Sodium Hydroxide Catalyzed Monodispersed High Surface Area Silica Nanoparticles

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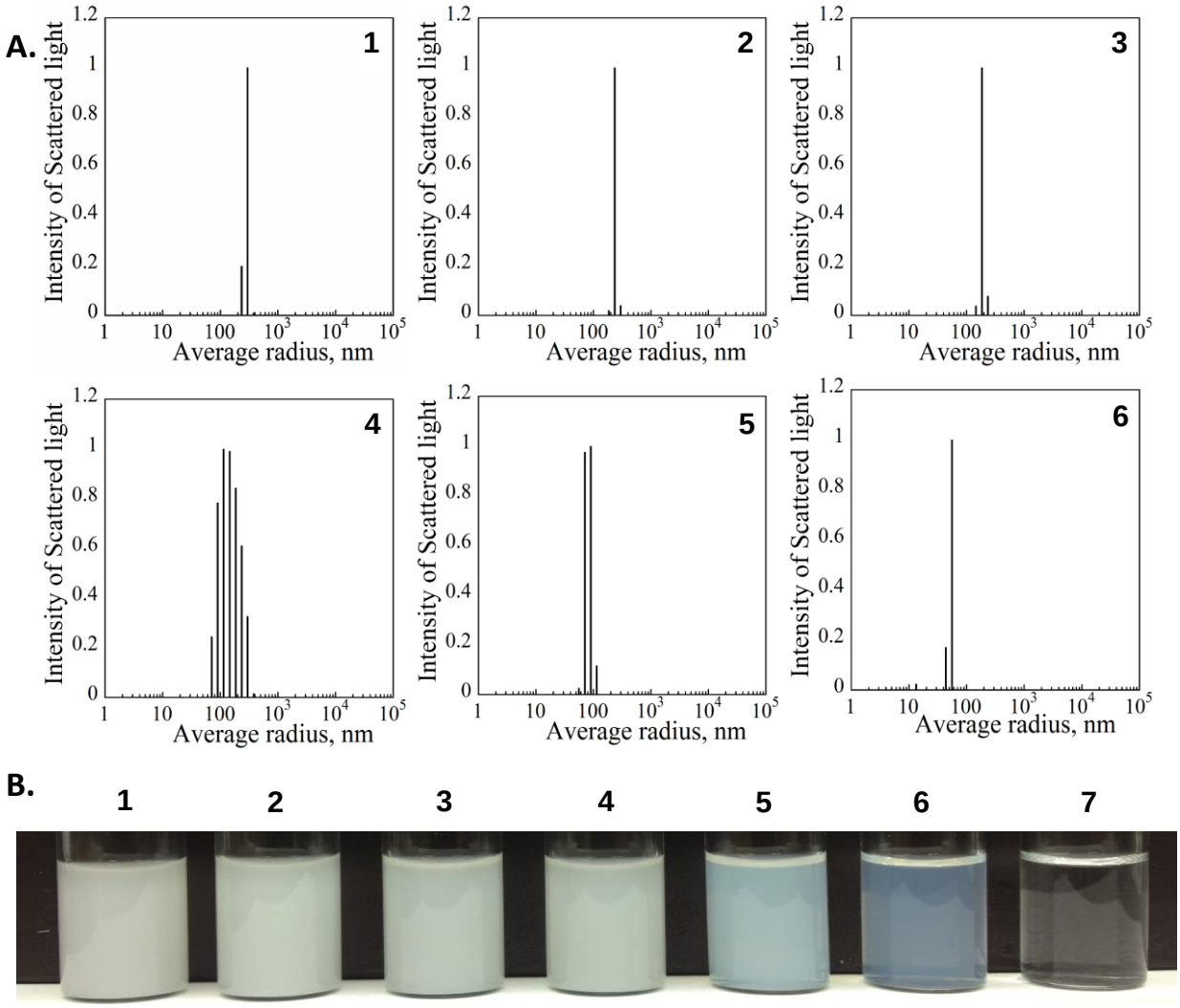
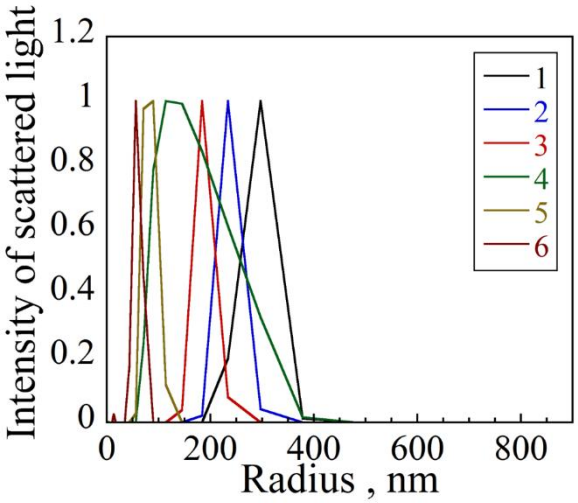
Abstract

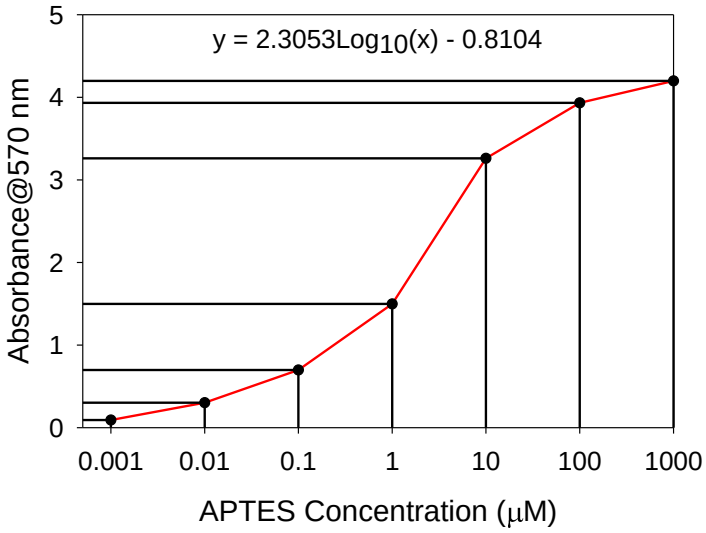
Understanding of the synthesis kinetics and our ability to modulate medium conditions allowed us to generate nanoparticles via an ultra-fast process. The synthesis medium is kept quite simple with tetraethyl orthosilicate (TEOS) as precursor and 50% ethanol and sodium hydroxide catalyst. Synthesis is performed under gentle conditions at 20 ^{o}C for 20 minutes. Long synthesis time and catalyst-associated drawbacks are most crucial in silica nanoparticle synthesis. We have addressed both these bottlenecks by replacing the conventional Stober catalyst, ammonium hydroxide, with sodium hydroxide. We have reduced the overall synthesis time from 20 h to 1/3 h, ~60-fold decrease, and obtained highly monodispersed nanoparticles with 5-fold higher surface area than Stober particles. We have demonstrated that the developed NPs with ~3-fold higher silane can be used as efficient probes for biosensor applications.



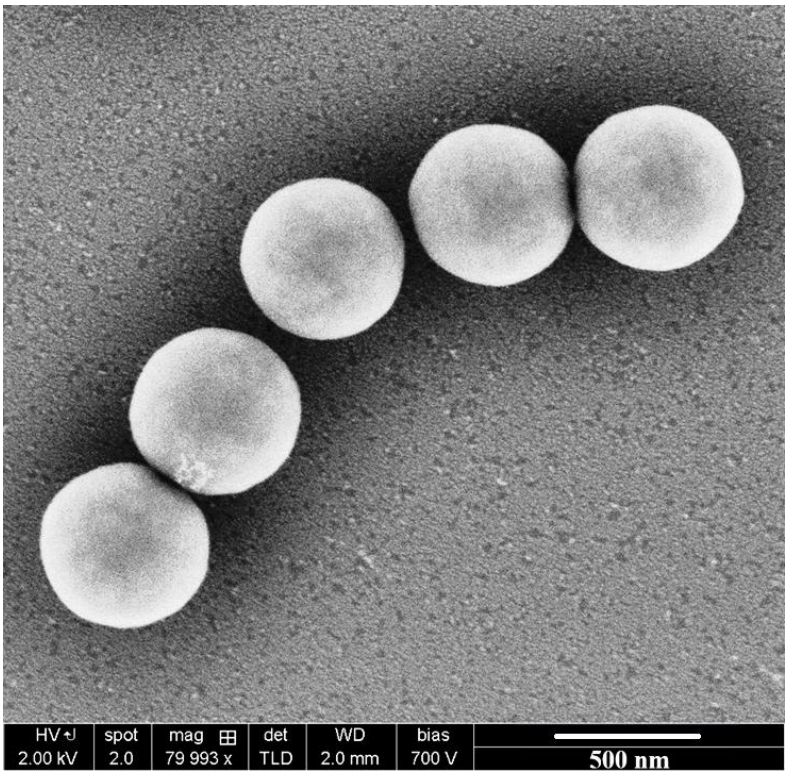
SI Figure 1. A. Dynamic Light Scattering analyses-based NP population distribution along various sizes for different NaOH concentrations. **B.** Images of different SiNPs as per the sequence from 'A'. The sizes of the particles decrease from 1 to 7. Samples 1 to 7 correspond to formulations with different NaOH concentrations ranging 20 mM to 0, respectively.



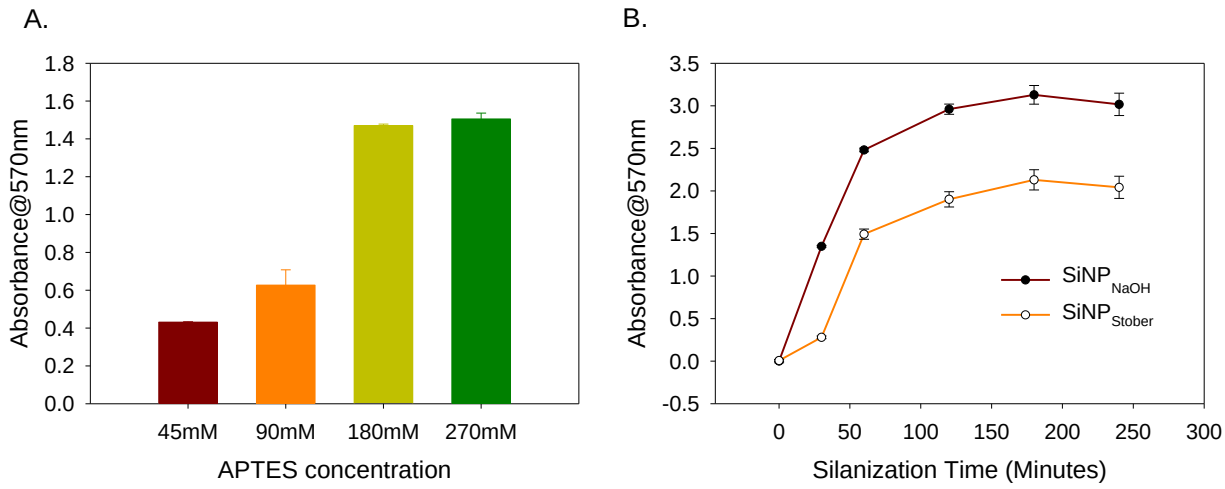
SI Figure 2. Average radius of different silica nanoparticles obtained from dynamic light scattering.



SI Figure 3. Standard curve for analyzing data obtained with ninhydrin on silanized SiNPs. Various known concentrations of APTES were prepared by directly diluting stock APTES concentration in 100 µL ninhydrin (20 mg/mL) followed by incubating at 100 ^{o}C for 10 min. Absorbance was recorded for each sample at 570 nm against ethanol background.



SI Figure 4. Scanning micrograph of Stober nanoparticles.



SI Figure 5. Ninhydrin assay for silanization optimization. (A) Stober particles with four different APTES concentrations. Optimized APTES concentration of 180 mM was employed for analyzing APTES loading efficiency on NaOH- and Stober Silica nanoparticles (B).

Table 1: Different synthesis procedure of silica nanoparticles with their advantages and disadvantages

Method	Advantages	Disadvantages
Reverse microemulsion[1, 2]	• Coating with different functional groups • Mesoporous • Precise control over size	• Lengthy post processing (removal of surfactants) and sample work outs • High cost
Chemical vapor condensation[3, 4]	• Synthesized in powder form • Can be synthesized in bulk amount, thus useful in industries	• Hard to control morphology (size and shape) • Poor control of phase composition • Powder exposure; Health risk
Sol-gel: Stober and modified method, ammonia as catalyst[5, 6, 7]	• Mild condition • Pure and homogeneous particles	• Time • Reproducibility due to ammonia • Removal of ammonia • Sometimes controlling the size
Microwave-assisted heating[8,9,10]	• Fast synthesis • Can be employed in industry using continuous flow reactor	• Microwave exposure; Health risk • High cost • Poor control over size and shape of particles • Poor solvent penetration

Table 2: Optimization of water-ethanol concentration for the synthesis of sodium hydroxide mediated silica nanoparticle: NaOH concentration: 20 mM, TEOS concentration 90 mM*

Volumetric Ratio (Water : Ethanol)	Result
10:90	Gel formation
20:80	Gel formation
30:70	Gel + Particles
40:60	Particles; poorly dispersed
50:50	Particles; well dispersed
60:40	Cloudiness; No particles
70:30	No nucleation

*TEOS at 90 mM concentration was chosen to have a higher TEOS concentration as the starting point

Table 3: Optimization of tetraethyl orthosilicate concentration at 20 mM sodium hydroxide concentration in 1:1 ratio of water-ethanol medium

TEOS concentration (mM)	Result
11.25	No particles
22.5	Cloudiness (no particles) + Gel formation
45	Particles
67.5	Particles
90	Particles; well dispersed
112	Particles; poorly dispersed

Table 4: Optimization of sodium hydroxide concentration at 90 mM tetraethyl orthosilicate concentration in 1:1 ratio of water-ethanol medium

NaOH concentration (mM)	Result
4	No particles
8	No particles
10	Particles
20	Particles
50	Gelation
100	Gelation

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