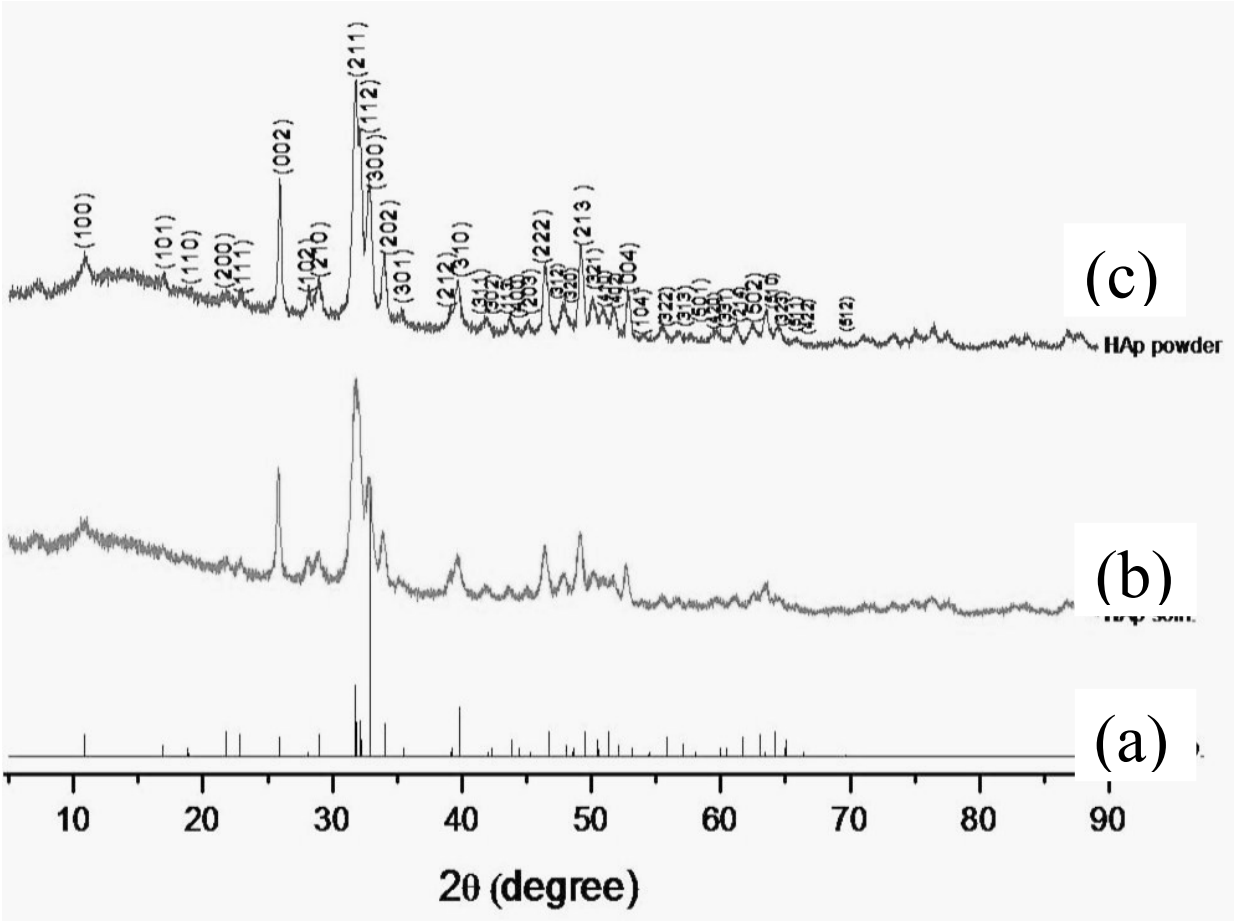

Fig. S1 XRD pattern of: (a) HAp standard reflection patterns [$Ca_{10}(PO_4)_6(OH)_2$] , (b) HAp solution (dried), (c) HAp powder (standard sample).

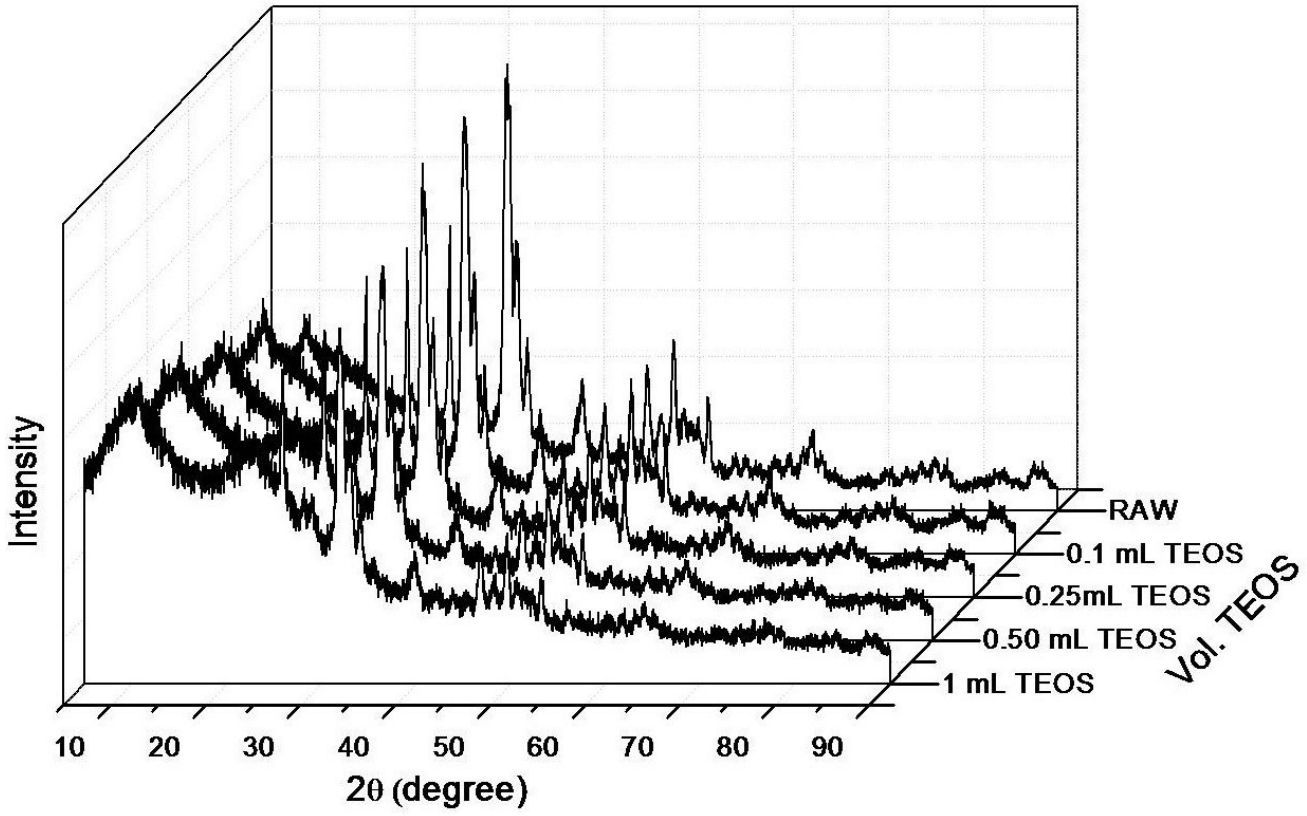

Fig. S2. XRD pattern of (RAW) dried HAp powder as well as nano-sized HAp powder encapsulated by (0.1 mL TEOS) SiO_2, (0.25 mL TEOS) SiO_2, (0.50 mL TEOS) SiO_2, and (1.0 mL TEOS) SiO_2.

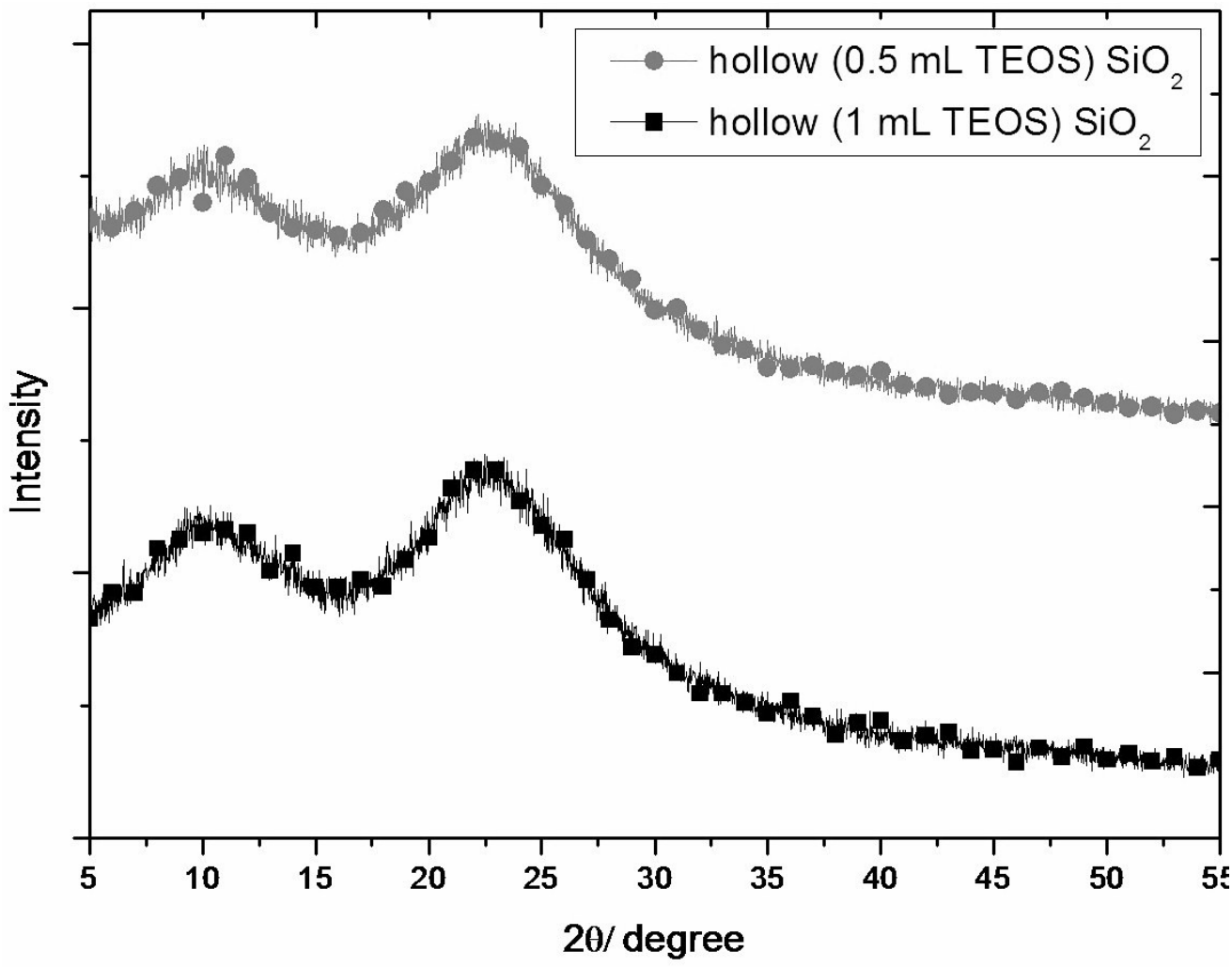

Fig. S3. XRD pattern after acid treatment exhibit amorphous phase (0.50 mL TEOS, (●)) SiO_2, and (1.0 mL TEOS, (■)) SiO_2.

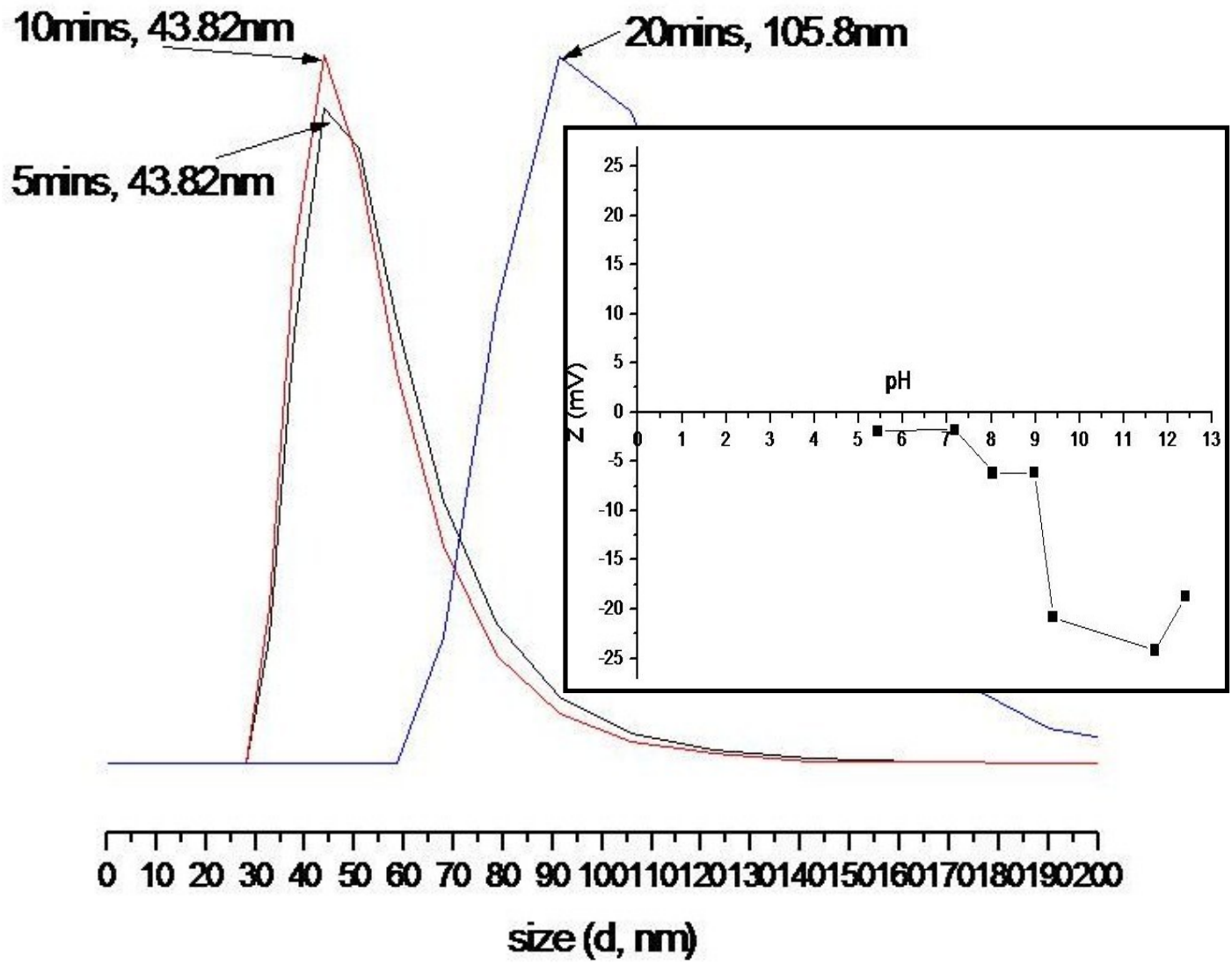

Fig. S4. Particle size distribution of HAp`s solution (specific gravity of 1.001-0.999) at different ultrasonic time interval. Inset is the zeta potential of the HAp nanoparticles. .

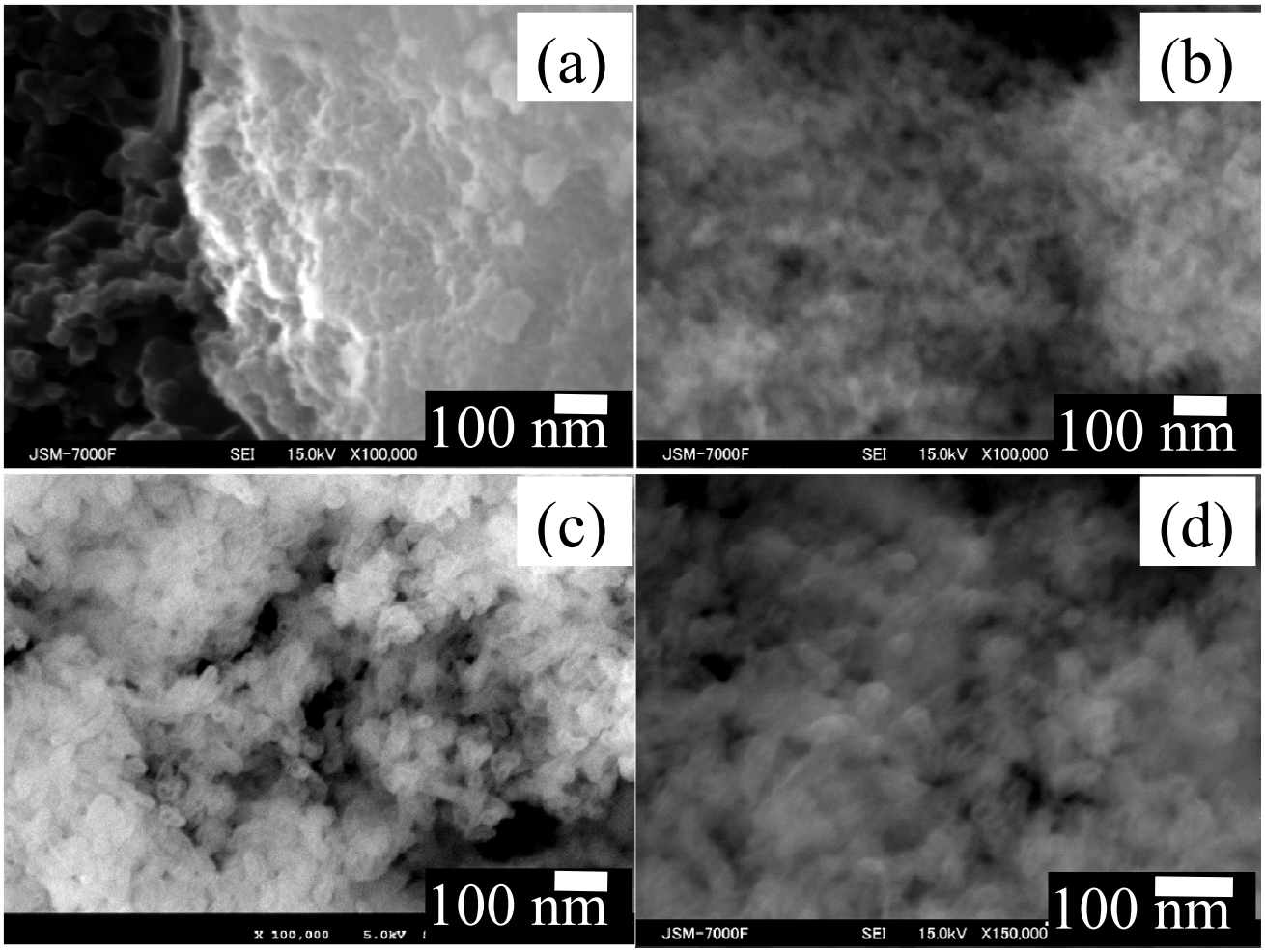

Fig. S5. SEM images (bar line 100 nm): Acid treated samples of nano-sized hollow (0.1 mL TEOS) SiO_2 (a), (0.25 mL TEOS) SiO_2 (b), (0.5 mL TEOS) SiO_2 (c), and (1 mL TEOS) SiO_2 (d).

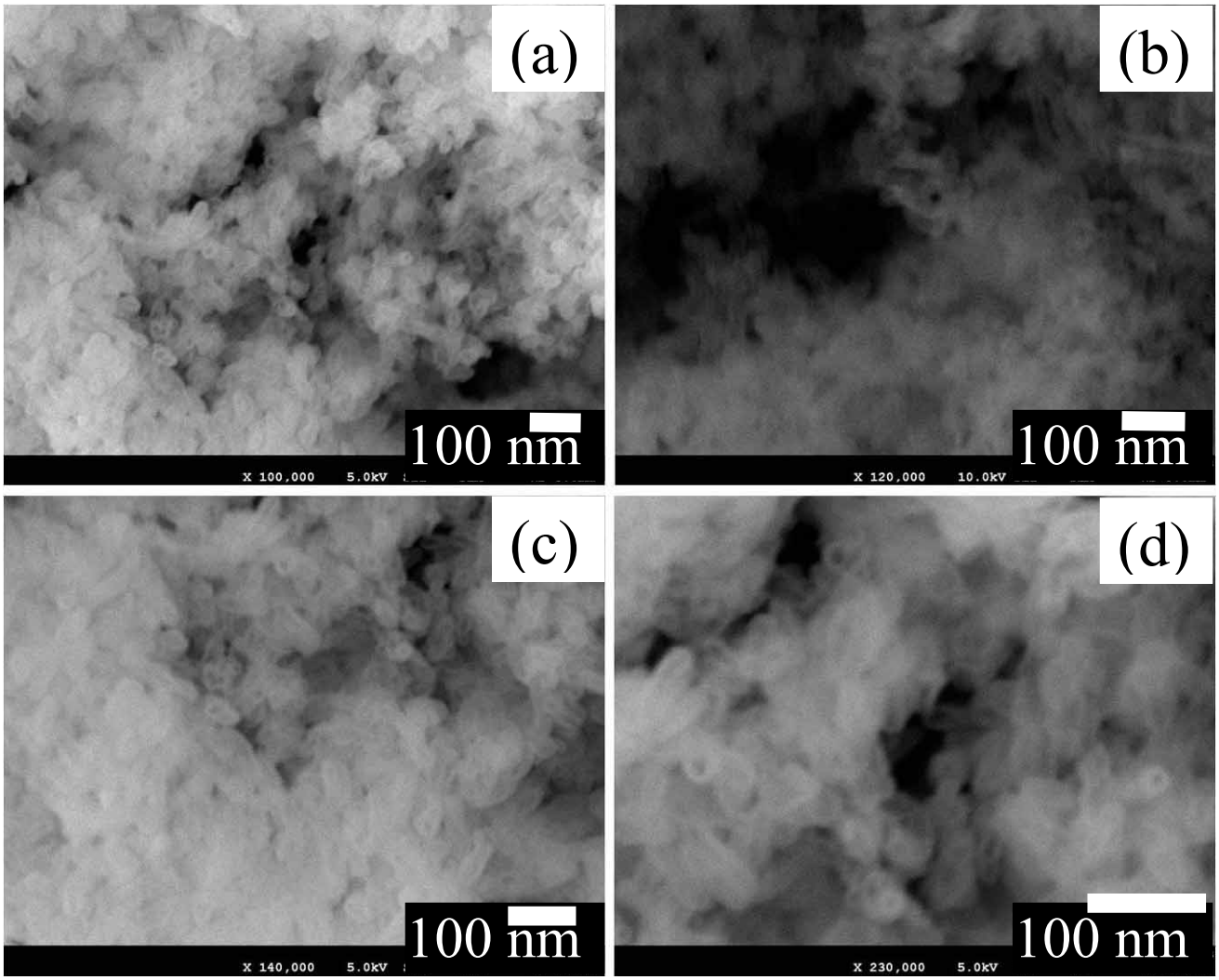

Fig. S6. SEM images (bar line 100 nm) : Acid treated samples of nano-sized hollow (0.5 mL TEOS) SiO_2 magnified at (a) X100,000, (b) X 120,000 (c) X 140,000 and (d) X230,000

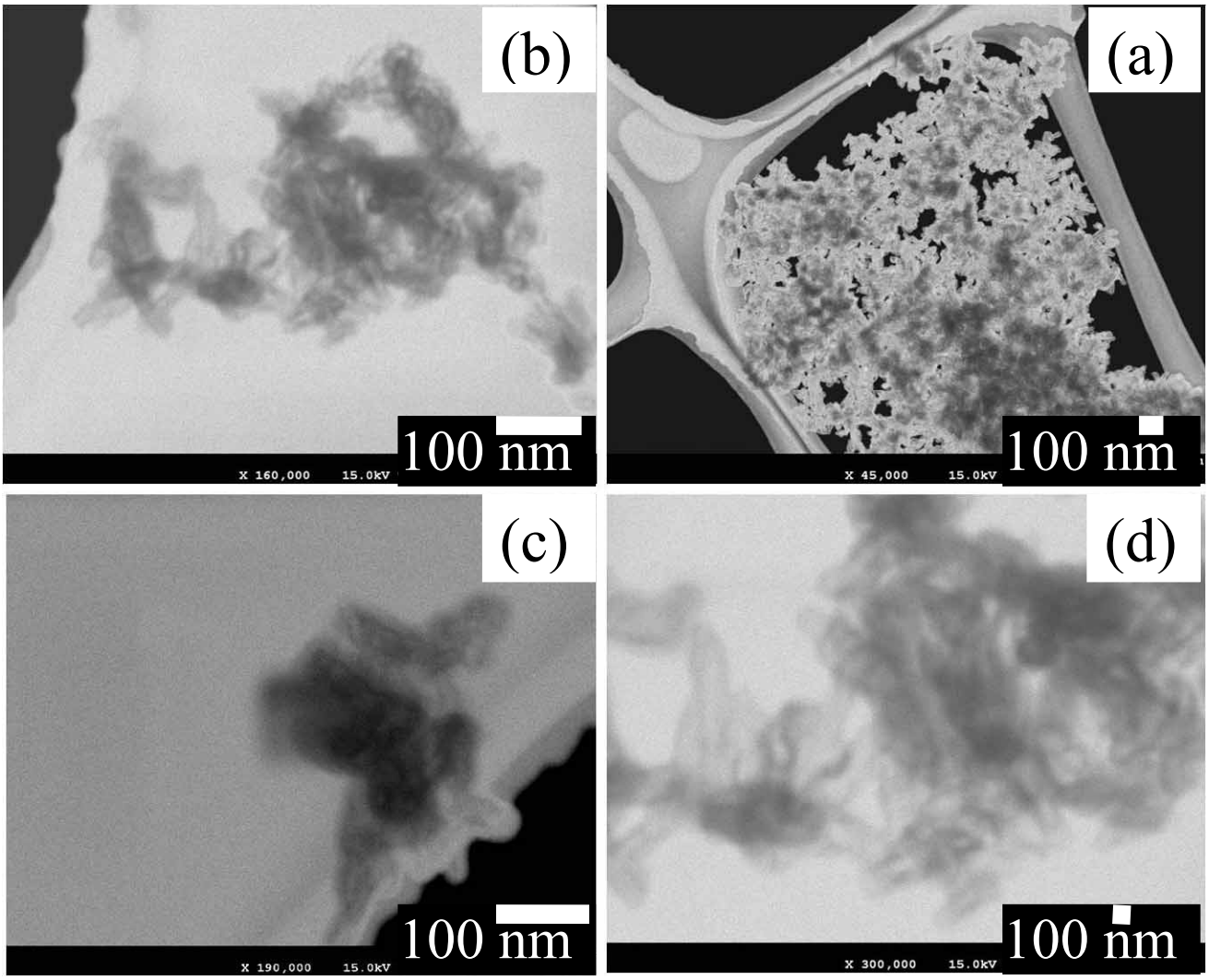

Fig. S7. STEM images (line bar 100 nm [a,b,c] while 10 nm [d]) : Acid treated samples of nano-sized hollow (0.5 mL TEOS) SiO_2 magnified at (a) X140,000, (b) X 45,000 (c) X 190,000 and (d) X300,000.

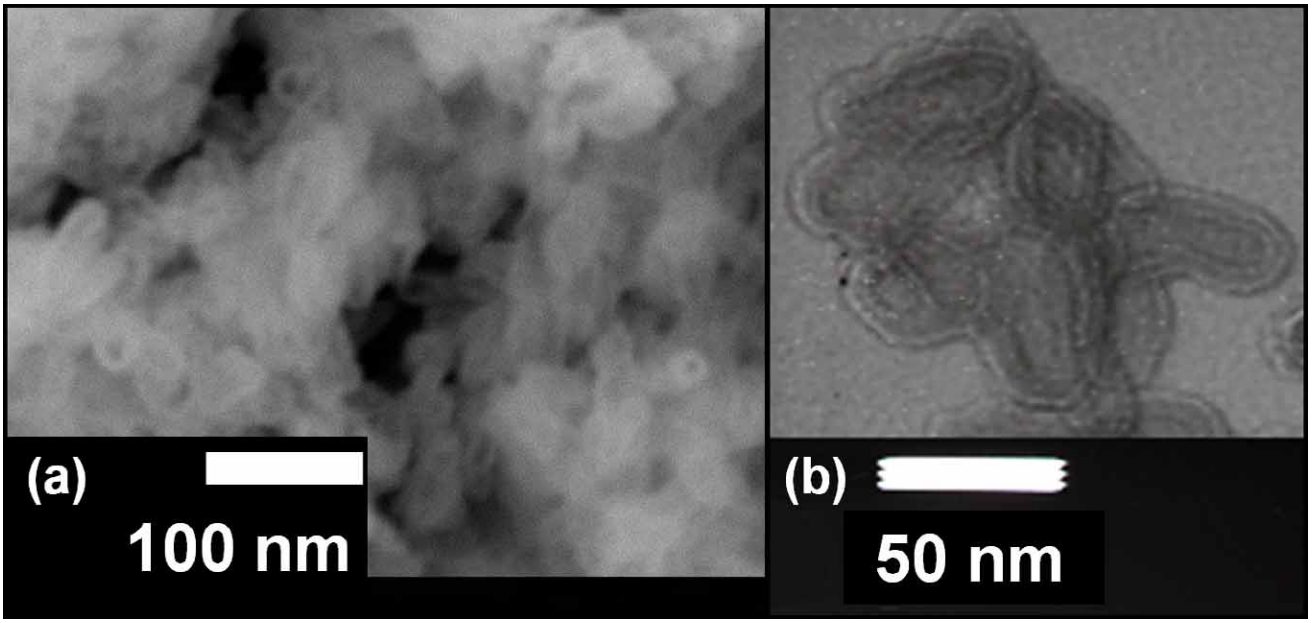

Fig. S8 SEM (a) and TEM (b) images: Acid treated samples of nano-sized hollow (0.5 mL TEOS) SiO_2

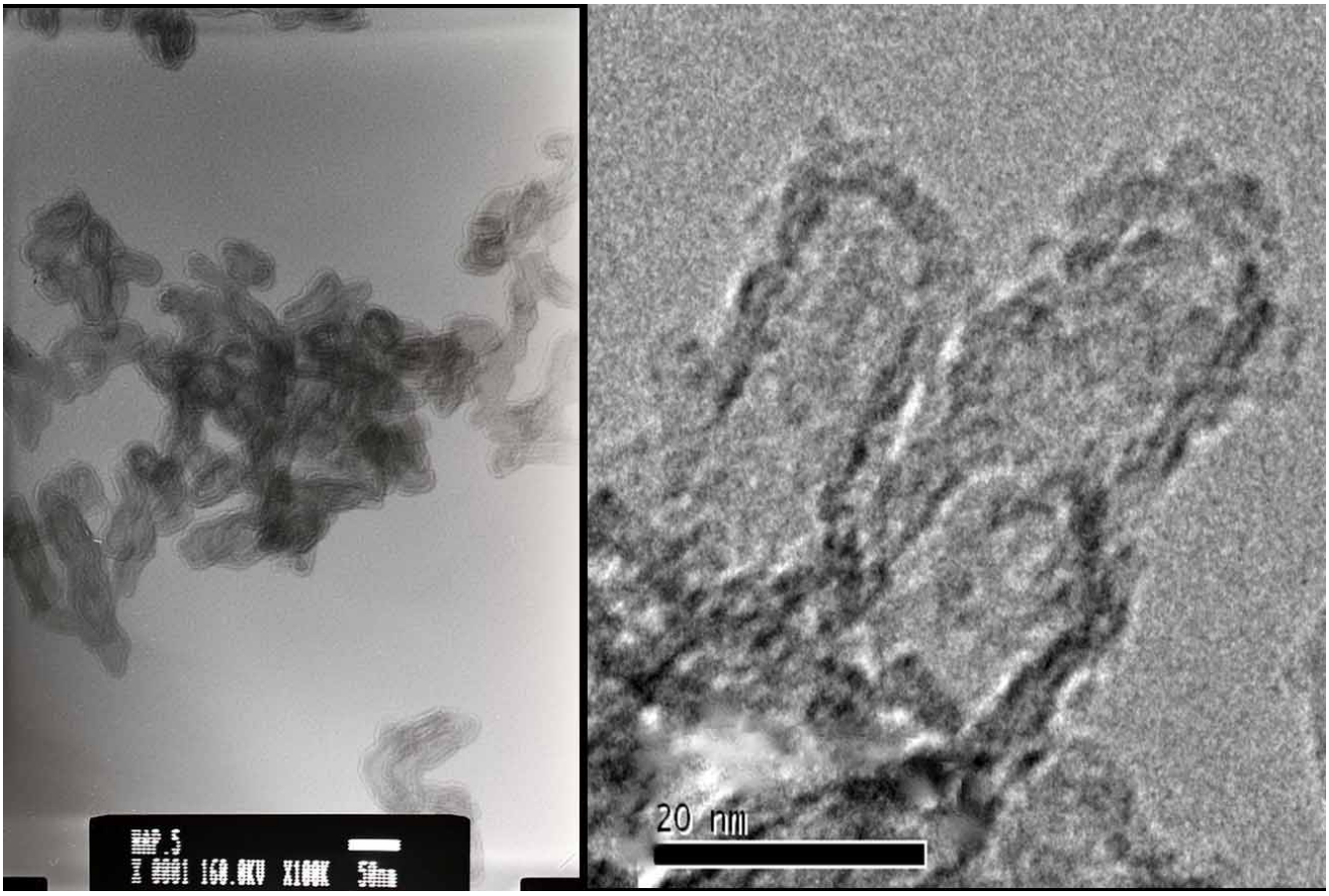

Fig. S9 TEM images: Acid treated samples of nano-sized hollow (0.5 mL TEOS) SiO_2

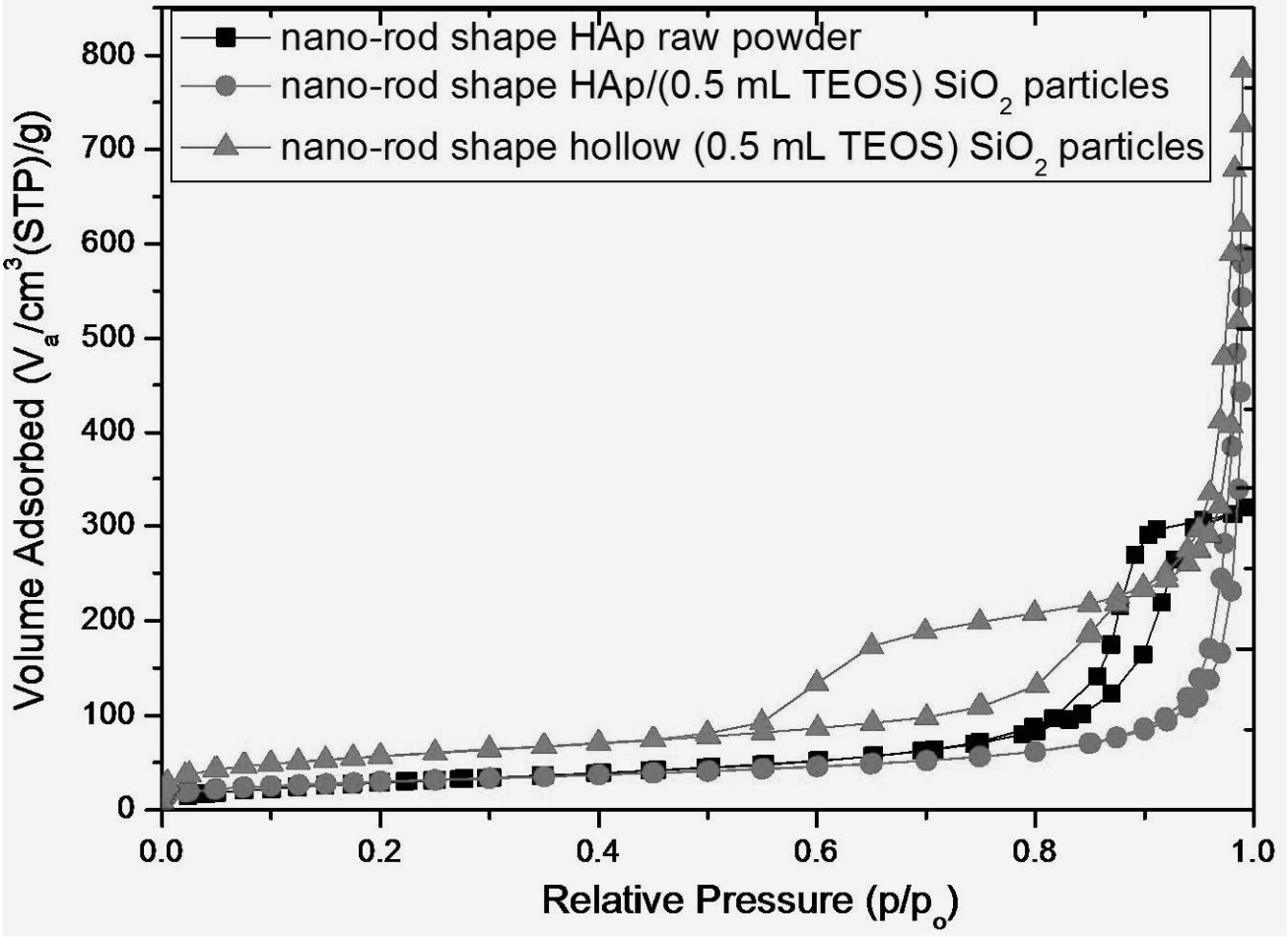

Fig. S10 Nitrogen adsorption-deporption isotherms of nano-rod (spindles) shape HAp nanoparticles raw powder (■), core-shell HAp/ SiO_2 nanoparticles (●) and hollow spindle-shape (rod) nano-size hollow silica particles (▲) synthesized at ambient temperature.

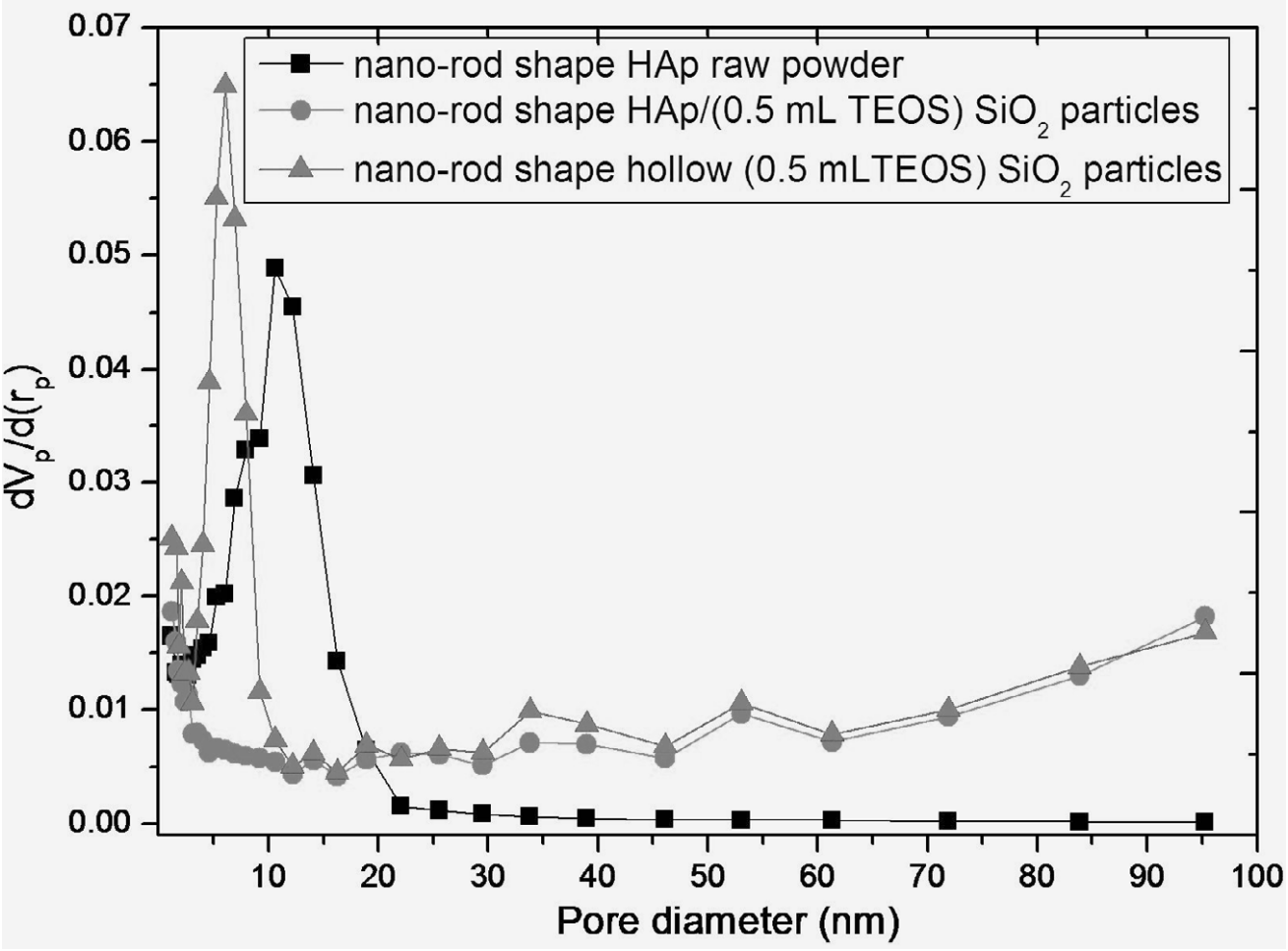

Fig. S11 BJH differential pore size distribution of nano-rod (spindle) shape HAp nanoparticles raw powder (■), core-shell HAp/ SiO_2 nanoparticles (●) and hollow spindle-shape (rod) nano-size hollow silica particles(▲) synthesized at ambient temperature.

TABLE S1 Physicochemical properties of the the Nanostructure HAp/SiO_2 particles

Material	Pore Volume (cm^3/g , BET)	Cavity diameter (nm,, BJH)	Surface Area (m^2/g , BET)
HAp powder (solution dried)	0.4912	10.65	111.7
HAp/(0.5 mL TEOS) SiO_2	0.8981	1.21	108.8
Hollow (0.5 mL TEOS) SiO_2	1.18	6.06	204.0