Stable Luminous Nanocomposite of $CsPbX_3$ Perovskite Nanocrystal Anchored on Silica for Multicolor Anti-counterfeit Ink and White-LED

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Experimental

Materials and Chemicals:

$PbBr_2$ (99.90%), $PbCl_2$ (99.90%) PbI_2 (99.90%), Cs_2CO_3 (99.99%), octadecene (ODE, 90%), oleic acid (OA, 90%, AR), oleylamine (OLA, 90%, AR), trimethoxy(octadecyl)silane (TMODS, 90%), 3-aminopropyltriethoxysilane (APTES, 99%), vinyltrimethoxysilane (VTMS, 98%), thioglycolic acid (TA, 90%, AR) and tetraethoxysilane (TEOS, >98%) were purchased from Aladdin and used as received without purification. Silicone resin and phosphor fluorescent powder (red) were purchased from Shenzhen Looking Long Technology co., LTD and used as received without purification. All the other solvents were used as received without any purification.

Preparation of silica (SiO_2) NPs:

SiO_2 NPs were synthesized via the modified Stöber method:[1] a solution of TEOS (8 ml), EtOH (150 ml), ammonium hydroxide (12 ml) and deionized H_2O (30 ml) was introduced into a 250 ml round-bottom glass flask and mixed homogenously with a magnetic stirrer. The hydrolysis and condensation reaction of TEOS was carried out under continuous magnetic stirring at a rate of 700 r/min at 50 ℃, from which SiO_2 NPs were obtained as a suspension after 24 h.

Preparation of octadecyl/propylamine-capped silica (CA-SiO_2) NPs:

Octadecyl/propylamine-capped silica NPs were synthesized using the following procedures (Supporting information, Scheme S1). When the above SiO_2 NPs suspension was cooled to room temperature, a mixture of APTES (4 ml) and TMODS (4 ml) was injected gradually. After the magnetic stirring was continued for another 24 h, the white capped SiO_2 NPs (CA-SiO_2) powder was obtained by removing the residual reactant and ammonium hydroxide through five cycles of centrifugation/redispersion in ethanol and water, and finally drying in a vacuum oven at 50 ℃ for 24 h. Similarly, propylamine-capped silica (A-SiO_2) NPs and octadecyl/carboxyl-capped silica (CC-SiO_2) NPs were synthesized using the procedures outlined in Scheme S2.

Preparation of propylamine-capped silica (A-SiO_2) NPs:

When the pristine SiO_2 NPs suspension was cooled to room temperature, an aliquot of APTES (4 ml) was injected. After the magnetic stirring continued for another 24 h, the white functional SiO_2 NP (A-SiO_2 NP) powder was obtained by removing the residual reactant and ammonium hydroxide through five cycles of centrifugation/redispersion in ethanol and water, and finally drying in a vacuum oven at 50 ℃ for 24 h.

Preparation of octadecyl/carboxyl-capped silica (CC-SiO_2) NPs:

Octadecyl/carboxyl-capped silica (CC-SiO_2) NPs were synthesized using the procedures outlined in Scheme S2. When the above SiO_2 NP suspension was cooled to room temperature, a mixture of vinyltrimethoxysilane (VTMS, 4 ml) and TMODS (4 ml) was injected gradually. After the magnetic stirring was continued for another 24 h, the white functional SiO_2 NPs powder was obtained by removing the residual reactant and ammonium hydroxide through five cycles of centrifugation/redispersion in ethanol and water, and finally drying in a vacuum oven at 50 ℃ for 24 h.

When the above SiO_2 NPs disperse in ethanol, a calculated amount of thioglycolic acid (TA) and photoinitiator was injected. After UV light irradiation (365 nm, 0.5 $W \cdot cm^{-2}$) for 2 h, the white octadecyl/carboxyl-capped silica (CC-SiO_2) NPs powder was obtained by removing the residual reactant through five cycles of centrifugation/redispersion in ethanol and water, and finally drying in a vacuum oven at 50 ℃ for 24 h.

***In-situ* growth of $CsPbX_3$ NCs on capped CA-SiO_2 NPs ($CsPbX_3$@CA-SiO_2):**

$CsPbX_3$@CA-SiO_2 composites were prepared following a modified procedure.[2] A typical synthetic procedure is described in Scheme 1. Cs_2CO_3 (0.1 mmol), $PbBr_2$ (0.2 mmol) or equivalent PbI_2, $PbBr_2$/$PbCl_2$ and $PbCl_2$, CA-SiO_2 NPs (0.3 g), ODE (10 mL), OLA (0.3 mL), and OA (1 mL) were mixed and heated under vigorous stirring at 150 ℃. The reaction was cooled in an ice/water bath in 5 min. The centrifugation/redispersion procedure was repeated three to five times in toluene, after which the solid precipitate was collected for characterization. The resulting composite was dried in a vacuum oven overnight before being stored for future use. A control sample was made from physically blended silica NPs with $CsPbBr_3$ NCs.

Stability Tests:

To evaluate the stability in water, all composite films were immersed in air-free de-ionized water stored in the dark at room temperature and PL intensity was subsequently measured over time. Separately, colloidal suspensions of $CsPbX_3$@CA-SiO_2 were stored under vacuum at room temperature and subjected to UV light irradiation (365 nm, 0.5 $W\cdot cm^{-2}$) over different period of times. The aged samples were then subjected to further characterization.

Anti-counterfeiting inks for patterning:

The composites were dispersed in toluene at a concentration of 0.2 $g\cdot mL^{-1}$. Pre-designed seals with customized "XJTU" patterns were wetted with the above suspension and then pressed against filter papers to transfer the designed patterns.

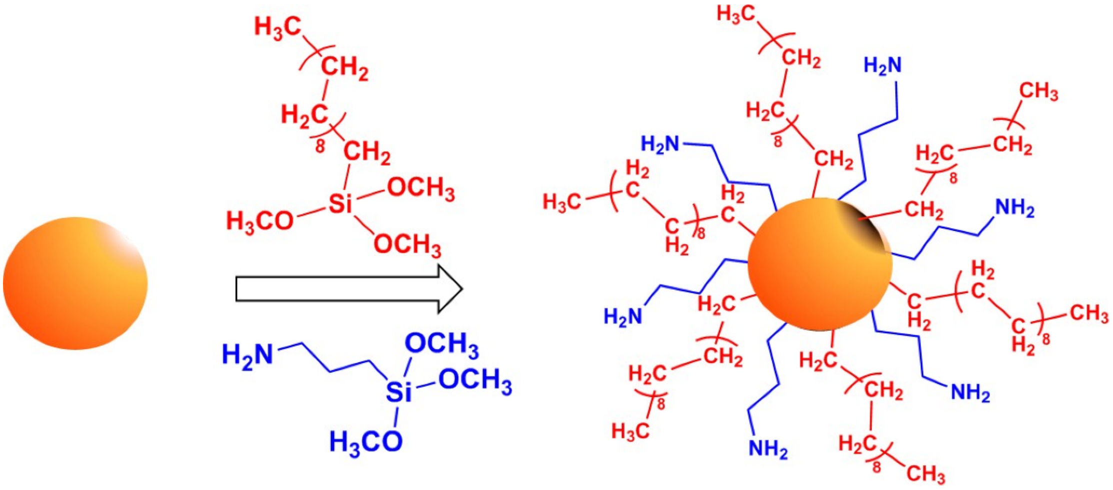
White LED device fabrication:

To fabricate white LEDs, a blue (460 nm) LED chip was used to excite the green (520 nm for $CsPbX_3$@CA-SiO_2) and red composites (660 nm, YAG fluorescent powder). Firstly, the YAG phosphors (0.3 g) were dispersed in silicon resin (3 g) after vigorous stirring, and the resulting mixture was directly coated onto blue LED chips and thermally cured at 40 °C for 30 min and then 120 °C for 60 min. Then, the composites film was prepared similarly as above, which would be stowage onto the upper surface of YAG-based LED devices by mixing with silicon resin, followed by two-stage thermal curing, to give the fabricated WLED devices.

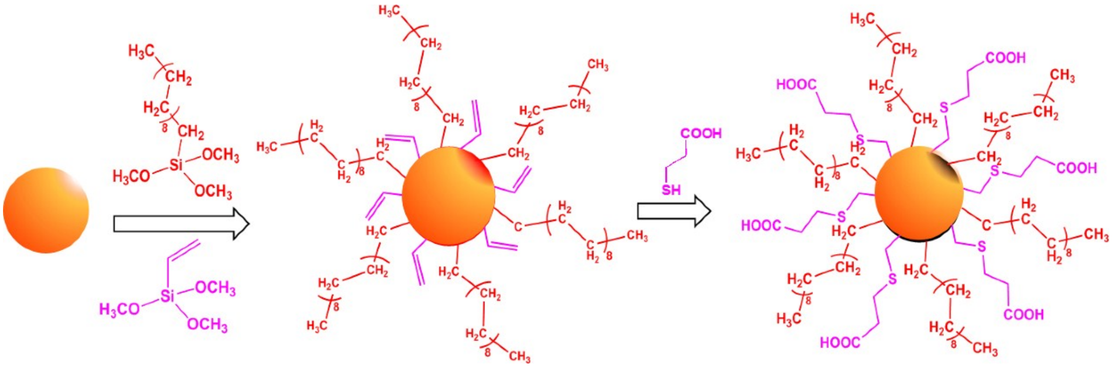
Characterization Methods:

Ultraviolet and visible absorption (UV-vis) spectra of colloidal solutions were collected using a Cary 5000 UV-Vis-NIR spectrophotometer. Fluorescence spectra and absolute photo-luminescent quantum yields (PLQYs) were collected using an integrated sphere, recorded on an Edinburgh Instruments FLS920 spectrophotometer.

FTIR spectrometer for the chemical structures were collected using a Tensor 27 of Bruker Optics. PXRD data were acquired using a Bruker AXS D8 Discover X-Ray Diffractometer at a wavelength of Cu K (1.79 Å). X-Ray photoelectron spectroscopy (XPS) measurement for elemental composition was processed about the composites powder by an AXIS ULTRA (England, KRATOS ANALYTICAL Ltd) using an Al mono Kα X-ray source (1486.6 eV) operated at 150 W. SEM images were acquired on a JEOL 7800F Field Emission Scanning Electron Microscope. TEM and high-resolution TEM (HR-TEM) data were acquired on a FEI G_2F_{30} electron microscope operated at 200 kV with a Gatan SC 200 CCD camera.



Scheme S1. Schematic illustration of the octadecyl/propylamine capped silica (CA-SiO_2).



Scheme S2. Schematic illustration of the octadecyl/carboxyl capped silica NPs (CC-SiO_2).

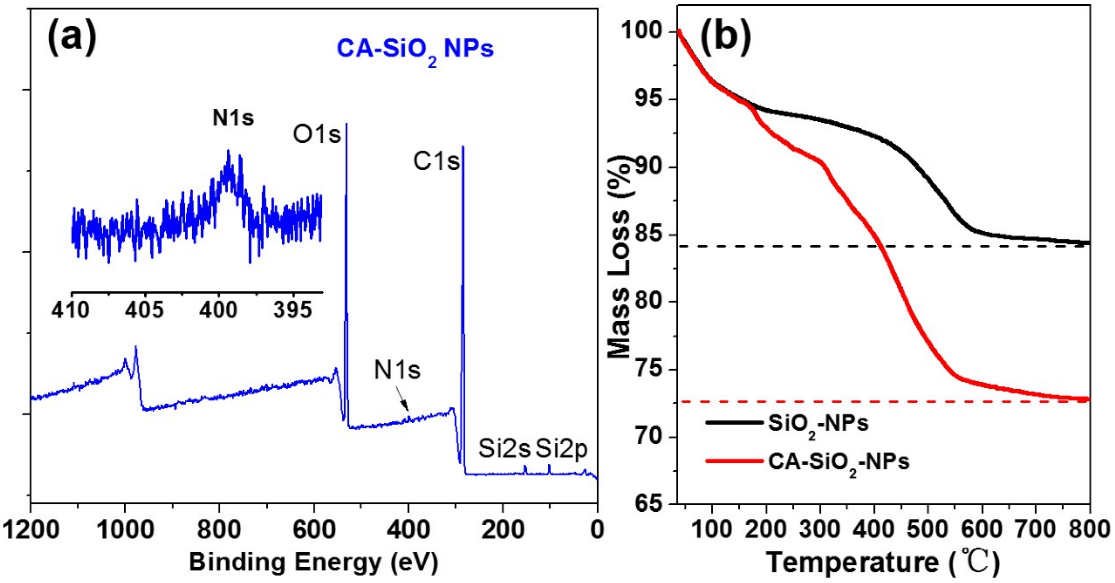


Figure S1. (a) Elemental composition of functionalized silica (CA-SiO_2) by XPS. The inset is a higher magnification of N1s. (b) Thermogravimetry analysis plots of the primal and capped silica (CA-SiO_2).

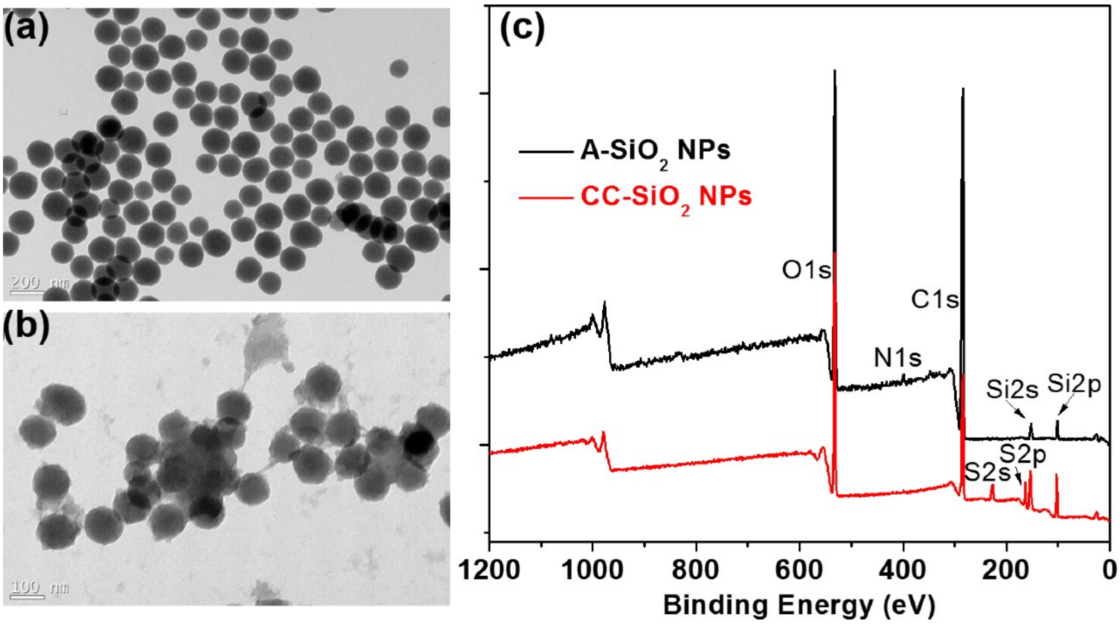


Figure S2. TEM images of A-SiO_2 NPs (a) and CC-SiO_2 NPs (b). (c) High-resolution X-ray photoelectron spectra (XPS) analysis with a survey scan of A-SiO_2 NPs and CC-SiO_2 NPs.

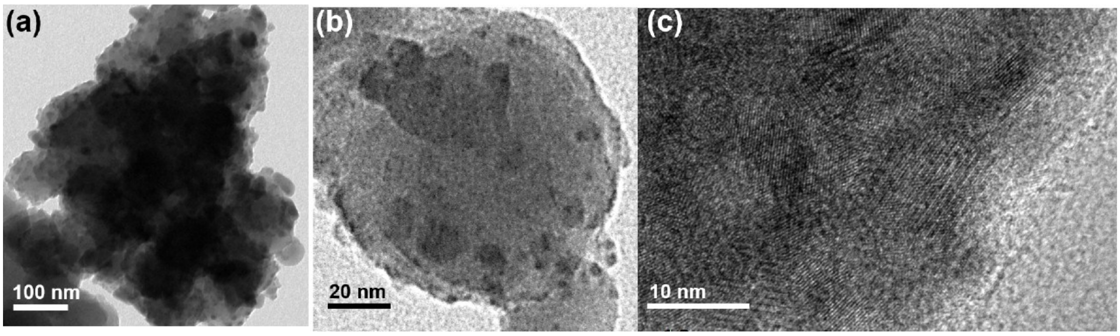


Figure S3. TEM (a, b) and HR-TEM (c) images of $CsPbBr_3$@CA-SiO_2 composites.

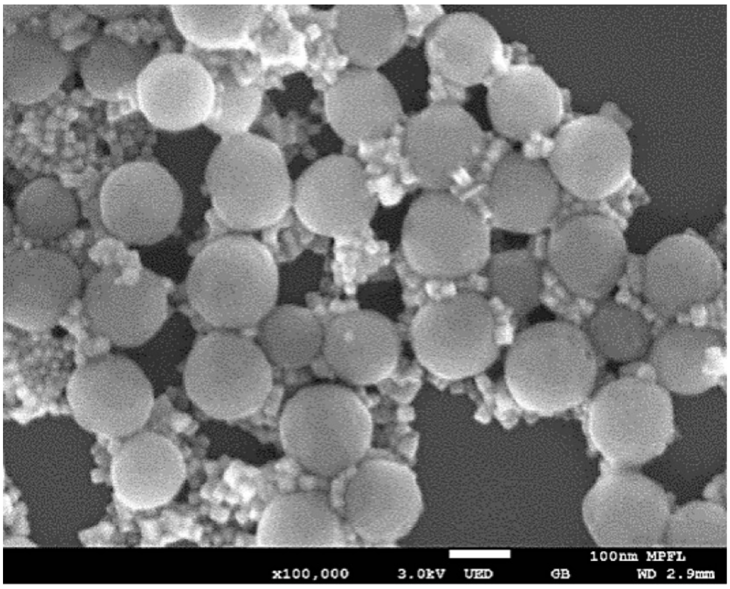


Figure S4. SEM images of the blend sample of CA-SiO_2 and $CsPbBr_3$ NCs.

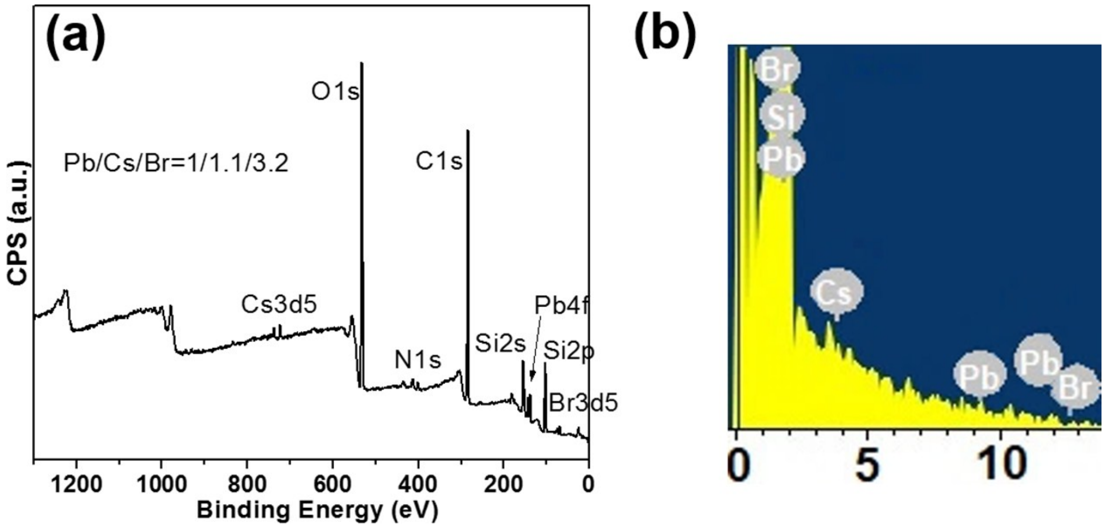


Figure S5. (a) High-resolution X-ray photoelectron spectra (XPS) analysis with a survey scan. (b) SEM-EDS elemental compositions.

Samples	**Emission peak/ nm**	**PLQY/ %**
$CsPbBr_3$@CA-SiO_2	**520**	**76**
$CsPbCl_3$@CA-SiO_2	**427**	**28**
$CsPbI_3$@CA-SiO_2	**650**	**67**
$CsPbBr_3$@A-SiO_2	**524**	**55**
$CsPbBr_3$@CC-SiO_2	**523**	**40**

Table S1. Summary of the optical properties of the composites obtained from different structures.

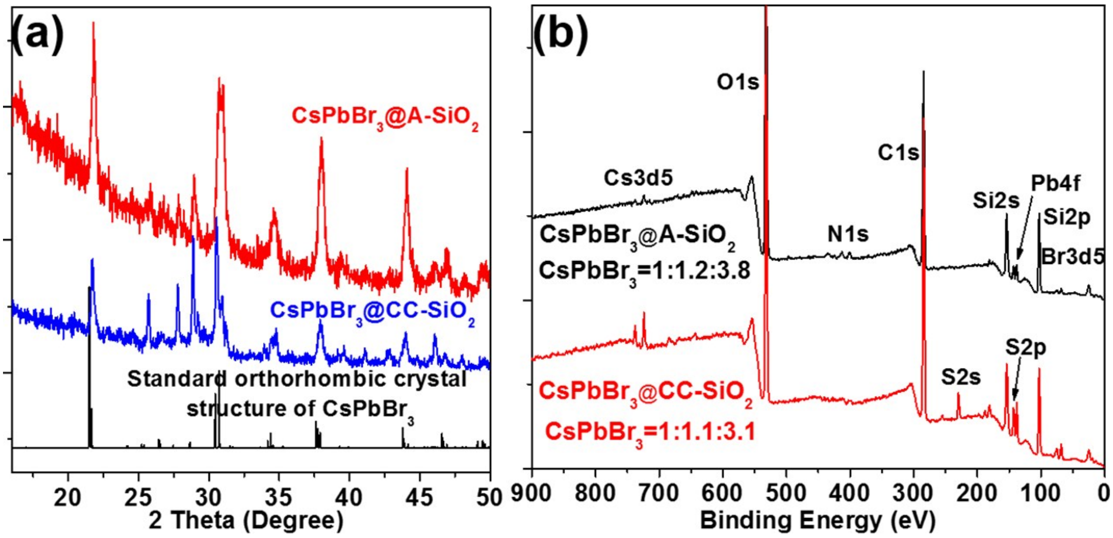


Figure S6. (a) PXRD pattern and the standard orthorhombic crystal structure of $CsPbBr_3$. (b) High-resolution XPS analysis with a survey scan.

PXRD analysis confirm the bulk crystallinity of as-prepared $CsPbBr_3$@A-SiO_2 and $CsPbBr_3$@CC-SiO_2, corresponding to the orthorhombic crystal structure of $CsPbBr_3$ NCs (Figure S6a). Furthermore, the elemental composition of $CsPbBr_3$@A-SiO_2 and $CsPbBr_3$@CC-SiO_2 from XPS analysis confirms that the composite contains all the elements (Cs3d5, O1s, N1s, C1s, Si2s, Pb4f and Br3d5) expected from the $CsPbBr_3$ NCs and capped SiO_2 NPs (Figure S6b). The elemental ratios for Cs:Pb:Br measured by XPS amount to 1:1.2:3.8 and 1:1.1:3.1 for $CsPbBr_3$@A-SiO_2 and $CsPbBr_3$@CC-SiO_2, respectively, which match well with the expected ratio of $CsPbBr_3$.

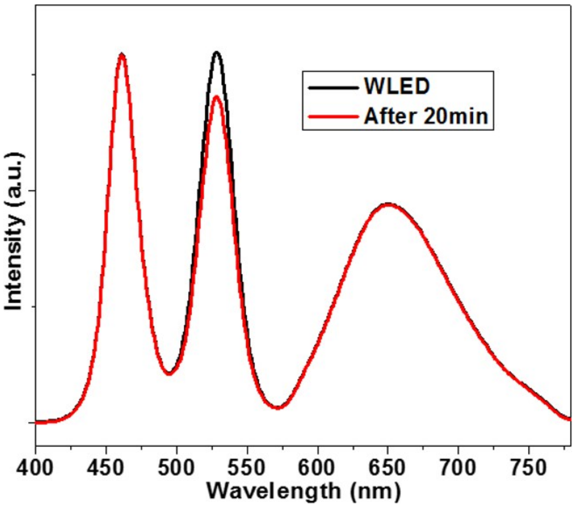


Figure S7. EL emission spectra of the WLED before (black curve) and after 20 min (red curve).

References

1. X. Li, Y. Wang, H. Sun and H. Zeng, *Adv. Mater.,* 2017, **29**, 1701185-1701194.
2. S. Werner, F. A. and B. Ernst, *J. Colloid Interf. Sci.,* 1968, **26**, 62-69.