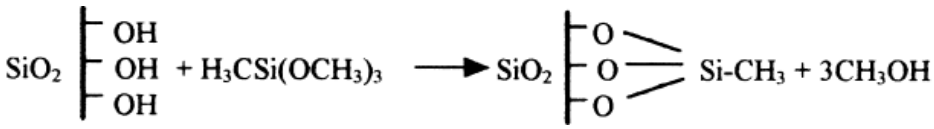
Preparation of hydrophobic SiO_2:Eu gels:

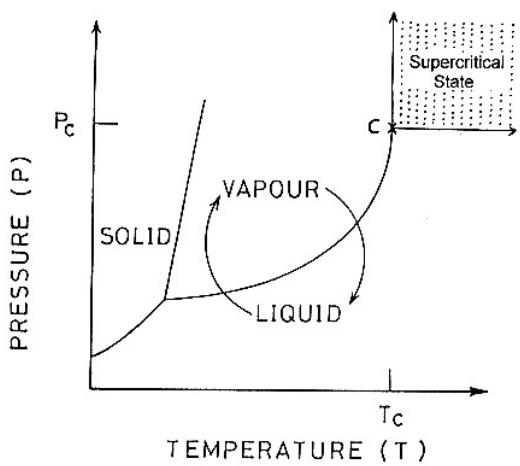
Under basic conditions, it has been found that the rate of hydrolysis of tetramethoxysilane (TMOS) is faster than that of methyltrimethoxysilane (MTMS). Hence, in a mixture containing TMOS and MTMS, TMOS is preferentially hydrolyzed in the early stages of the reaction, during which MTMS acts as a co-solvent. Therefore, the core of the primary particles will not contain any alkyl group. The formation of a three-dimentional solid SiO_2 network is achieved by the hydrolysis and polycondensation of methanolic TMOS in the presence of the ammonia catalyst as per the following chemical reaction:

$$xSi(OCH_3)_4 + 2xH_2O \xrightarrow{MeOH} xSiO_2 + 4xCH_3OH$$

When the sufficient amount of TMOS gets hydrolyzed, the MTMS hydrolysis becomes faster and proceeds as follows:



In this way the SiOH groups react towards the formation of a permanently hydrophobic SiO_2 gel surface. In the presence of dopant Eu^{3+} ions and co-dopant Al^{3+} ions the gelation takes place and after aging for a day, the gels were thermolyzed in an autoclave at supercritical conditions of MeOH to obtain hydrophobic SiO_2:Eu gels. This work presented is a novel method to improve the luminescent properties of rare-earth ions in sol-gel monoliths by making them hydrophobic and isolating the rare-earth ions from the vibrations of the residual OH groups and avoiding the clustering of ions. The phase diagram and the list of some common solvents with their supercritical parameters are given in the Figure S1.



Solvent	T_c (°C)	P_c (atm.)
MeOH	240	78.7
EtOH	243.1	63.1
H_2O	374	217.72
Acetone	235	47
Liq. CO_2	31.1	73

Figure S1: Phase diagram showing the supercritical state and the data showing various solvents and their supercritical parameters.

X-ray Photoelectron Spectroscopy of $SiO_2:Eu^{3+}$ nanophosphor:

The x-ray photoelectron spectroscopy (XPS) measurement was carried out using a Perkin Elmer 1257 model, operating at a base pressure of ~5 × 10^{-8} Torr at 300 K with a non-monochromatized AlKα line at 1486.6 eV and a hemispherical sector analyzer capable of 25 meV resolution. The overall instrumental resolution was about 0.3 eV. Pass energy for general survey scan and core level spectra was kept at 143.05 and 71.55 eV respectively.

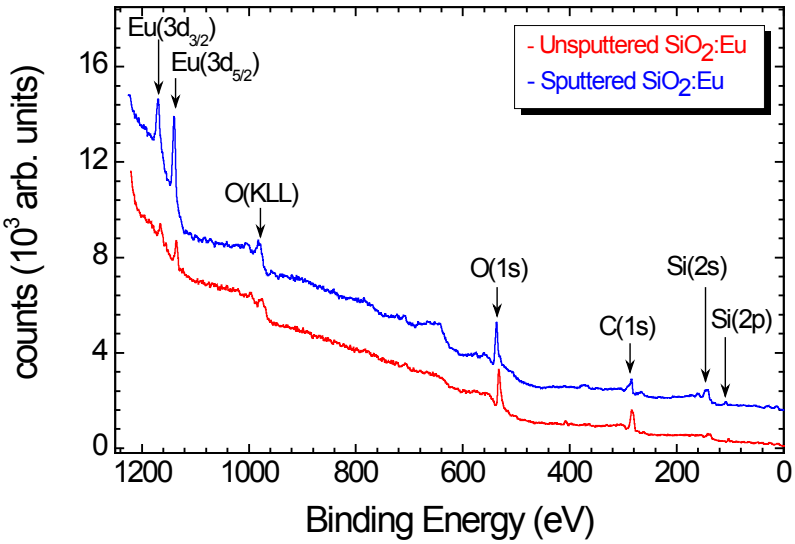


Figure S2: XPS survey scan spectra of sputtered and unsputtered nanoparticles of $SiO_2:Eu^{3+}$ recorded with photon energy of AlKα (hv = 1486.6 eV)

Using XPS studies, we tried to characterize the surface and chemistry of $SiO_2:Eu^{3+}$ nanoparticles. Figure S2 shows the survey spectra of $SiO_2:Eu^{3+}$ nanoparticles acquired in the range of 0-1200 eV. Corrections due to charging effects were taken care of by using C 1s as an internal reference and the Fermi edge of gold sample. Peak areas were obtained by integrating the appropriate signal after data analysis. During photoemission studies, small specimen charging was observed, which was later calibrated by assigning the C 1s signal at 285 eV. Survey spectra of Figure S2 show sharp peaks of C 1s (285 eV), O 1s (533 & 537 eV), Si 2p (103 & 106 eV), while Eu $3d_{3/2}$ and $3d_{5/2}$ were observed at 1165 & 1170 and 1135 & 1140 eV for unsputtered and sputtered respectively. The distinct two state of Eu $3d_{3/2}$ and $3d_{5/2}$ observed because of spin-orbit splitting. The appearance of Si2p at 103 eV confirms the SiO_2. The binding energies of various elements match very well with the peaks observed for standard $SiO_2:Eu^{3+}$. Sputtering was performed using Ar+ ions with 4 keV beam energy and 20 mA emission current for 5 min at a base pressure of 9.0 x 10^{-7} Torr. The effect sputtering causes a removal of impurity such as C and enhanced Eu_2O_3 state. The presence of C is an obvious consequence from the air atmosphere and the organics used for the preparation of Eu^{3+} doped in silica matrix.

PL Lifetime Decay Measurements of SiO_2:Eu^{3+} nanophosphor:

Photoluminescence lifetime decay measurements are non-destructive and powerful means commonly used for optical characterization of semiconductors. The free carrier or exciton lifetime, an important parameter related to material quality and device performance, can be obtained by lifetime data. It has been observed that the value of decay constants (τ_1) decrease under 350 nm excitation and respective peak (max) emission with increased dopant (Eu^{3+}) ion concentration. In other words, the intrinsic silica gel has the maximum decay constant of 16.54 µs, whereas, SiO_2 gel with Eu ion concentration of 0.1 mol-% has a decay constant of 0.95 µs. The decay constants generated by exponential fitting of other samples are indicated in below. It is a clear indication that the luminescence efficiency of the radiative recombination is strongly related to the decay time of a particular transition. The secondary decay constants (τ_2) observed for some samples in the present study indicates that the samples consists of multiple surface states that either promote the recombination to take place faster or quench the luminescence non-radiatively.

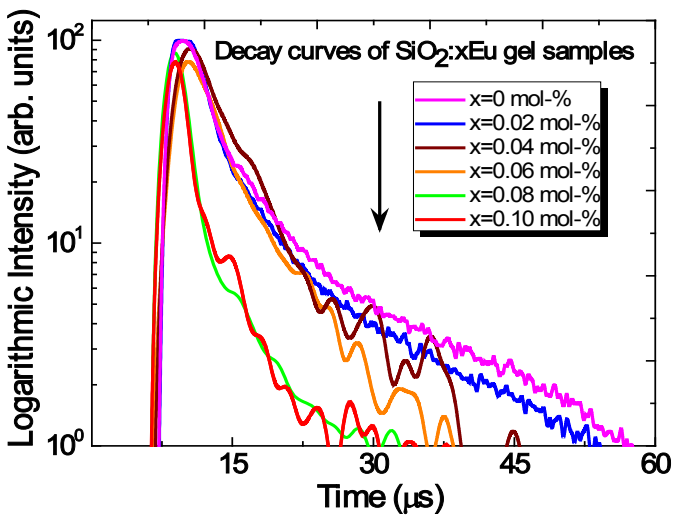


Figure S3: The room-temperature photoluminescence decay curves of SiO_2:xEu^{3+} gel samples under 350 nm excitation and respective emission peaks of the samples depicted in Figure 3. The Eu concentration (x) has been varied from 0-0.1 mol-% at a step of 0.02 mol-%.

PL Lifetime Data for SiO_2:xEu gel samples at 350 nm excitation and respective peak (max) emission:

Eu concentration	Decay Constants		
(mol-%)	τ_1 (microseconds)	τ_2 (microseconds)	χ^2
X=0 (Intrinsic silica)	16.54	4.52	2.246
X=0.02	10.05	1.37	2.995
X=0.04	8.38	0.961	1.228
X=0.06	2.89	6.47	0.961
X=0.08	1.93	7.05	0.853
X=0.10	0.95	12.23	0.433