Electronic Supplementary Information

for

Nanosized MEL zeolite and GeSe₂ chalcogenide layers as functional building blocks of tunable Bragg stacks

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Fig. S1 (a) Dynamic light scattering curve for MEL nanocrystals dispersed in ethanol. The average hydrodynamic diameter is 120 nm. (b) X-ray diffraction pattern of MEL nanocrystals. The XRD pattern exhibits Bragg peaks typical for the MEL type crystalline structure.



Fig. S2 Surface of a) MEL type zeolite and b) $GeSe_2$ layer. Scale bar = 1 micron. MEL particles have almost spheroidal shape with a diameter in the range 110 -130 nm that is consistence with the crystal size determined by DLS measurements. $GeSe_2$ film is smooth, homogenous and dense as it is expected for the amorphous structure.



Fig. S3 Side view of multilayer consisting of MEL type zeolite and $GeSe_2$. Scale bar = 500 nm. The two layers are clearly distinguished. It is seen that the MEL crystals are packed and form porous layer, while the $GeSe_2$ layer is smooth and free of pores.

Calculation of Transmittance and Reflectance of multilayered system

The transfer matrix method for calculation of transmittance T and reflectance R of the stack is applied [1]. Each layer is described with a single matrix called characteristic matrix. If the refractive index and thicknesses of the layers are represented by n_i and d_i , then the characteristic matrices M_P and M_S of each layer for p and s – polarization can be written in the form:

$$M_{P} = \begin{pmatrix} \cos\Delta_{i} & \frac{-in_{i}\sin\Delta_{i}}{\cos\theta_{i}} \\ \frac{-i\cos\theta_{i}\sin\Delta_{i}}{n_{i}} & \cos\Delta_{i} \end{pmatrix} \text{ and } M_{S} = \begin{pmatrix} \cos\Delta_{i} & \frac{-i\sin\Delta_{i}}{n_{i}\cos\theta_{i}} \\ -in_{i}\cos\theta_{i}\sin\Delta_{i} & \cos\Delta_{i} \end{pmatrix}, (1)$$

(The polarization is a property of light that describes its oscillations. All types of oscillations can be presented by two orthogonal modes of oscillations called "p" and "s" pollarization).

In eq.1 $\Delta_i = 2\pi n_i d_i \cos \theta_i / \lambda$ is the optical phase thickness of the layer and θ_i is connected with the angle of incidence θ_0 by the Snell-Decarte's law $(n_0 \sin \theta_0 = n_i \sin \theta_i)$,

where n_0 is the refractive index of incident medium. In our case $n_0 = 1$ because the incident medium is air.

If the multilayered stack composed of q pairs of high (H) and low (L) refractive index layers, it can be presented by the matrix multiplication:

$$Q_P = (n_s/n_0)^* I^* H^* (LH)^{q*S}, \text{ for p-polarization}$$
(2)

$$Q_{S}=0.5*I^{*}H^{*}(LH)^{q}*S, \quad \text{for s-polarization,}$$
(3)

where the sign "*" denotes matrix multiplication, the matrices H and L are the characteristic matrices M_P and M_S for high and low refractive index materials, respectively; I and S are the characteristic matrices of the two surrounding media, air and Si - substrate in our case with refractive indices n_0 and n_s respectively:

$$I_{P} = \begin{pmatrix} 1 & \frac{-n_{0}}{\cos \theta_{0}} \\ 1 & \frac{-n_{0}}{\cos \theta_{0}} \end{pmatrix}, I_{S} = \begin{pmatrix} 1 & \frac{-1}{n_{0} \cos \theta_{0}} \\ 1 & \frac{1}{n_{0} \cos \theta_{0}} \end{pmatrix},$$
$$S_{P} = \begin{pmatrix} \frac{-1}{\cos \theta_{s}} & \frac{1}{\cos \theta_{s}} \\ \frac{-\cos \theta_{s}}{n_{s}} & \frac{\cos \theta_{s}}{n_{s}} \end{pmatrix}, S_{S} = \begin{pmatrix} 1 & 1 \\ -n_{s} \cos \theta_{s} & n_{s} \cos \theta_{s} \end{pmatrix}$$
(4)

Transmittance and reflectance of the stack for both polarization are finally obtained from the respective matrix elements Q(i,j):

$$T_{P} = \frac{n_{s} \cos \theta_{s}}{n_{0} \cos \theta_{0}} \left| \frac{1}{Q_{P}(1,1)} \right|^{2} \text{ and } T_{S} = \frac{n_{s} \cos \theta_{s}}{n_{0} \cos \theta_{0}} \left| \frac{1}{Q_{s}(1,1)} \right|^{2}$$
(5)

$$R_{P} = \left| \frac{Q_{P}(2,1)}{Q_{P}(1,1)} \right|^{2} \text{ and } R_{S} = \left| \frac{Q_{S}(2,1)}{Q_{S}(1,1)} \right|^{2}$$
(6)

In our case $\theta_0 = 0$ and $\theta_i = \theta_0$ (normal incident) and *T* and *R* for both polarization are the same.

As we have already determined the refractive index of the layers (n_L) for zeolite and (n_H) for GeSe₂, we can calculate their quarter wave thicknesses as $d_i = \lambda_c/4n_i$, i=L, H, where λ_c is the centre of the reflectance band. Using Eqs. 1 to 5, the R as a function of number of bi-layers q can be calculated.

Optical characterization of single layer

For optical characterization the $GeSe_2$ layers were deposited simultaneously on two types of substrates: optical glass BK7 and Si-wafer. Optical constants (refractive index, *n* and extinction coefficient, *k*) and thickness, *d* were calculated from transmittance and reflectance measurements at normal light incidence (zero angle of incidence) using already developed calculating procedure [2,3].

For spin coated films, a different approach was used since no the same thickness of the layers is obtained on both substrates. The n, k and d of the zeolite layers deposited onto Si-substrates were determined from reflectance measurements at normal incidence using Wemple -DiDomenico dispersion equations for n [4] and exponential decay function for k:

$$n(E) = \sqrt{1 + \frac{E_0 E_d}{E_0^2 - E^2}}, \qquad k(E) = a_0 \exp(\frac{E}{A}), \qquad (7)$$

where *E* is the light energy in the measured spectral range. The coefficients E_0 , E_d , a_0 and *A* in Eq. 7 along with the thickness of the layer were determined through minimization of a goal function *G* (Eq. 8) consisting of the discrepancies between measured R_{meas} and calculated R_{calc} reflectance spectra. A non-linear subspace trust region method combining the interior-reflective Newton method with a preconditioned conjugate gradients method is used for the minimization [5]:

$$G(E_d, E_0, a_0, A, d) = \sum_i \{R_{meas} - R_{calc}\}^2,$$
(8),

where *i* is the number of the points in the used spectral range of wavelengths.

For accurate and unambiguous minimization one needs proper initial values for the unknown parameters. Because such information is not available we used the approach presented in elsewhere [6]. Briefly, the minimization procedure was run using a wide grid of initial values for the unknown parameters and the error function *Err* of the minimization was calculated as the residual value of the goal function at each solution:

$$Err = \sqrt{\sum_{i} \left| G(E_d, E_0, a_0, A, d) \right|^2} .$$
(9)

The values of E_0 , E_d , a_0 , A and d in the global minimum of *Err* are used as initial values in the next minimization step, and the calculation algorithm is continuously repeated until the value of *Err* at the minimum does not change any longer. The values for E_0 , E_d , a_0 , A, from the final solution were substituted in Eq. 7, and the n and k values for the layer were obtained.

Calculation of the optical response of bi-layers exposed to analytes

The optical response of bi-layer system can be calculated using the data for refractive index and thickness changes of single layer when exposed to the analytes. Eqs. 1, 4, 5, 6 and 10 were used to calculate R of the bi-layer before and after exposure to the analyte; the data for refractive index and thicknesses of the single layers before and after exposure were used.

$$Q_{PS} = (n_s/n_0) * I * HL * S \tag{10}$$

References

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