

# INCUBATION AND INVESTIGATION OF MESOPOROUS THIN LAYERS

Emőke Volentíru, Dániel Zámbó, Mátyás Dabóczi, Éva Kunsági-Máté, Jánosné Kabai, Zoltán Hórvölgyi



Budapest University of Technology and Economics

Department of Physical Chemistry and Materials Science, Center for Colloid Chemistry, H-1521 Budapest, Hungary

web.fkt.bme.hu/~colloid

## Introduction

Nowadays, mesoporous sol-gel coatings (inorganic oxides with semiconducting or dielectric properties) are of great interest due to their advantageous optical properties and of their photoactivity. The formation of porous system is enabled by using additives (templates, e.g. surfactants) during the preparation process of a sol-gel layer.

The purpose of this work was the preparation of sol-gel ( $\text{SiO}_2$ ,  $\text{TiO}_2$ ) layers on solid surfaces of high porosity containing opened pores. Our experiments mainly focused on the investigation of incubation processes of porous system with different (salt-, dye-) solutions.

## Keywords

Sol-gel coatings, porous system, opened pores, incubation, storage capacity, release time

## Synthesis of precursor sols

Silica and titania precursor sols were prepared in ethanolic media by the acid-catalyzed controlled hydrolysis of tetraethyl orthosilicate and tetrabutyl orthotitanate, respectively. In order to form layers with porous system cationic (cetyltrimethylammonium bromide, (CTAB)) and non-ionic (triblock copolymers: Pluronic PE10300, Pluronic P123) surfactants were used as templates.

## Preparation of coatings

Sol-gel films on glass or silicon substrates were prepared from the precursor sols by the dip-coating method. Prior to film deposition solid substrates were cleaned with 2-propanol and distilled water. The deposited films were annealed at elevated temperature.

*Main steps of dip-coating (Fig.1.):*

1. dipping the substrate into the precursor sol
2. withdrawing the substrate from the sol with constant speed
3. solvent evaporation, heat treatment at elevated temperature

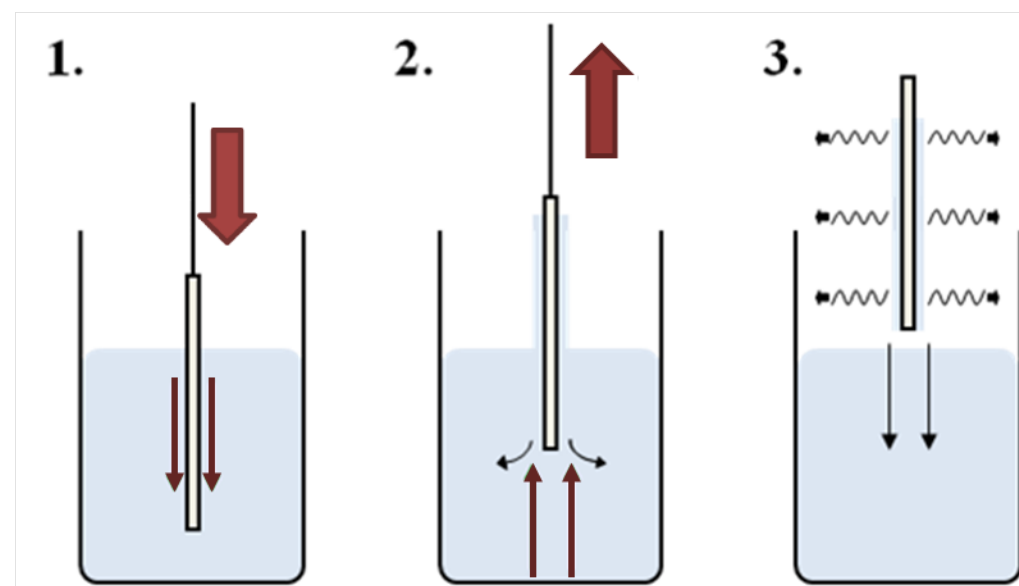


Fig.1. Sol-gel film preparation by dip-coating

## Investigation methods

Coatings on glass substrates were studied by UV-Vis spectroscopy. Thickness, refractive index and porosity (Lorentz-Lorenz) values were determined analyzing the transmittance spectra in terms of thin layer optical models. Porosity of the coatings was assessed by ellipsometric porosimetry. On silica powder model samples X-ray diffraction and simultaneous TG-DTA MS measurements were carried out. The incubation process of the resulting porous system with different solutions (silver nitrate, gold(III) chloride, Rhodamine 6G) was studied by UV-Vis spectroscopy measurements.

## RESULTS

### Optical properties of coatings

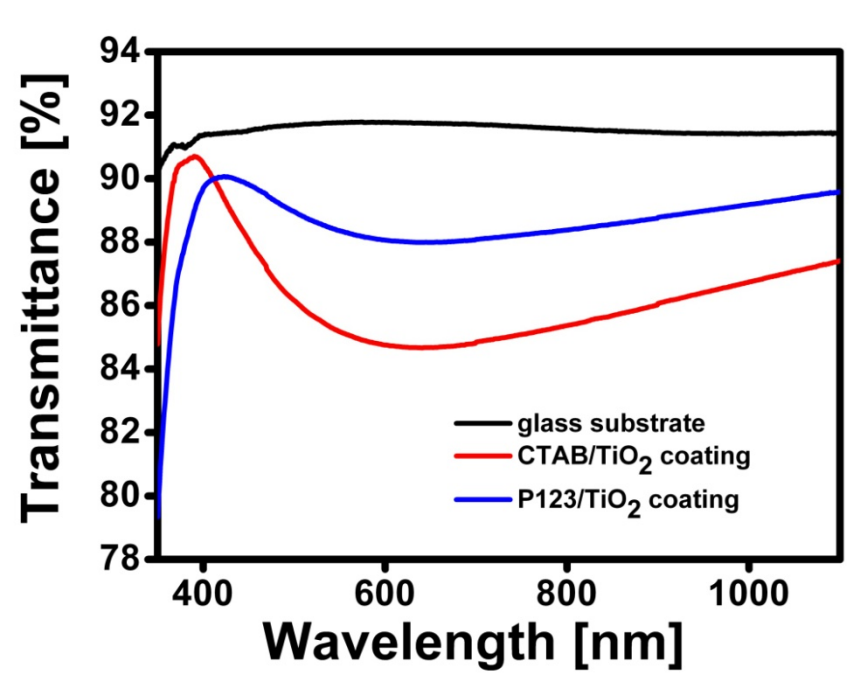


Fig. 2. Transmittance spectra of porous  $\text{TiO}_2$  coatings

| sample               | d (nm)      | n                  | porosity (%)  |
|----------------------|-------------|--------------------|---------------|
| CTAB/ $\text{TiO}_2$ | $106 \pm 2$ | $1.627 \pm 0.010$  | $42 \pm 0.76$ |
| P123/ $\text{TiO}_2$ | $121 \pm 4$ | $1.548 \pm 0.006$  | $48 \pm 0.48$ |
| CTAB/ $\text{SiO}_2$ | $163 \pm 4$ | $1.385 \pm 0.017$  | $13 \pm 3$    |
| chitosan             | $103 \pm 9$ | $1.529 \pm 0.0124$ | -             |

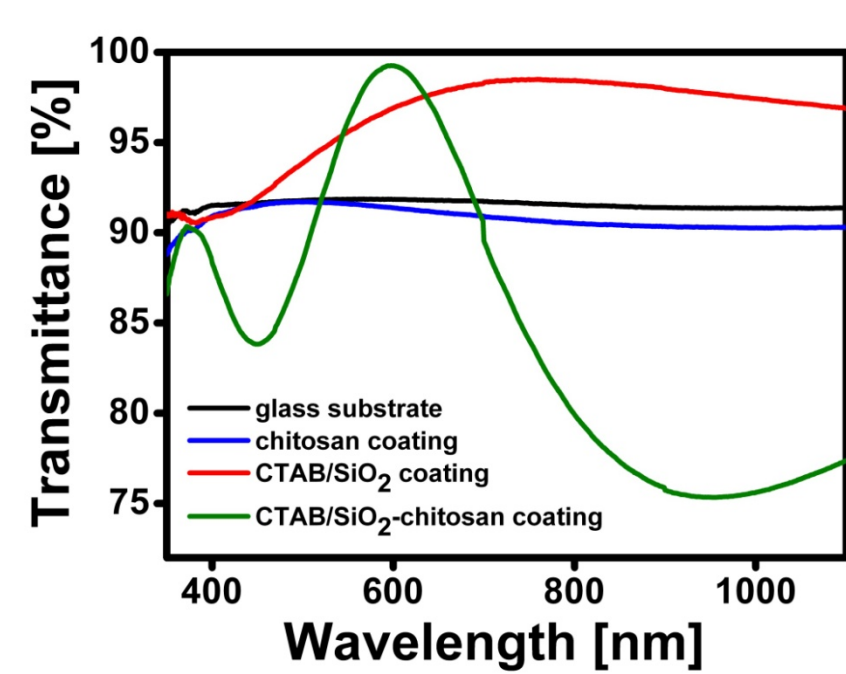


Fig. 3. Transmittance spectra of porous  $\text{SiO}_2$ , chitosan and combined coatings

### Ellipsometric porosimetry measurements

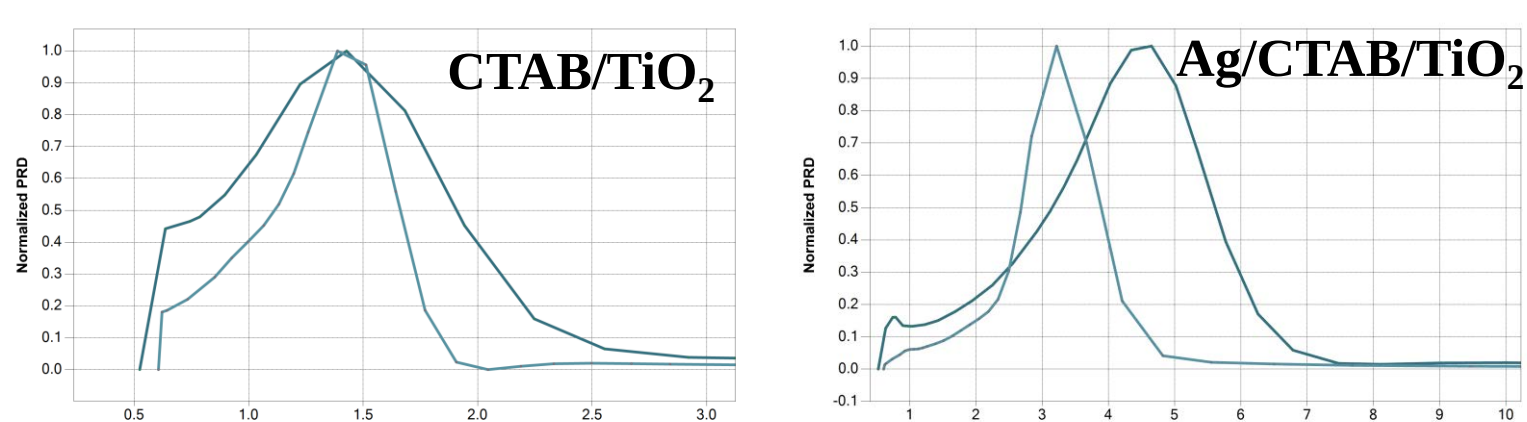


Fig. 4. Pore size distribution of CTAB/ $\text{TiO}_2$  (left) and Ag doped CTAB/ $\text{TiO}_2$  (right) coatings

| sample                        | porosity (%) | d <sub>pores (ads)</sub> (nm) | d <sub>pores (des)</sub> (nm) | n     | d (nm) |
|-------------------------------|--------------|-------------------------------|-------------------------------|-------|--------|
| CTAB/ $\text{TiO}_2$          | 29.8         | 2.8                           | 2.8                           | 1.735 | 92.1   |
| Ag doped CTAB/ $\text{TiO}_2$ | 36.8         | 9.4                           | 6.4                           | 1.701 | 89.8   |

| sample                           | porosity (%) | d <sub>pores (ads)</sub> (nm) | d <sub>pores (des)</sub> (nm) | n     | d (nm) |
|----------------------------------|--------------|-------------------------------|-------------------------------|-------|--------|
| CTAB/ $\text{SiO}_2$             | 27.6         | 2.42                          | 2.76                          | 1.312 | 129    |
| Pluronic PE10300/ $\text{SiO}_2$ | 34.6         | 3.82                          | 3.16                          | 1.283 | 127    |

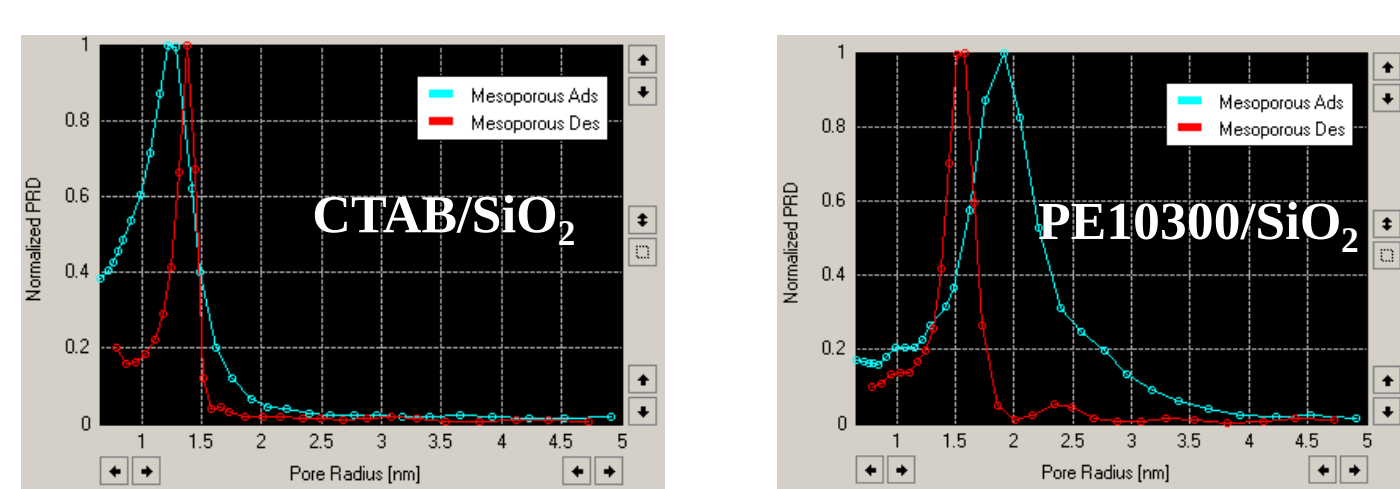


Fig. 5. Pore size distribution of CTAB/ $\text{SiO}_2$  (left) and Pluronic PE10300/ $\text{SiO}_2$  (right) coatings

### XRD and TG/DTA-MS measurements

In order to get information about the colloidal structure of coatings and for revealing the processes that take place during the heat treatment X-ray diffraction and simultaneous TG/DTA-MS measurements were carried out on porous silica powder model samples prepared by identical way than that of the coating.

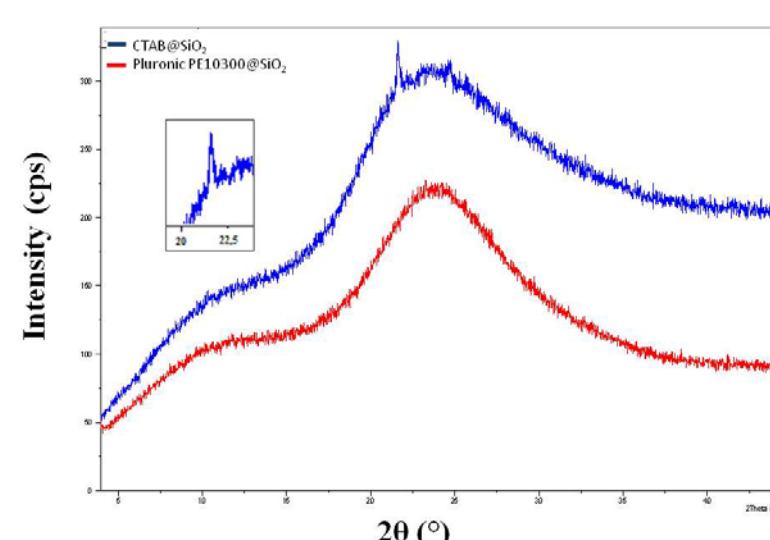


Fig.6. XR diffractogram of CTAB/ $\text{SiO}_2$  and Pluronic PE10300/ $\text{SiO}_2$  samples

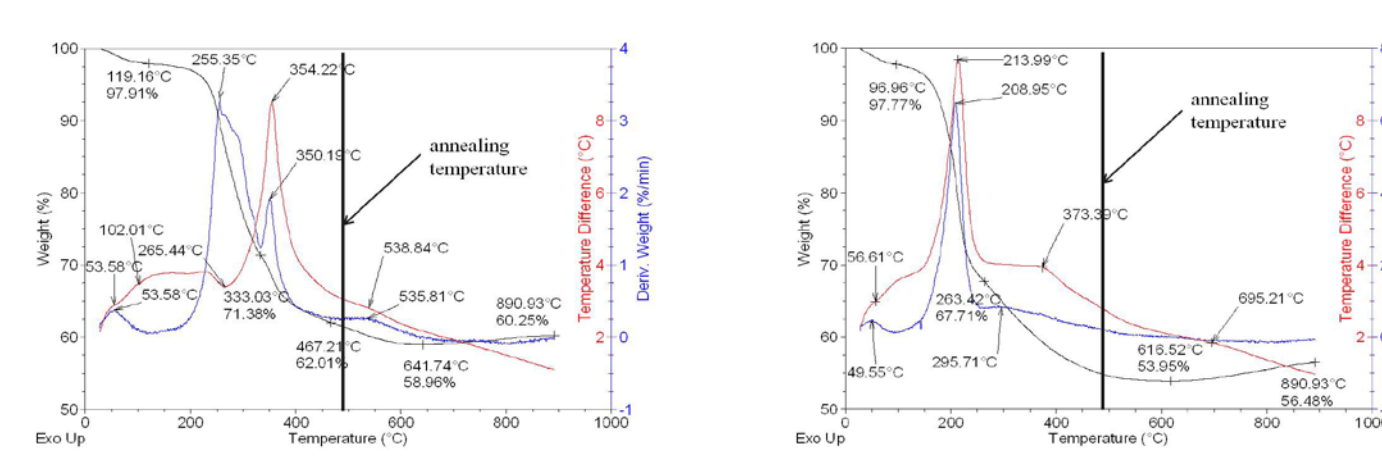


Fig. 7. TGA- DTA images of CTAB/ $\text{SiO}_2$  (left) and Pluronic PE10300/ $\text{SiO}_2$  (right) samples

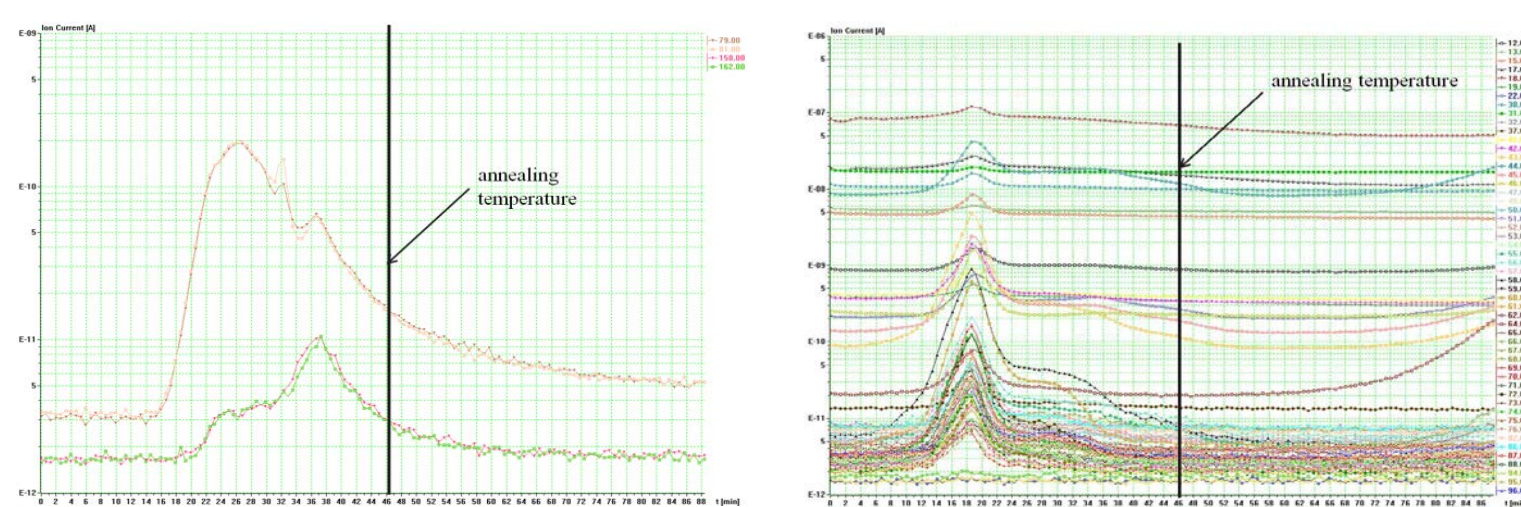


Fig. 8. TG/DTA-MS MID images of CTAB/ $\text{SiO}_2$  (left) and Pluronic PE10300/ $\text{SiO}_2$  (right) samples

### Investigation of incubation processes

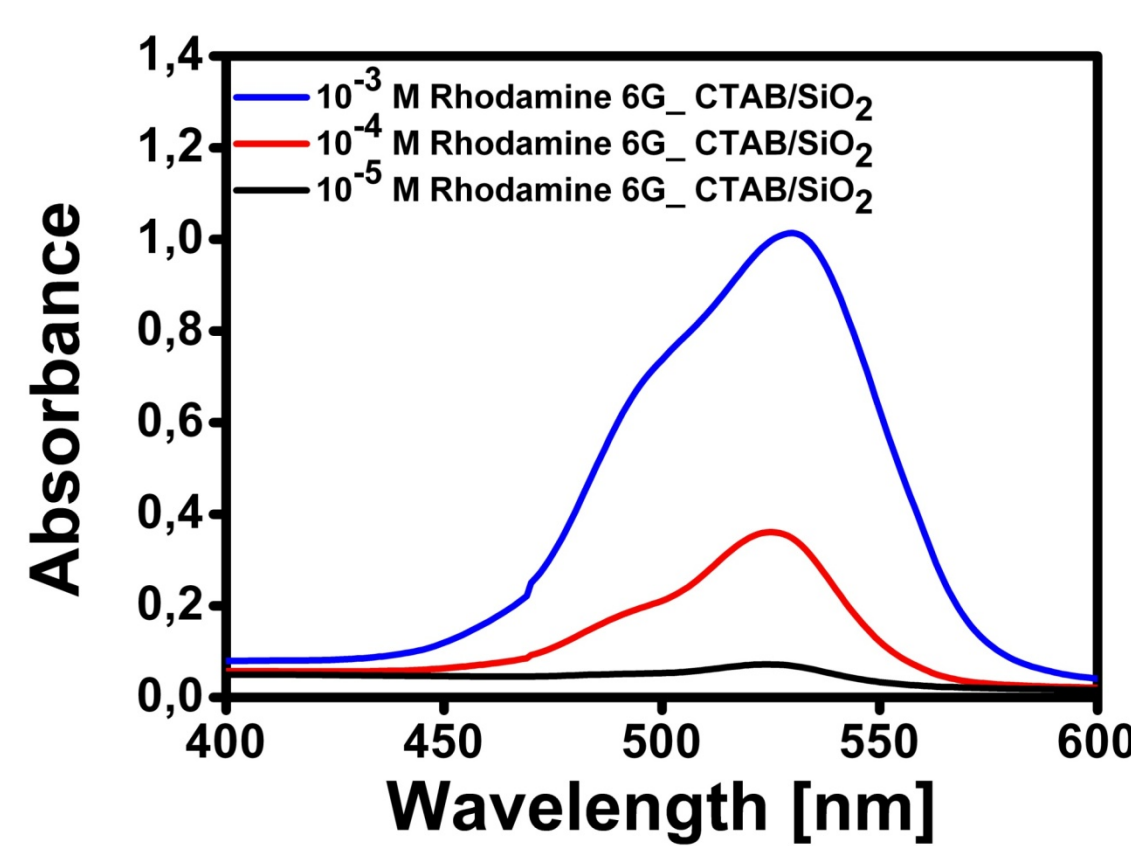


Fig. 9. Absorbance spectra of CTAB/  $\text{SiO}_2$  coatings after incubation with R6G solutions

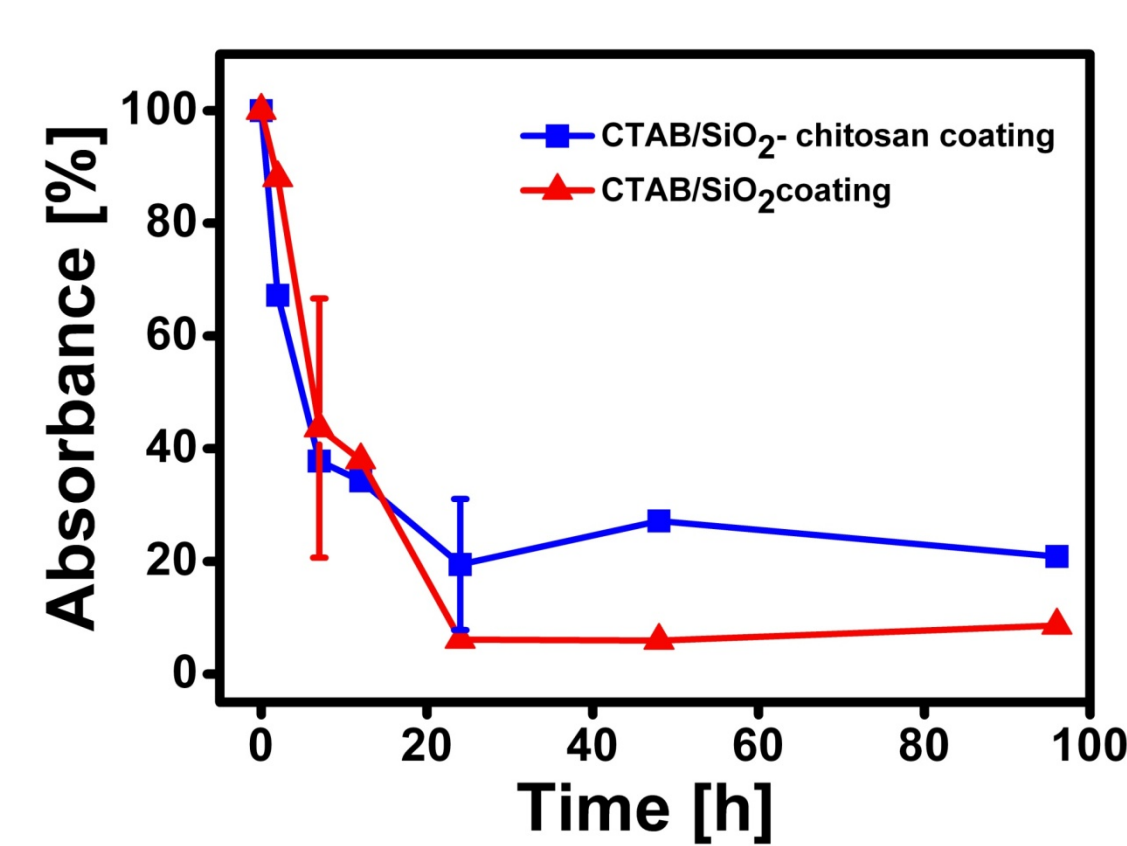


Fig.10. Absorbance spectra of R6G containing buffer solutions released from CTAB/ $\text{SiO}_2$  and CTAB/ $\text{SiO}_2$  - chitosan coatings as a function of time

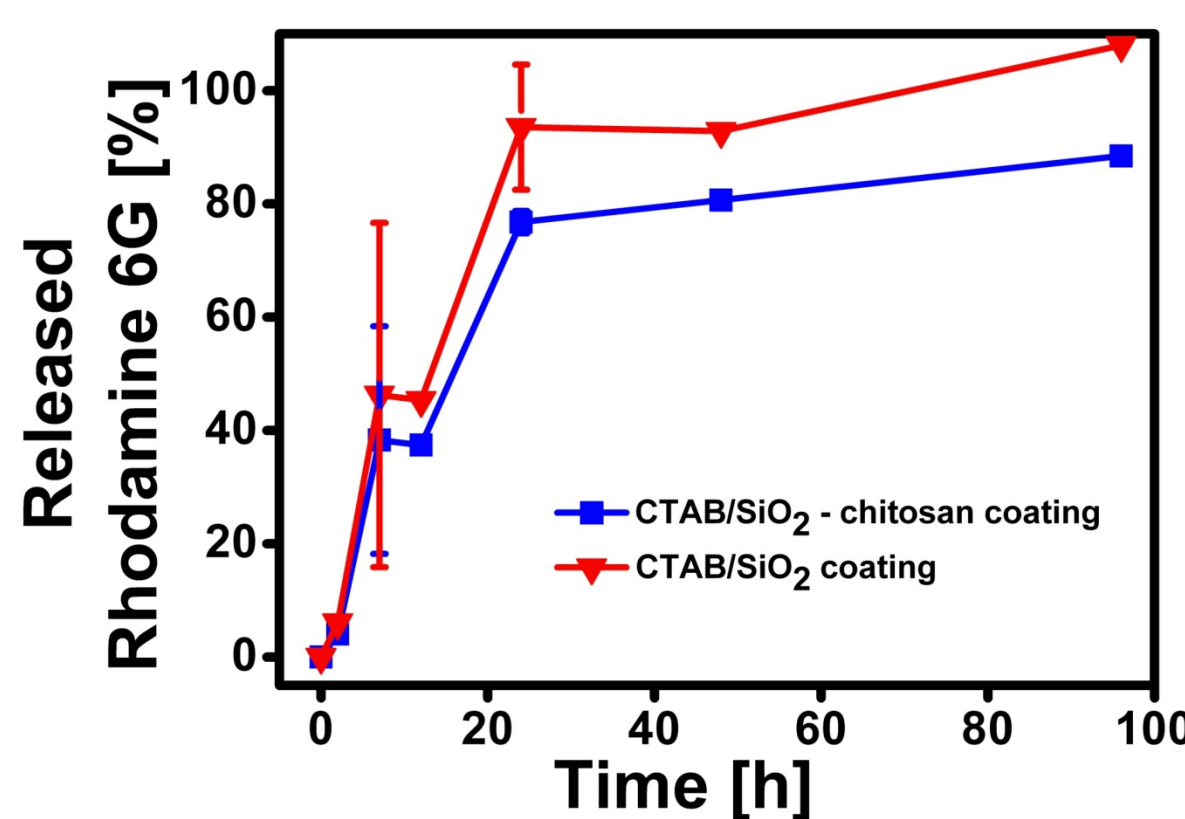


Fig. 11. Percentage of the released R6G from CTAB/ $\text{SiO}_2$  and CTAB/ $\text{SiO}_2$  - chitosan coatings as a function of time

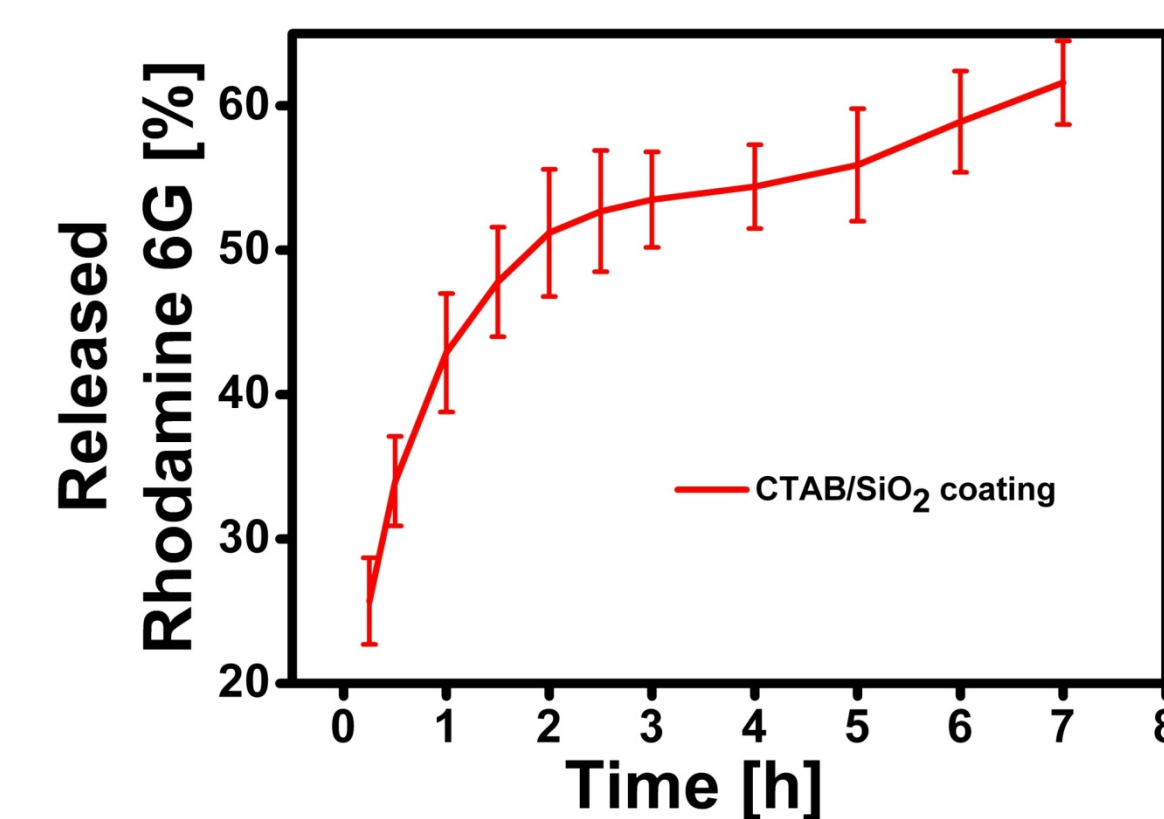


Fig. 12. Percentage of the released R6G from CTAB/ $\text{SiO}_2$  coating as a function of time

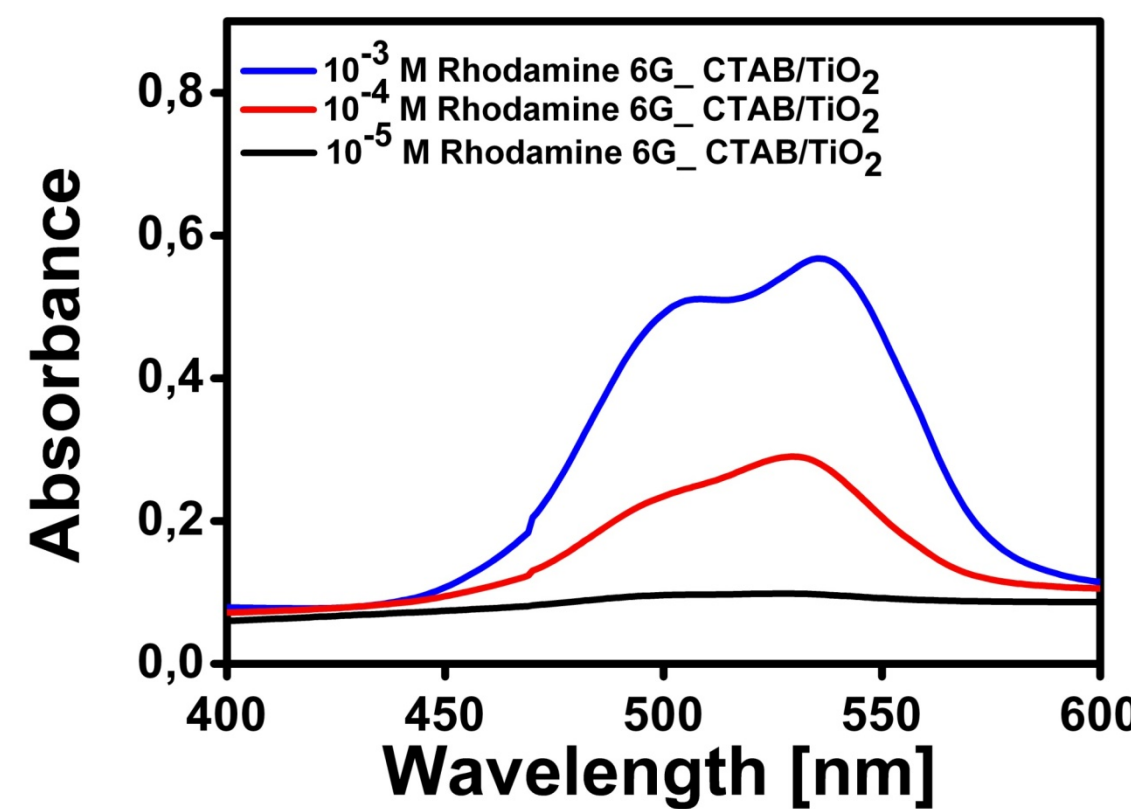


Fig. 13. Absorbance spectra of CTAB/  $\text{TiO}_2$  coatings after incubation with R6G solutions

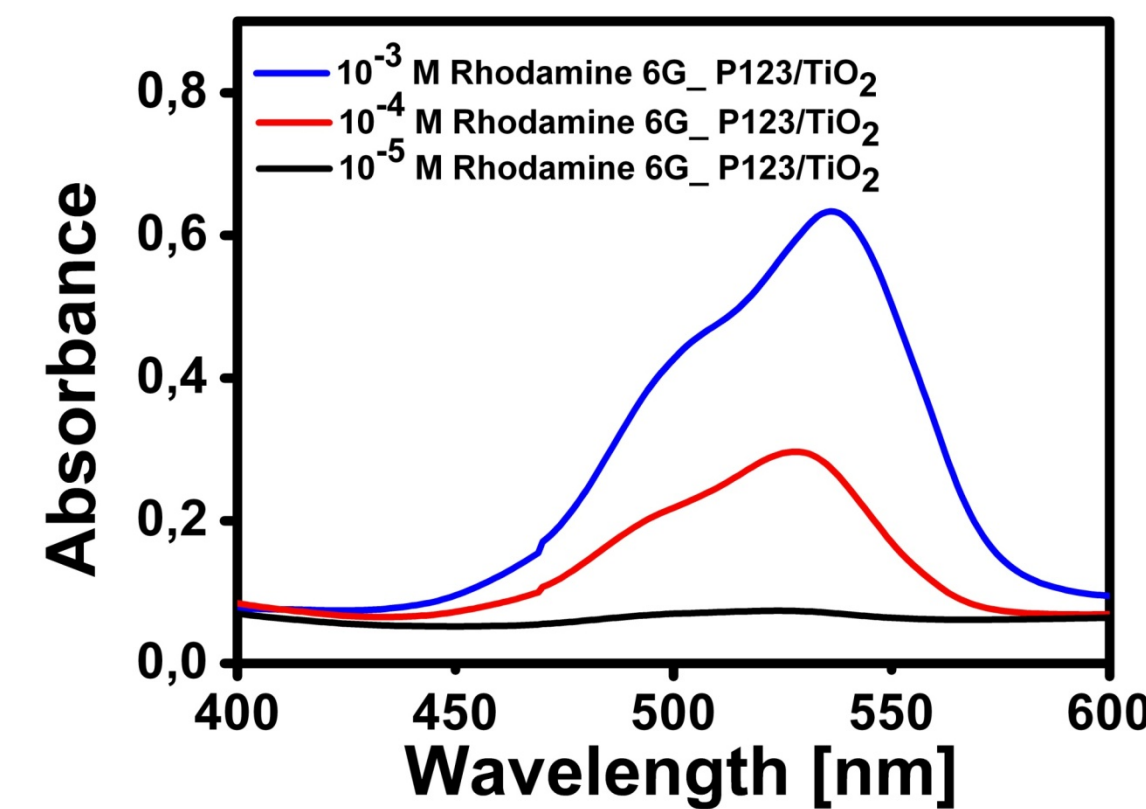


Fig. 14. Absorbance spectra of P123/  $\text{TiO}_2$  coatings after incubation with R6G solutions

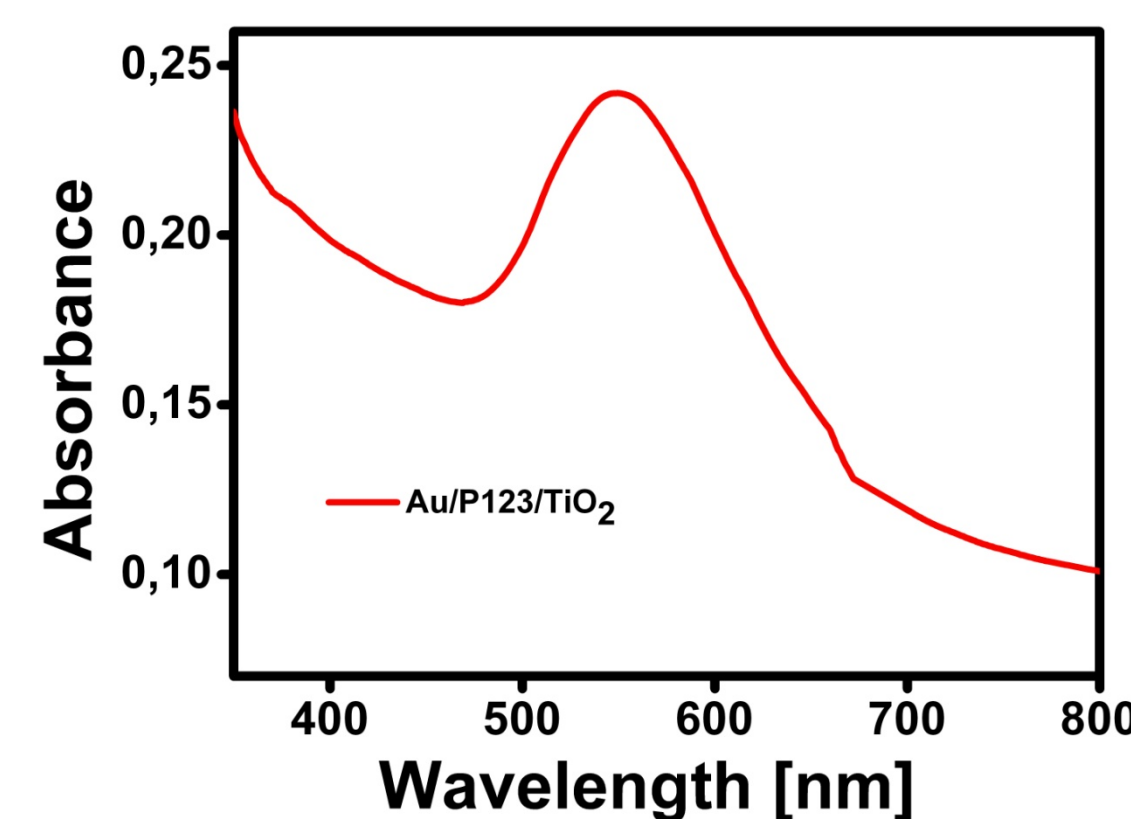


Fig. 15. Absorbance spectra of Au/CTAB/  $\text{TiO}_2$  film

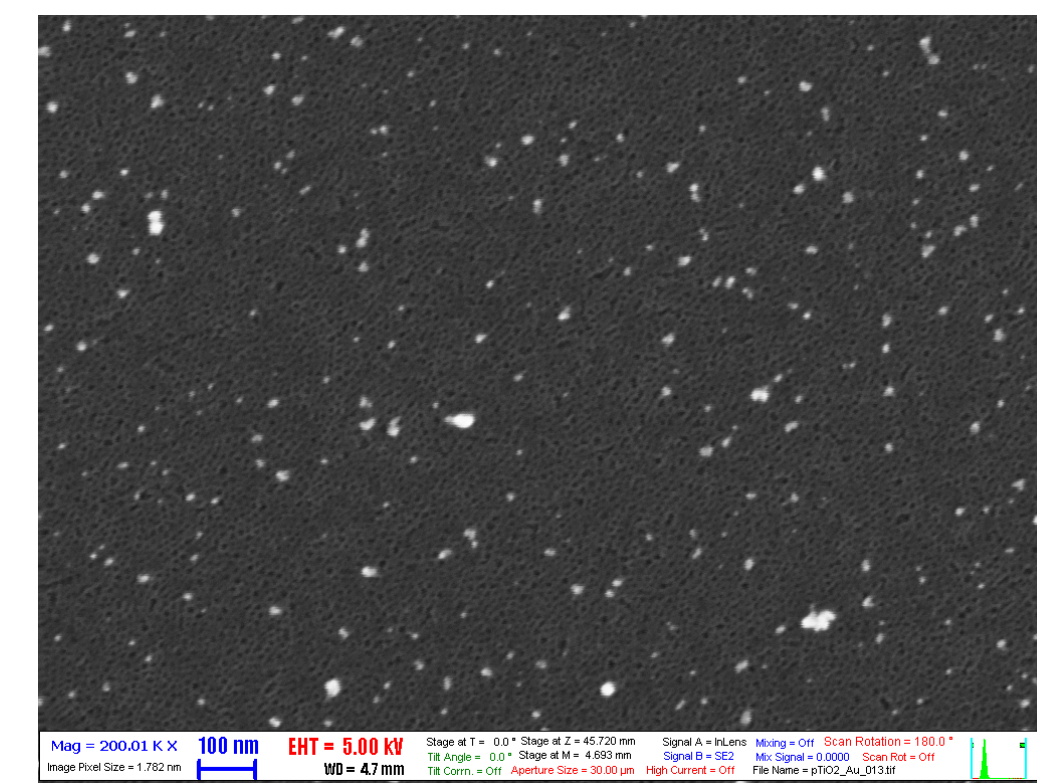


Fig. 16. FESEM image of Au/CTAB/  $\text{TiO}_2$  film

**Summary:** The prepared porous coatings are suitable for the model investigation of incubation and releasing phenomena.

**Acknowledgement:** The authors thank to E. Hild, P. Basa, A. Deák, J. Madarász, N. Nagy, Zs. Zolnai, Zs. Mőring for their help in this work. The financial support of the Hungarian Scientific Research Fund (OTKA CK 78629), the New Széchenyi Plan (TÁMOP-4.2.1/B-09/1/KMR-2010-0002), NKTH - A\*STAR Hungarian - Singaporean Bilateral S&T International Co-operation (BIOSPONA), and of the National Development Agency (Hungarian-French Bilateral Co-operation, PHONOSEL, TÉT\_11-2-2012-0008) is gratefully acknowledged.