Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Low intensity, continuous wave photodoping of ZnO quantum dots. Photon energy and particle size effects

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Supporting Information

S-1 Capping action of ethylene glycol on ZnO quantum dots

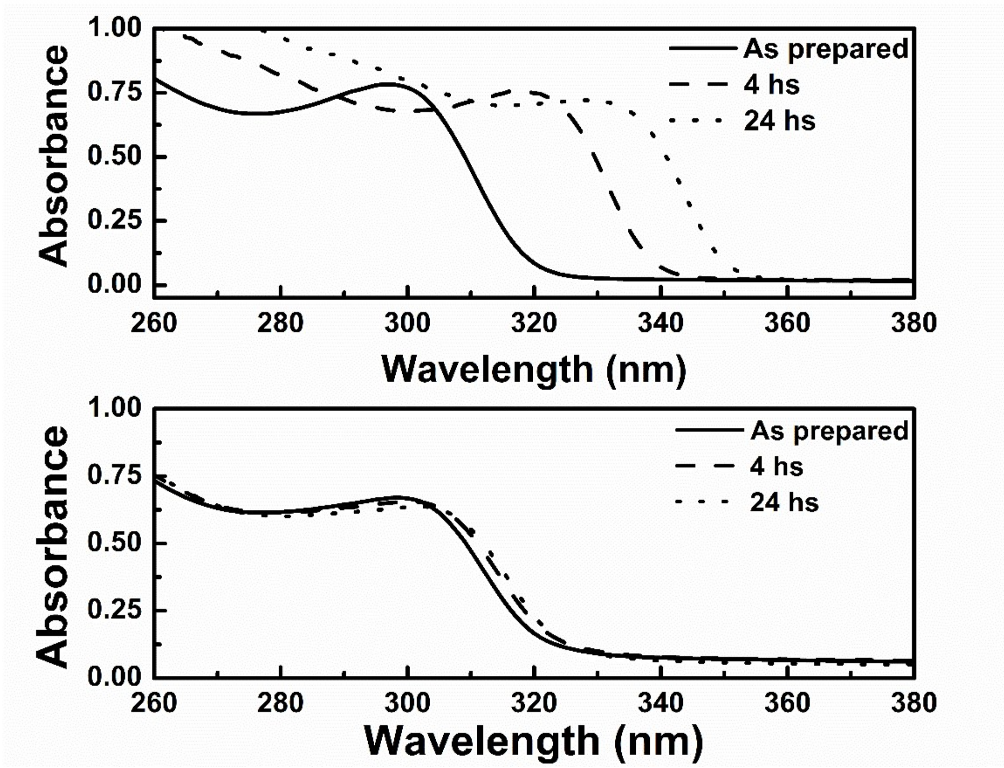

Figure S1: Comparison between the room temperature evolution of the UV absorption spectra of ZnO QDs synthesized at T_R = 0 °C, after a 1:20 dilution in ethanol (top) or ethylene glycol (bottom).

S-2 Size distribution

The mean size of the particles and its distribution was obtained using the procedure developed by Pesika.[1]

For dilute concentrations, the absorbance, A, of a sol at any wavelength is related to the total volume of particles with radius greater or equal to the size corresponding to the absorption onset. Thus, for spherical particles

$$A(r) \propto \int_r^{\infty} \frac{4}{3}\pi r^3 n_P(r)dr \qquad \text{(E1)}$$

where $n_P(r)$ is the particle size distribution. It follows from eq. (1), that the particle size distribution is related to the local slope of the absorption spectrum:

$$n_P(r) \propto -\frac{dA/dr}{4/3\,\pi r^3} = n_P^*(r) \qquad \text{(E2)}$$

Using the above expression, we obtained the size distribution for each sample. For all the samples the distributions could be fitted to a Gaussian function, as shown in Figure S2 for sample B.

Sample	T_R (°C)	$\langle r \rangle$(nm)	σ(nm)
A	0	1.70	0.06
B	25	2.10	0.11
C	65	2.65	0.16

Table S2: Mean particle size and dispersion obtained from the fit of the distribution to a Gaussian function

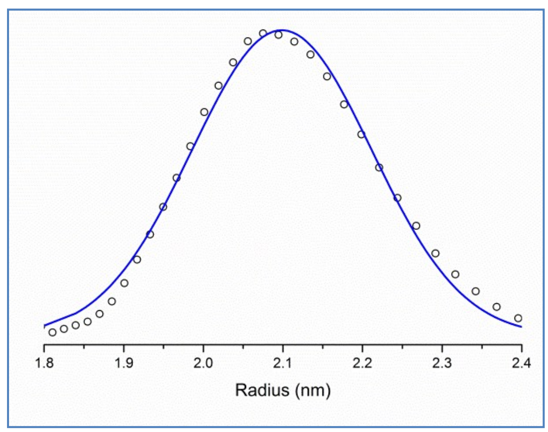

Figure S2: Particle size distribution obtained from the absorbance spectra of the ZnO nanoparticles synthesized at 25 °C (sample B) after ethylene glycol capping.

S-3 Spectrophotometric determination of MV^{2+} photoreduction rates

Typical spectrophotometric determination of MV^{2+} photoreduction rates.

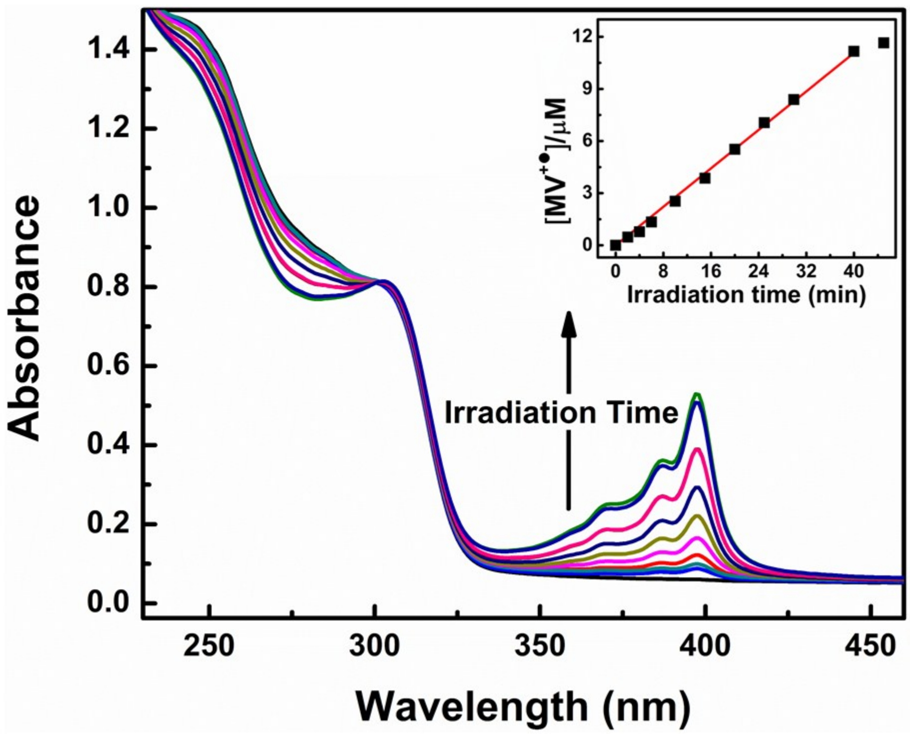

Figure S3: Time evolution of the UV-Vis absorption spectra obtained during the MV^{2+} anaerobic photoreduction in the presence of EG-capped ZnO QDs (Sample A). Irradiation wavelength 303 ± 5 nm. Inset [$MV^{+\bullet}$] as a function of irradiation time. The photoreduction rate can be readily obtained from the slope.

S-4 Effective mass model

Neglecting the polarization terms, the use of standard models under the Brus effective mass approximation[2,3] makes possible to correlate the position of the conduction, $E^{BC}(r)$, and valence band, $E^{BV}(r)$, under confinement according to:[4]

$$E^{BC}(r) \cong E^{BC}(\infty) + \frac{h^2}{8r^2 m_e^*} - 0.9\frac{e^2}{4\pi\varepsilon_0\varepsilon_r r} \qquad \text{(E3)}$$

$$E^{BV}(r) \cong E^{BV}(\infty) + \frac{h^2}{8r^2 m_h^*} - 0.9\frac{e^2}{4\pi\varepsilon_0\varepsilon_r r} \qquad \text{(E4)}$$

$$E_g(R) = E^{BC}(R) - E^{BV}(R) = E_g(\infty) + \frac{h^2}{8r^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - 1.8\frac{e^2}{4\pi\varepsilon_0\varepsilon_r r} \qquad \text{(E5)}$$

In the above equation m_e^*, m_h^* are the effective mass of the electron ($0.28m_e$), and the hole ($0.59m_e$), respectively, m_e the electron mass, r the radius of the particle, ε the dielectric constant of ZnO, and ε_0 the permittivity of free space.[5, 6]

References

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