Effect of Surface Defects on Auger Recombination in Colloidal CdS Quantum Dots

Supporting Information

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A TEM image of typical GSH capped CdS QDs and X-ray diffraction (XRD) patterns.

A TEM image of typical GSH capped CdS QDs are shown in Figure S1a. Crystal structures and spherical particles are clearly observed. X-ray scattering images were recorded on a RIGAKU R-AXIS IV imaging plate diffractometer with a camera length of 800 mm. The X-ray source was nickel-filtered copper K_α radiation from a rotating-anode X-ray generator (Rigaku Ultrax18). Figure S1a presents XRD patterns of CdS QDs capped with MA, OA and GSH. A comparison of the XRD patterns of CdS QDs with zinc blende and wurtzite patterns of bulk CdS (solid line in Figure S1a) shows that MA and OA capped CdS QDs were zinc blende structure. Although GSH capped CdS QDs were reported to exhibit zinc blende structure [ref. 34 in the main text], they exhibit wurtzite structure in our experiments even though the similar synthetic procedures as ref. 34 were used. The theoretical calculation reported that the difference of the crystal structure in CdS QDs gives only a slight effect to electronic structures

such as the fine-structure splitting of hole states [ref. 38 in the main text]. Therefore, the crystal structure does not affect Auger recombination dynamics.

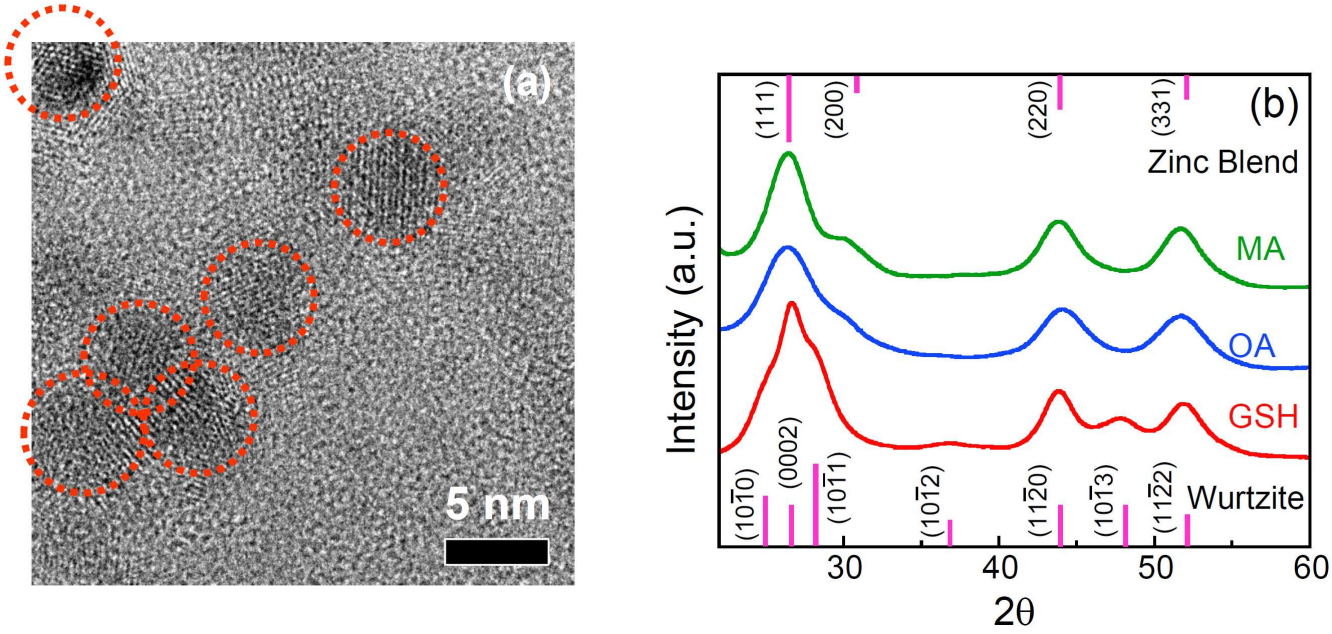

Figure S1. A TEM image of typical GSH capped CdS QDs (a) and XRD diffraction patterns of CdS QDs (b).

Transient absorption spectra and population dynamics at the $1S_{3/2}$(h)-1*S*(e) peak of MA capped CdS QDs

As similar to OA and GSH capped CdS QDs, we measured transient absorption spectra of MA-capped CdS QDs. Figure S1 display transient absorption spectra and dynamics at the $1S_{3/2}$(h)-1*S*(e) peak of MA-capped CdS QDs. These spectra and dynamics are very similar to those of OA-capped CdS QDs.

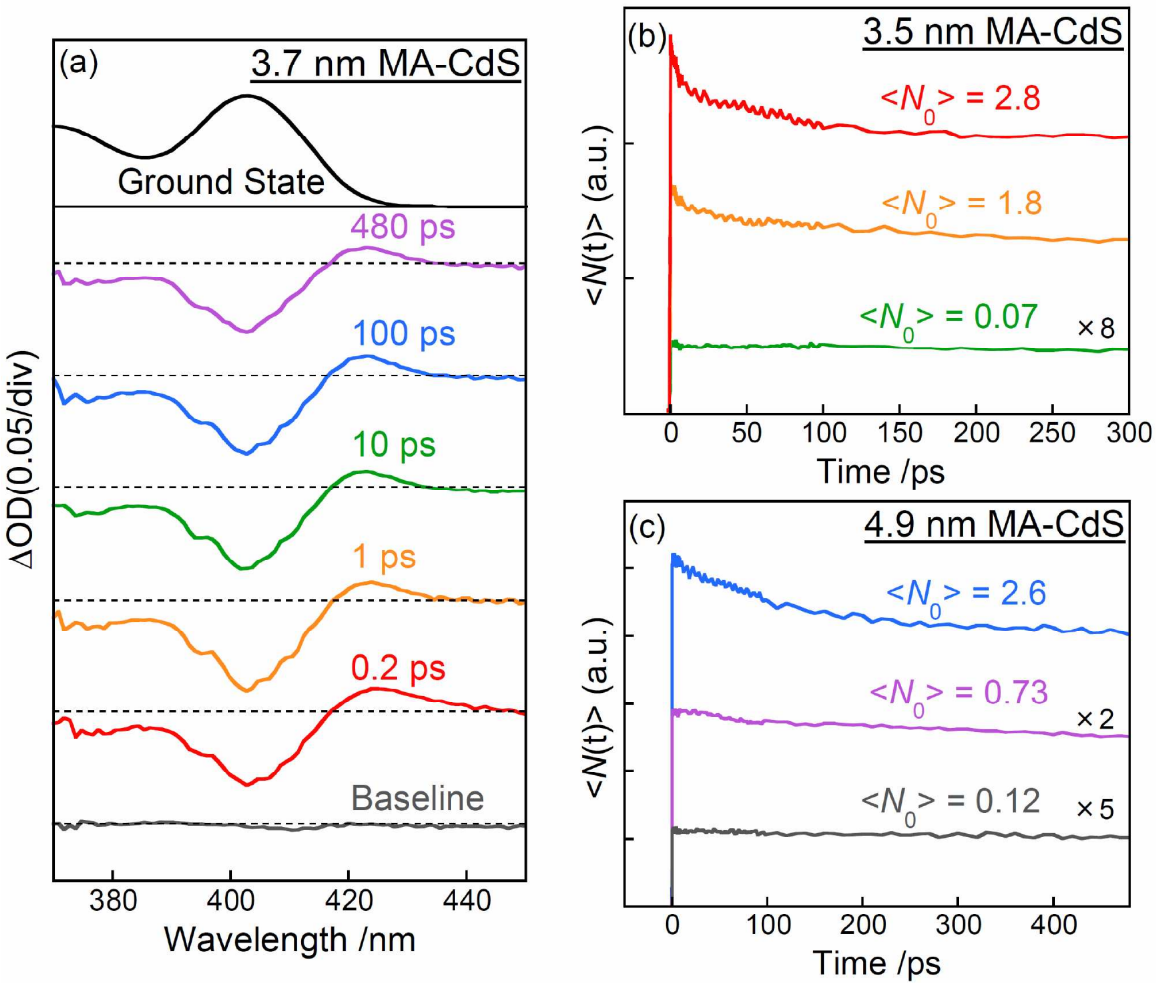

Figure S2. Transient absorption spectra with D = 3.7 nm (a) and Population dynamics of the $1S_{3/2}$(h)-1S(e) state of MA capped CdS QDs with D = 3.5 nm (b) and 4.9 nm (c).

Analysis of the growth kinetics at the bleaching peak of OA and GSH capped CdS QDs

By pulse-convolution analysis, we obtained the rise time to be ~190 fs in both samples. This rise time is probably due to the lifetime of Auger-type energy transfer. This result indicates that capping reagents does not affect hot electron relaxation in this size.

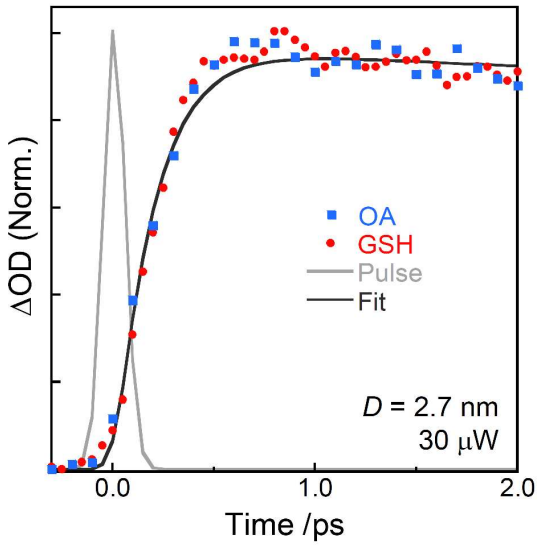

Figure S3. Growth kinetics at the bleaching peak of OA and GSH capped CdS QDs.

Surface-related transient absorption of GSH capped CdS QDs

We show broad-range transient absorption spectra at different time delay of GSH, OA and MA capped CdS QDs in Figure S5a (Excitation intensity: 30 μW). Broad positive transient absorption is observed at longer wavelength region of GSH capped CdS QDs (Figure S5a). Their transient absorption spectra at typical time delay are shown in Figure S5b (Excitation intensity: 60 μW) for the comparison of the signal at longer wavelength region. The ratio between the bleaching signal and the positive signal of GSH capped CdS QDs is a little larger than those of OA and MA capped CdS QDs. However, we cannot analyze the dynamics because of the very low signal. Kambhampati reported that the broad positive absorption is probably due to the transition from the band-edge single exciton state to a higher continuum state [ref. 33 in the main text]. By considering the luminescence properties of GSH capped CdS QDs, absorption owing to surface charge trapping may be superimposed in longer wavelength region.

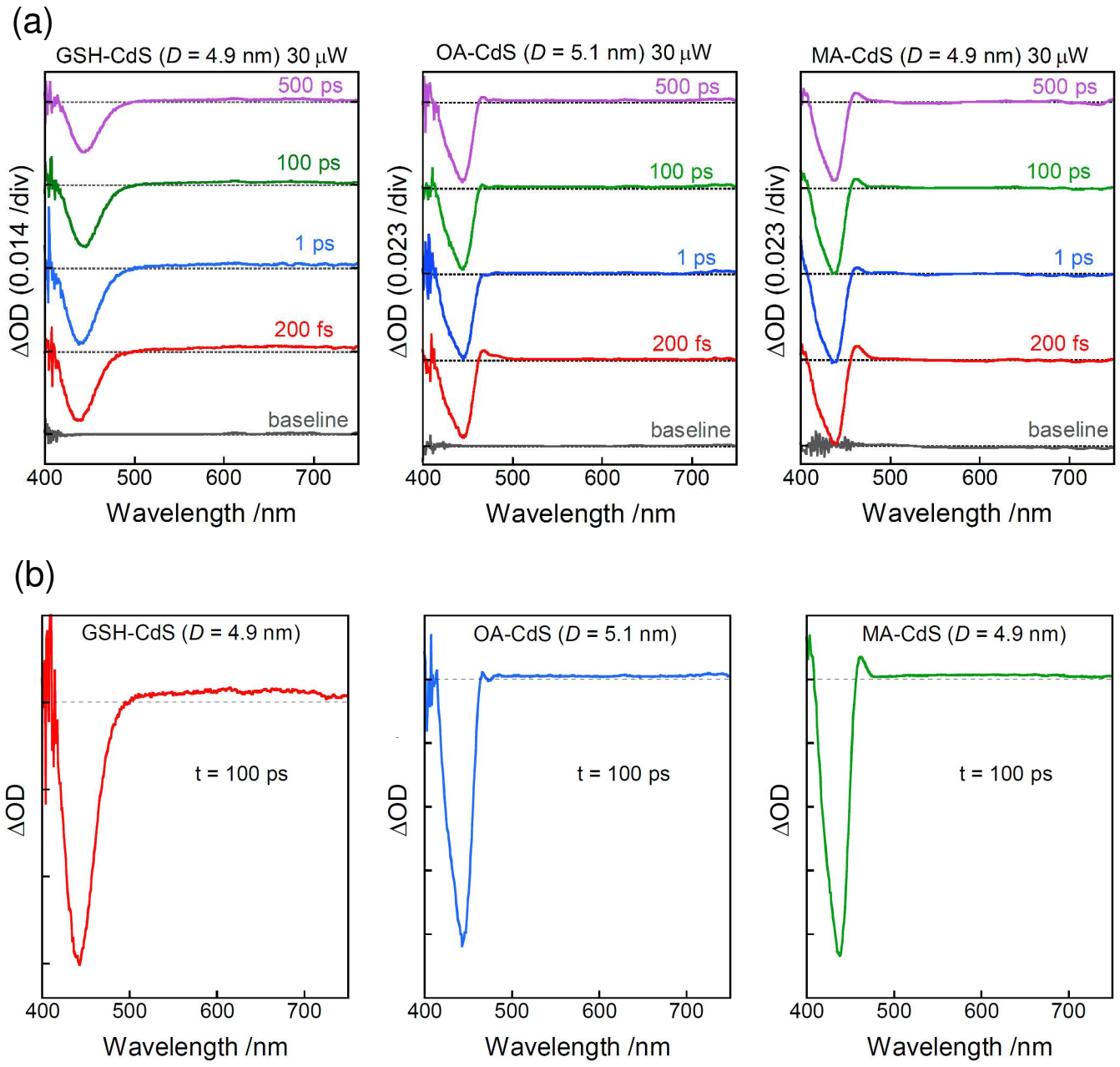

Figure S4. (a) Wide-range transient absorption spectra of GSH, OA and MA capped CdS QDs at different time delays. (b) Transient absorption spectra at the typical time delay for the comparison of surface-related spectra. Excitation intensity is 30 μW for (a) and 60 μW for (b).

Analysis of the positive transient absorption of OA capped CdS QDs

A positive transient absorption is observed at the longer wavelength of the $1S_{3/2}$(h)-$1S$(e) transition in OA and MA capped CdS QDs. Dynamics at the positive peak are shown in Figure S4(a). The absolute values of these signals is plotted as a function of the pump intensity in Figure S4(b). The positive signal is linearly proportional to the pump intensity, which is similar trend with the $1S_{3/2}$(h)-$1S$(e) signal.

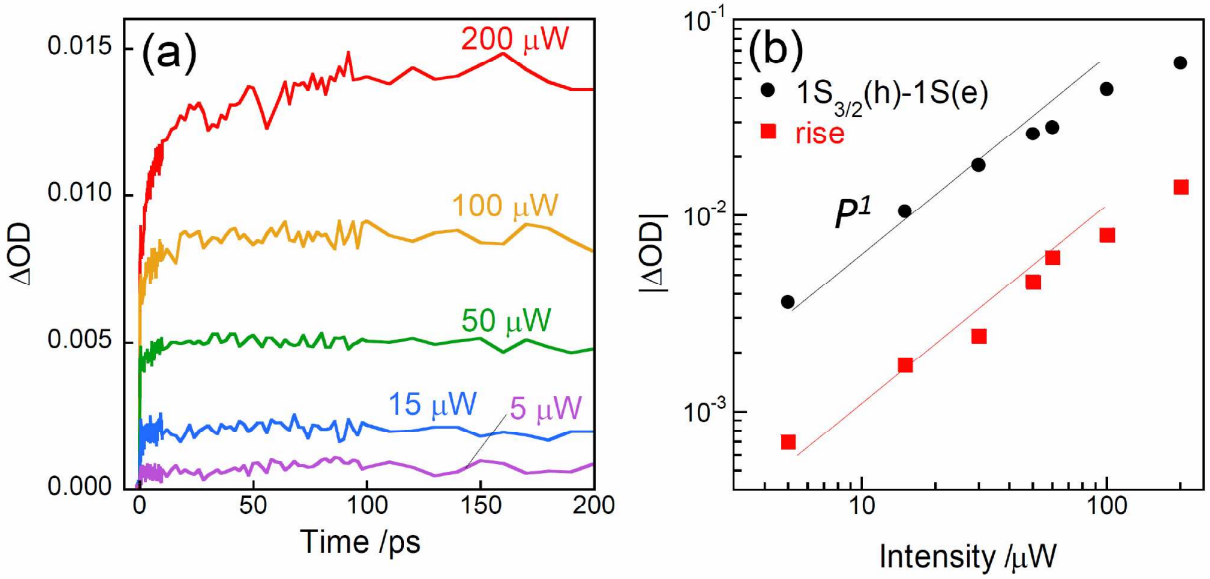

Figure S5. Transient absorption dynamics at the positive peak located at the longer wavelength of the $1S$ bleaching of OA capped CdS QDs (D = 2.7 nm) (a). The intensity dependence of the positive peak (b). P denotes the pump intensity.