

## Supporting Information for

### A General Method to Label Metal Oxide Particles with Fluorescent Dyes Using Aryldiazonium Salts

*Jean-François Dechézelles, Nebewia Griffete, Hervé Dietsch and Frank Scheffold\**

[\*] Dr. J-F. Dechézelles, Dr. N. Griffete, Prof. Dr. Frank Scheffold.  
Department of Physics and Fribourg Center for Nanomaterials, University of Fribourg  
Chemin du musée 3, CH-1700 Fribourg, Switzerland, E-mail: [frank.scheffold@unifr.ch](mailto:frank.scheffold@unifr.ch)  
Dr. H. Dietsch  
Adolphe Merkle Institute and Fribourg Center for Nanomaterials, University of Fribourg  
Route de l'ancienne papeterie CP 209, CH-1723 Marly 1, Switzerland

**Synthesis of silica particles:** Silica spheres are synthesized following the Stöber-Fink-Bohn method.<sup>[31]</sup> 161 mL of absolute ethanol, 8 mL of ammonia (25 % in water) and 59 mL of deionized water are introduced in a round flask. The mixture is homogenized at room temperature while stirring at 400 rpm. 22 mL of TEOS is added and after few minutes, the solution starts to become turbid indicating the presence of silica particles. The solution is left under stirring for 6 hours. Finally the silica particles suspension is washed by applying different cycles of centrifugation / dispersion in water cycles. Silica particles are labeled with RITC as described in the main text.

**Characterization of the dye-labeled silica particles:** As shown in Figure SI-1, in the spectral region between 1700 and 600 cm<sup>-1</sup>, one notices several bands that can be associated to the phenyldiazonium and its precursor. The spectrum of 4-aminophenyldiazonium salt shows a characteristic N≡N diazonium absorbance band ( $\nu_{\text{N}\equiv\text{N}} = 2225 \text{ cm}^{-1}$ ) not present for the phenylenediamine spectrum. This shows the success of the reaction step. A pair of bands is also present at 1500 and 1575 cm<sup>-1</sup> which corresponds to the aromatic C=C stretching vibrations.<sup>[30]</sup>

The chemical reaction of phenyldiazonium grafting onto metallic oxide surface involves the release of N<sub>2</sub> with the disappearance of the N≡N group absorbance band.<sup>[17]</sup> Indeed we do not

observe the  $\text{N}\equiv\text{N}$  stretching mode band at  $2225\text{ cm}^{-1}$  in the labeled particles spectra, indicating the successful grafting of aminophenyl onto the inorganic surface (data not shown).

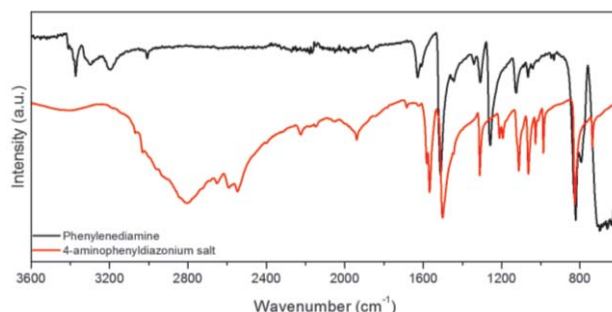


Figure SI-1. ATR-IR spectra of 4-aminophenyldiazonium salt and its precursor.

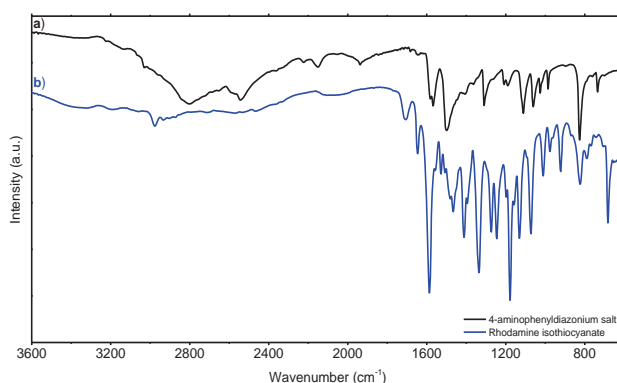


Figure SI-2. ATR-IR spectra of a) 4-aminophenyldiazonium, b) Rhodamine isothiocyanate (RITC).

For a closer analysis we present in Figures SI-3 an enlarged view of the ATR-IR spectra of bare silica particles, aminophenyl-modified particles and phenylrhodamine labeled silica particles. Two bands at  $1520$  and  $1575\text{ cm}^{-1}$  appear for the diazonium salt and aminophenyl-grafted silica particles. They can be attributed to the aromatic  $\text{C}=\text{C}$  stretching vibrations. In the case of the diazonium salt (Figure SI-2), one of them is stronger and shifted at  $1500\text{ cm}^{-1}$ . These bands also appear in the spectrum of the rhodamine-labeled particles (Figure SI-3). Common spectral features are also present between bare silica and modified silica particles, as indicated by dashed lines in Figure SI-3. The combined evidence drawn from the IR spectra strongly suggests the successful covalent grafting of the molecules onto the surface of the inorganic particles by taking advantage of the diazonium salts chemistry approach outlined

above. Finally we assess the success of the silica dye labeling synthesis by the analysis of real-space fluorescent microscopy images (Figure SI-4).

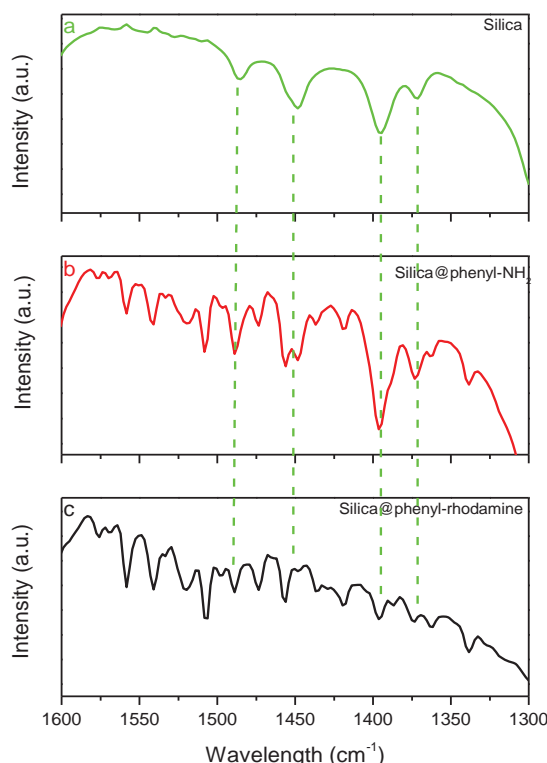


Figure SI-3. Enlarged view of one region of the ATR-IR spectra of a) silica particles, b) phenyl-NH<sub>2</sub> labeled silica particles and c), phenylrhodamine labeled silica particles.

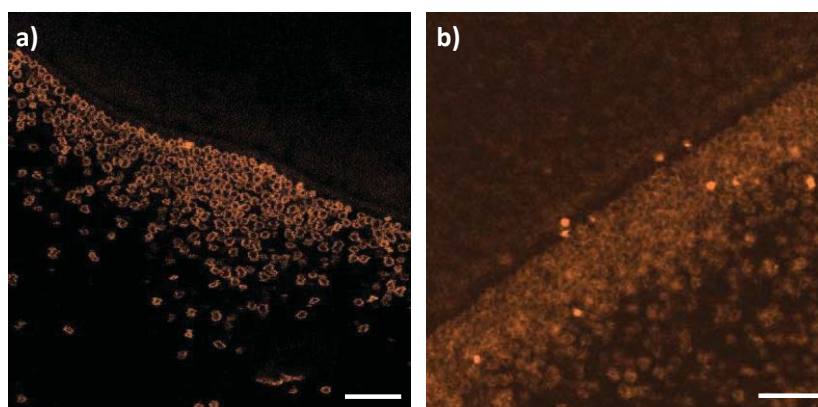


Figure SI-4. LSCM image of the silica particles labeled with rhodamine (RITC) following the first protocol (a) and the second protocol (b). Scale bars: 5  $\mu\text{m}$ .

**Characterization of the dye-labeled silica particles:** A thermogravimetric analysis (TGA) is performed, in the temperature range of 20–800  $^{\circ}\text{C}$  with a heating rate of 10  $^{\circ}\text{C min}^{-1}$  under a flow of air at 80  $\text{ml. min}^{-1}$  on bare silica particles and after the reaction with aminophenyldiazonium salt.

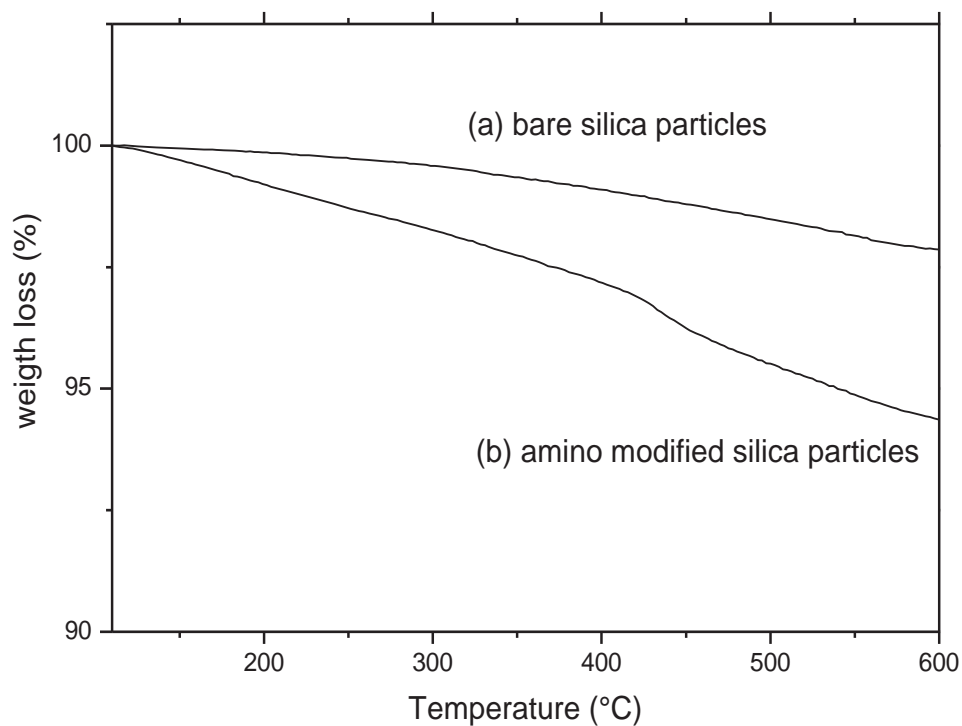


Figure SI-5. Thermogravimetric analysis of (a) bare silica and (b) phenyl-NH<sub>2</sub> labeled particles. A substantially increased weight loss is observed for the latter case.