

# Supplementary information

## Optical Quantum Confinement and Photocatalytic Properties in Two-, One-, and Zero-Dimensional Nanostructures

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### 1. Key data for potential dependent absorption spectroscopy

**Table S1.** Key data for potential dependent absorption spectroscopy for ZnO quantum dots with diameters between 4.4 and 8.6 nm utilized for analysis of Burstein-Moss bleach discussed in main article. The potentials (V) are all reported *versus* the normal hydrogen electrode (NHE). The flatband potential ( $E_{fb}$ ) reported in the table is determined by electrochemical impedance spectroscopy (EIS).

| Sample | $E_g$<br>[eV] | $d$<br>[nm] | $E_{cb}$ B<br>(V) | $E_{cb}$ J<br>(V) | $E_{fb}$ M<br>1225 Hz<br>(V) | $E_{fb}$ M<br>3160 Hz<br>(V) | $dE_g/dU$ | U at $I_{min}$<br>(V) |
|--------|---------------|-------------|-------------------|-------------------|------------------------------|------------------------------|-----------|-----------------------|
| 1      | 3.57          | 4.39        | -0.83             | -0.79             | -0.60                        | -0.62                        | -1.30     | -0.76                 |
| 2      | 3.53          | 4.89        | -0.79             | -0.77             | -0.59                        | -0.61                        | -1.16     | -0.68                 |
| 3      | 3.52          | 4.91        | -0.76             | -0.72             | -0.50                        | -0.53                        | -1.30     | -0.69                 |
| 4      | 3.51          | 5.10        | -0.77             | -0.75             | -0.53                        | -0.54                        | -1.48     | -0.72                 |
| 5      | 3.50          | 5.22        | -0.76             | -0.74             | -0.54                        | -0.55                        | -1.46     | -0.70                 |
| 6      | 3.49          | 5.36        | -0.75             | -0.72             | -0.51                        | -0.53                        | -1.15     | -0.68                 |
| 7      | 3.49          | 5.42        | -0.71             | -0.68             | -0.50                        | -0.57                        | -1.26     | -0.67                 |
| 8      | 3.45          | 6.15        | -0.75             | -0.75             | -0.49                        | -0.50                        | -0.68     | -0.69                 |
| 9      | 3.45          | 6.19        | -0.73             | -0.73             | -0.51                        | -0.52                        | -0.76     | -0.69                 |
| 10     | 3.43          | 6.65        | -0.71             | -0.73             | -0.49                        | -0.52                        | -0.57     | -0.69                 |
| 11     | 3.43          | 6.72        | -0.70             | -0.72             | -0.52                        | -0.53                        | -0.72     | -0.70                 |
| 12     | 3.42          | 7.08        | -0.69             | -0.70             | -0.46                        | -0.48                        | -0.74     | -0.65                 |
| 13     | 3.42          | 7.12        | -0.68             | -0.69             | -0.45                        | -0.47                        | -0.85     | -0.66                 |
| 14     | 3.42          | 7.15        | -0.68             | -0.72             | -0.49                        | -0.50                        | -0.50     | -0.67                 |
| 15     | 3.42          | 7.19        | -0.68             | -0.72             | -0.45                        | -0.46                        | -0.60     | -0.66                 |
| 16     | 3.41          | 7.30        | -0.66             | -0.65             | -0.44                        | -0.46                        | -0.52     | -0.60                 |
| 17     | 3.40          | 8.01        | -0.64             | -0.65             | -0.67                        | -0.83                        | -0.84     | -0.38                 |
| 18     | 3.39          | 8.56        | -0.63             | -0.68             | -0.86                        | -1.20                        | -0.48     | -0.41                 |

### 2. Derivation of the joint density of states, equation (8) in the main manuscript

Equation (4) in the main article is

$$T_{v \rightarrow c} = \frac{2\pi}{\hbar} \int_{BZ} \frac{1}{4\pi^3} |H'_{vc}|^2 \delta(E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega) d\mathbf{k} \quad (S1)$$

Considering a direct transition (no change in the crystal momentum between the initial,  $\mathbf{k}_i$ , and final states,  $\mathbf{k}_f$ ), the perturbation matrix element between the corresponding states is then effectively independent of the  $\mathbf{k}$ -vector within the BZ, and can be taken outside the integral to obtain

$$T_{v \rightarrow c} = \frac{2\pi}{\hbar} |H'_{vc}|^2 g_{vc}(\hbar\omega) \quad (S2)$$

where

$$g_{vc}(\hbar\omega) = \int_{BZ} \frac{1}{4\pi^3} \delta(E_c - E_v - \hbar\omega) d\mathbf{k} \quad (S3)$$

$g_{vc}(\hbar\omega)$  is here the joint density of states. Evaluation of the integral in (S3) can be performed by using the integral properties of the delta function

$$\int_a^b g(x) \delta(f(x)) dx = \sum_{x_0} g(x_0) \left| \frac{\partial f(x)}{\partial x} \right|_{x=x_0} \quad (S4)$$

with  $f(x_0)=0$  and  $a < x_0 < b$ . To ensure that  $f(x_0)=0$  in the interval  $[a, b]$ . A constant energy difference surface between S and S+dS (between the valence and conduction band), valid at each  $\mathbf{k}$ -point in the Brillouin zone have to be constructed with  $d\mathbf{k} = dS d\mathbf{k}_n$  where  $d\mathbf{k}_n$  is a wave vector normal to S. Since  $|\nabla_{\mathbf{k}} E| = dE/dk_n$ , the constant energy difference can be expressed as

$$d\mathbf{k} = dS d\mathbf{k}_n = dS \left[ \frac{d(E_c - E_v)}{|\nabla_{\mathbf{k}}(E_c - E_v)|_{E_c - E_v = \hbar\omega}} \right] \quad (S5)$$

Utilizing  $d\mathbf{k}$  in (S3),(S4) and integrate over the constant  $d(E_c - E_v)$  one obtain

$$g_{vc}(\hbar\omega) = \frac{1}{4\pi^3} \int \frac{dS}{|\nabla_{\mathbf{k}}(E_c - E_v)|_{E_c - E_v = \hbar\omega}} \quad (S6)$$

and can be calculated if the functional form of  $E_c$  and  $E_v$  is known. Close to the band edges, the band structure energy can be expanded (with a truncation after the second order term) as

$$E_v(\mathbf{k}) = E_v(\mathbf{k}_0 + \boldsymbol{\kappa}) = E_v(\mathbf{k}_0) + \frac{1}{2} \sum_{\alpha\beta} \frac{\partial^2 E}{\partial k_\alpha \partial k_\beta} \kappa_\alpha \kappa_\beta \quad (S7)$$

$$E_c(\mathbf{k}) = E_c(\mathbf{k}_0 + \boldsymbol{\kappa}) = E_c(\mathbf{k}_0) + \frac{1}{2} \sum_{\alpha\beta} \frac{\partial^2 E}{\partial k_\alpha \partial k_\beta} \kappa_\alpha \kappa_\beta \quad (S8)$$

where  $\mathbf{k}$  is the crystal momentum,  $\mathbf{k}_0$  is the crystal momentum at the band edge at the  $\Gamma$ -point  $E_v$  is the valence band energy,  $E_c$  is the conduction band energy, and  $\boldsymbol{\kappa}$  is the crystal momentum in reciprocal space for two linear independent directions,  $\alpha$  and  $\beta$ .

For isotropic parabolic dispersion close to the band edges, the electrons and holes can be described by a constant direction-independent parameter the effective mass), where the electrons and holes are described as effectively free carriers close band edges *via*

$$E_v(\mathbf{k}) = E_v(0) - \frac{\hbar^2 \mathbf{k}^2}{2m_p^*} \quad (S9)$$

$$E_c(k) = E_c(0) + \frac{\hbar^2 k^2}{2m_n^*} \quad (\text{S10})$$

with notations taken from the main article. Utilizing equation (7) in the main article and the energy difference in (S6) we have

$$|\nabla_k (E_c - E_v)| = \frac{\hbar^2 k}{m_{red}^*} \quad (\text{S11})$$

which together with (S6) gives the joint density of states

$$g_{vc}(\hbar\omega) = \frac{1}{4\pi^3} \left[ 4\pi k^2 \left( \frac{m_{red}^*}{\hbar^2 k} \right) \right]_{E_c - E_v = \hbar\omega} = \frac{1}{2\pi^2} \left( \frac{2m_{red}^*}{\hbar^2} k \right)_{E_c - E_v = \hbar\omega} \quad (\text{S12})$$

Expressing  $k = (2m_{red}^*/\hbar^2)^{1/2} (\hbar\omega - E_g)^{1/2}$  we then have

$$g_{vc}(\hbar\omega) = \frac{1}{2\pi^2} \left( \frac{2m_{red}^*}{\hbar^2} \right)^{3/2} (\hbar\omega - E_g)^{1/2} \quad (\text{S13})$$

Which is equation (8) in the main article.

### ***Justification:***

A justification of eqn (S13) can be done by reformulating the density of states on the energy scale,  $g(E)$ , from the definition  $g(E)dE = 2g(k)dk$  where a factor of 2 is introduced from the two electron spins allowed for each  $k$  state. This gives  $g(E) = 2g(k) / (dE/dk)$  where  $dE/dk$  is the  $E$ - $k$  dispersion curve valid under isotropic bands. The number of states per unit volume in  $k$ -space is  $1/2\pi^3$  for the incremental volume between  $k$  and  $k+dk$  ( $4\pi k^2 dk$ ) and give  $g(k) = k^2 / 2\pi^2$ .

In the parabolic approximation for the conduction band (given by eqn. (S8) ) we have

$$g_c(E) = \frac{1}{2\pi^2} \left( \frac{2m_n^*}{\hbar^2} \right)^{3/2} (E - E_c)^{1/2} \quad (\text{S14})$$

The combined density of states,  $g_{jc}$ , can then be introduce *ad hoc* within the parabolic approximation by combining equation (S12) with (S9) and (S10), which leads directly to the joint density of states expressed from the reduced effective mass and the bandgap

$$g_{vc}(\hbar\omega) = \frac{1}{2\pi^2} \left( \frac{2m_{red}^*}{\hbar^2} \right)^{3/2} (\hbar\omega - E_g)^{1/2} \quad (\text{S15})$$

Although this leads to the same equation as equation (S13), the *ad hoc* replacement of separate effective masses to the reduced mass use the hidden assumption of the existence of a constant energy difference surface between the respective bands as shown above.