Low intensity, continuous wave photodoping of ZnO quantum dots – photon energy and particle size effects†

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The unique properties of semiconductor quantum dots (QDs) have found application in the conversion of solar to chemical energy. How the relative rates of the redox processes that control QD photon efficiencies depend on the particle radius (r) and photon energy (Er), however, is not fully understood. Here, we address these issues and report the quantum yields (Φs) of interfacial charge transfer and electron doping in ZnO QDs capped with ethylene glycol (EG) as a function of r and Er in the presence and absence of methyl viologen (MV2+) as an electron acceptor, respectively. We found that Φs for the oxidation of EG are independent of Er and photon fluence (ρ), but markedly increase with r. The independence of Φs on ρr ensures that QDs are never populated by more than one electron–hole pair, thereby excluding Auger-type terminations. We show that these findings are consistent with the operation of an interfacial redox process that involves thermalized carriers in the Marcus inverted region. In the absence of MV2+, QDs accumulate electrons up to limiting volumetric densities ρe,max that depend sigmoidally on excess photon energy $E^* = E_r - E_{BG}$ (r) where $E_{BG}$ is the r-dependent bandgap energy. The maximum electron densities: $\rho_{e,max} \sim 4 \times 10^{10}$ cm$^{-3}$, are reached at $E^* > 0.5$ eV, independent of the particle radius.

Introduction

The readily tunable optical and electrical properties of semiconductor QDs have found extensive applications in optoelectronics, light harvesting, solar energy conversion and photocatalysis.1–9 A key advantage is that QD properties can be tailored by modifying their chemical composition, size and shape.10 The distinctive feature that impacts the QD properties is the discreteness of the lower rungs of their electronic band manifolds.11 Thus, the excess electronic energy: $E^* = E_r - E_{BG}$, carried by the electron–hole pairs (e$^-$–h$^+$) generated by photons of wavelengths shorter than band-gap thresholds: $\lambda < \lambda_{BG}$, was expected to be slowed in QDs due to the larger mismatch of electronic vs. vibrational manifolds.12 The failure of such expectations,13,14 was ascribed to Auger-type processes that bypass the putative phonon bottlenecks.15–17

QDs can also become overcharged18 upon irradiation in the absence of suitable electron acceptors. The progressive filling of discrete conduction band levels leads to the occupation of upper levels by electrons that convert QDs in powerful reductants.19,20

Since the utilization of photoinduced carriers in QDs is determined by the competition between energy dissipation, electron accumulation and interfacial electron transfer, it is essential to understand how the relative rates of these processes depend on excitation energy and QD properties.21–25

Here, we address these issues in a quantitative experimental investigation of the photochemistry of ZnO QDs of various sizes driven by low intensity, continuous monochromatic beams under well-defined experimental conditions. Low intensity irradiation with monochromatic light in the presence of methyl viologen (MV2+) allows us to exclude Auger-type carrier terminations and investigate the effect of photon energy on the efficiency of interfacial electron transfer. Similar experiments in the absence of MV2+ let us probe the impact of r and $E_r$ on electron accumulation.

Experimental section

Materials

Methyl viologen dichloride hydrate, MV2+ (98%, Aldrich); zinc acetate dehydrate, Zn(CH$_3$COO)$_2$·2H$_2$O (Fluka); lithium
hydroxide, LiOH (Sigma-Aldrich); tetra-methyl-ammonium hydroxide, (Me₄)₅NOH (Sigma) were of the highest available purity and used as received. Ethanol, EtOH (Sintorgan); ethylene glycol, EG (Biopack); ethyl acetate (Sintorgan); heptane (Sintorgan) and dimethyl-sulfoxide, DMSO (chromatographic grade, Sintorgan) were used without further purification.

**Preparation of EG-capped ZnO QD sols**

EG-capped ZnO nanoparticle sols were prepared by two different procedures. In one of them, colloidal ZnO nanoparticles were synthesized via an alkaline hydrolysis/condensation reaction by slowly adding 6.25 mL of 0.55 M (Me₄)₅NOH in EtOH to 20 mL of 0.1 M Zn(CH₃COO)₂ in DMSO at room temperature.²⁶,²⁷ The reaction was stopped by precipitating the resulting ZnO nanoparticles with ethyl acetate. Nanoparticles were then suspended in neat EG and purified twice by a cycle involving precipitation with heptane and resuspension in EG. Alternatively, ZnO nanoparticles were prepared by the arrested alkaline hydrolysis of alcoholic solutions of Zn(CH₃COO)₂ in EtOH following the method reported by Pesika et al.,³⁰ see ESI-2.†

**Results and discussion**

MV⁺⁺ formation requires the presence of EG, we infer that the process controlling Φₛ is the oxidation of EG to glycolaldehyde, GA, reaction (R1):

\[ \text{HOCH₂–CH₂OH + 2h}⁺ = \text{HOCH₂–CHO + 2H}⁺ \]  

which proceeds in two steps via current doubling.³² The first step, reaction (R2), is deemed to yield strongly reducing z-hydroxyalkyl...
radicals, HOCH$_2$–C(\*)HOH, which subsequently inject an electron into the ZnO conduction band, $e_{CB}$, to produce GA, reaction (R3).

\[
\text{HOCH}_2\text{–CH}_2\text{OH} + \text{h}^+ = \text{HOCH}_2\text{–C(\*)HOH} + \text{H}^+ \quad \text{(R2)}
\]

\[
\text{HOCH}_2\text{–C(\*)HOH} = \text{HOCH}_2\text{–CHO} + \text{H}^+ + e_{CB}^- \quad \text{(R3)}
\]

We have shown that the kinetics of the evolution of the few electron–hole pairs generated under weak illumination falls in the stochastic regime and cannot be described by conventional kinetic laws involving continuum concentrations.\textsuperscript{2} Under such conditions, $\Phi$s are controlled by the faster charge transfer process, in this case the oxidation of EG.

### $\Phi$s as a function of particle radius, photon fluence and excess photon energy

$E_{BG}(r)$ band gap energies as a function of $r$ were evaluated from the onsets of light absorption as a function of photon energy (Fig. 1, inset). The energies of conduction band $E_{CB}(r)$ and valence band $E_{VB}(r)$ edges were calculated using Brus’s effective mass approximation.\textsuperscript{33–35} See ESI-4.\textsuperscript{†} The resulting parameters are summarized in Table 1.

Irradiation with photons of energies $E_\lambda > E_{BG}$ generates correlated $e^-\text{–h}^+$ pairs possessing excess energies: $E^* = E_\lambda - E_{BG}(r)$. Fig. 2 shows experimental $\Phi$s (from eqn (E1)) as a function of $E^*$ and $r$. It is apparent that $\Phi$s: (1) are independent of $E^*$ within experimental error, implying that the hot carriers produced by above-bandgap irradiation are thermalized before they engage in interfacial electron transfer, and (2) perhaps unexpectedly, increase dramatically with $r$ from $\Phi (1.70 \text{ nm}) = 3.2\%$ to $\Phi (2.65 \text{ nm}) = 25\%$.

We infer that relaxation rates of hot carriers are faster than the electron transfer processes that determine $\Phi$s under the present conditions.

The strict linear dependence of initial rates $R_0$ on $I_{\lambda, \lambda}$ (Fig. 3) implies that hole transfer competes with a pseudo first-order bimolecular $e^-\text{–h}^+$ recombination process.\textsuperscript{2} A pseudo first-order bimolecular carrier recombination process in turn is only possible if QDs contain at most a single electron–hole pair. Since Auger-type termination mechanisms require bi-excitons, i.e., the simultaneous presence of two or more carrier pairs, our experiments exclude Auger-type recombination.\textsuperscript{36}

Thus, the strong direct dependence of $\Phi$s on $r$ reflects the competition between electron transfer and $e^-\text{–h}^+$ first-order recombination under quantum confinement. Our interpretation of this finding is based on the dependence of transfer rates on free energy predicted by Marcus’s theory from the $E_{VB}$ shifts (to less positive values vs. vacuum), and a plausible dependence of $e^-\text{–h}^+$ recombination rates on $r$.

#### $\Phi$-Dependence on free energy

As pointed out above, in our experiments quantum yields represent the fraction of photogenerated holes that accept an electron from EG with a pseudo first-order rate constant $k_{ct}(r)$ in competition with a pseudo first-order (see above) $e^-\text{–h}^+$ recombination with a rate constant $k_{r}(r)$ (eqn (E3)).

\[
\Phi_\lambda(r) = \frac{k_{ct}(r)}{k_{r}(r) + k_{ct}(r)}
\]

\[\text{(E3)}\]
Anodic (EG oxidation) and cathodic (MV$^{2+}$ reduction) processes, of course, are not necessarily synchronous. We had shown that in the stochastic kinetic regime that applies to the evolution of a single e$^-$/h$^+$ pair it is the faster (rather than the slower) interfacial electron transfer process that determines $\Phi_s$. This is so because in this case once the more reactive carrier exits the particle, the remaining carrier must react before the arrival of another photon. By rearranging eqn (E3) we obtain eqn (E4), in which the ratio $k_{et}(r)/k_t(r)$ is expressed as an implicit function of $r$ via experimental $\Phi(r)$:

$$ f(r) = \frac{k_{et}(r)}{k_t(r)} = \left[ \frac{1}{\Phi(r)} - 1 \right]^{-1} \quad \text{(E4)} $$

Eqn (E4) is, of course, independent of any mechanistic considerations. The dependence of $k_{et}$ on $r$ arises from the $E_{VB}$ shifts due to quantum effects (shown in the inset of Fig. 4B). Under the approximations implicit in classical Marcus’s theory, $k_{et}$ is given by eqn (E5):

$$ k_{et}(r) = A \exp \left[ \frac{\left( \lambda + \Delta G^0(r) \right)^2}{4\Delta R_e k_B T} \right] \quad \text{(E5)} $$

In the above expression, $A$ is a frequency factor, $\Delta G^0(r)$ is the free energy change and $\lambda_{RE}$ the reorganization energy associated with hole transfer. We assume that $k_t$ is an inverse function of $r$, i.e.: $k_t = B r^{-n}$, with $1 \leq n \leq 3$. Stronger, $n > 3$ $r$-dependence is deemed to be unrealistic. Thus, $f(r)$ is given by eqn (E6):

$$ f(r) = C r^n \exp \left[ \frac{-\left( E_{VB}(r) - E^0(D) - \lambda_{RE} \right)^2}{4\lambda_{RE} k_B T} \right] \quad \text{(E6)} $$

$E^0(D)$ is the reduction potential for the one-electron oxidation of EG into its radical cation, $E_{VB}(r)$ the energy of the valence band edge of ZnO nanoparticles, $\lambda_{RE} = 0.5$ eV the reorganization energy, and $C$ is a constant $C = A/B$. Fig. 4B shows fits to the experimental results using $C$ and $E^0(D)$ as adjustable parameters for plausible $1 \leq n \leq 3$ values.

We found that experimental data could be fitted by using the following $\{C, E^0(D), n\}$ parameter sets: $\{0.485, 2.30 \text{ V}, 1\}$, $\{0.095, 2.37 \text{ V}, 2\}$, and $\{0.024, 2.40 \text{ V}, 3\}$. The main conclusion is that EG oxidation occurs in the Marcus inverted region. This conclusion is robust because hole transfer in the Marcus direct region would require a physically untenable strong inverse dependence of recombination rates on $r$, i.e.: $n \gg 3$.

**Electron photodoping**

The irradiation of EG-capped ZnO QD sols in the absence of the MV$^{2+}$ electron acceptor leads to perceptible changes. The UV spectra of ZnO QD sols shift to the blue region as expected from the progressive filling (bleaching) of low conduction band energy states. We quantified the spectral shifts by tracking the displacement of the wavelength corresponding to 50% absorption, $\lambda_{1/2}$. Fig. 5 shows how $\lambda_{1/2}$ evolves as a function of irradiation time for EG-capped ZnO QDs $r = 2.10$ nm sols. $\lambda_{1/2}$ closely follows a $\lambda_{1/2,\infty}(1 - \exp(-\beta t))$ saturation-type kinetics, where $\lambda_{1/2,\infty}$ is the limiting asymptotic value of $\lambda_{1/2}$, which is independent of photon fluence $\phi$, and $\beta$ is a first order rate constant that is an increasing function of $\phi$, i.e., saturation under larger photon fluences is reached in shorter illumination times $\tau_{\infty}$.

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**Fig. 4** (A) $\Phi_s$ as a function of QD radius $r$. Lines are putative quadratic regressions to the data. (B) Symbols: experimental data. Lines are calculated values from eqn (E6) with $n = 1$ (light blue, short dashed line); $n = 2$, (purple, dashed line); $n = 3$ (blue, dotted line). See text. Inset: Energy diagram showing the dependence of band edge positions on $r$.

**Fig. 5** Evolution $\lambda_{1/2}$ (the wavelength at 50% absorption) as a function of the irradiation time for EG-capped ZnO QDs. $r = 2.10$ nm, $[\text{ZnO}] = 0.78$ mM, $\lambda = 303 \pm 10$ nm, $I_0 = 2.27 \times 10^{-6}$ M s$^{-1}$.
The observed saturation-type kinetics corresponds to the filling of a fixed number of conduction band states that are available at the irradiation wavelength/photon energy in each experiment (see below). The electrons accumulated in the ZnO QD sols were titrated with MV2+ as described in the Experimental section. The results are shown in Table 2, where we present the limiting average number of electrons per particle, $n_{e}$, and the volumetric, $\rho_{ev}$, and surficial, $\rho_{es}$, electron densities as a function of excess photon energy $E^*$ for various particle radii.

For a given $r$, the dependence of $\rho_{ev}$ and $\rho_{es}$ on $E^*$ is consistent with the filling of $r$-dependent discrete conduction band levels which become quasi continuous above a $E_{CB} + 0.4$ eV threshold, as observed for particle radii above 2 nm.39–41 Fig. 6 shows a schematic representation of the levels that become accessible upon excitation at two selected irradiation wavelengths (303 and 330 nm) for different particle sizes.

On the other hand, Fig. 7 shows that both volumetric and surficial electron densities display a sigmoid dependence on $E^*$, with inflection points near $E^* = 0.43$ eV, reaching maximum values above $E^* \sim 0.5$ eV.

The sigmoid dependence on $E^*$ is consistent with a titration process in which conduction band levels are progressively filled by higher energy photons. It is apparent that electron–hole recombination is the dominant process above excess electron energies $E^* \sim 0.5$ eV, probably reflecting that the number of available states at these excess energies is no longer the limiting factor.

### Conclusions

Photochemical experiments involving low intensity, continuous wave, monochromatic irradiation of ethylene glycol-capped ZnO quantum dots of controlled size show that: (1) the quantum yields of interfacial redox processes increase with particle radius, a finding that can be accounted by the classical Marcus theory of electron transfer in the inverted region, and (2) in the absence of electron acceptors, ZnO quantum dots are charged with electron densities that depend sigmoidally on $E^*$ and reach a maximum at $E^* > 0.5$ eV. At smaller excess energies, the accumulated electron densities are determined by the number of discrete energy levels accessible to photons with energies exceeding the band gap.

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