Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information for

Carrier dynamics in quantum-dot sensitized solar cells measured by transient grating and transient absorption methods

The principle of the heterodyne transient grating method (Fig. 1S)

When a pump beam is incident on a transmission grating; an intensity pattern of an optical fringe is formed close to the grating. When a sample is placed near the transmission grating, it can be excited by the fringe pattern of the pump light. The refractive index of the liquid changes giving the same pattern as the optical fringe because of photochemical or photothermal processes; the pattern of refractive index change is called a transient grating. When another light beam (probe light) is incident on the transient grating, a part of the probe is transmitted (reference), or another part of the probe is once diffracted by the transmission grating and refracted by the transient grating into the same direction with the reference (signal). The intensity of the mixture of the signal and reference (heterodyne signal) was monitored as the time passed. When the transient grating is composed of an intermediate chemical species, the fringe pattern is gradually lost not only by the intrinsic lifetime of the species but also by the diffusion in the perpendicular direction to the fringe. We can recognize the signal decay was due to lifetime or diffusion by checking the dependence on the grating spacing because the decay time due to the diffusion process depends on it.

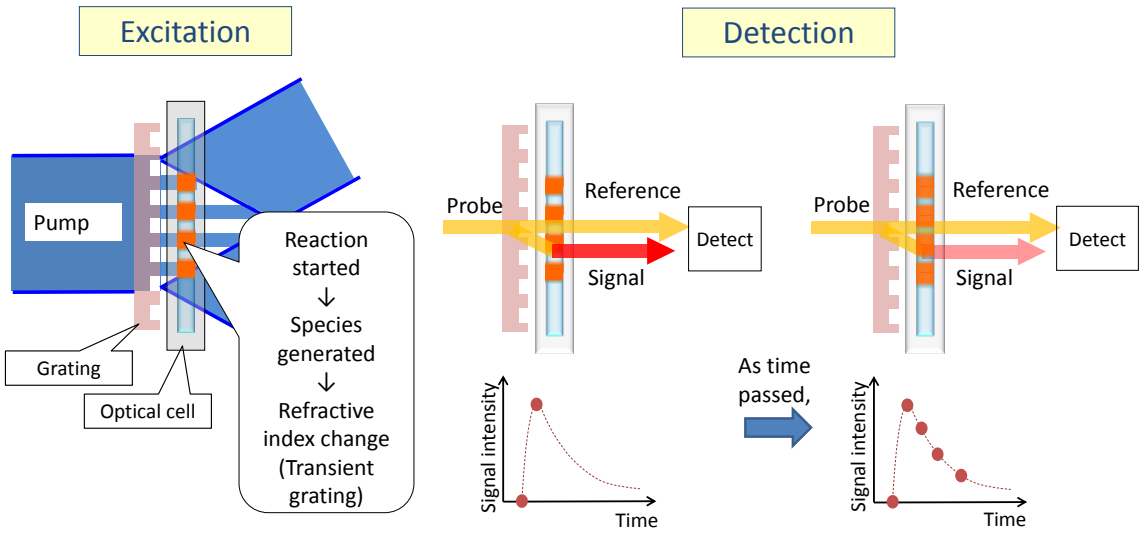

Fig.1S Schematic diagram of the heterodyne transient grating method.

SEM images of the TiO_2 electrode sensitized with CdSe

SEM images of the TiO_2 electrode before and after CdSe quantum dot growth were shown in Fig.2S. The electrode was made of anatase TiO_2 particles. From Fig.2S(a), the pore size of the TiO_2 electrode was on the order of tens of nanometers in diameter. The thickness of the TiO_2 electrode was 7 μm. The CdSe quantum dots were confirmed from Fig.2S(b) and the chemical composition was confirmed by XRD.

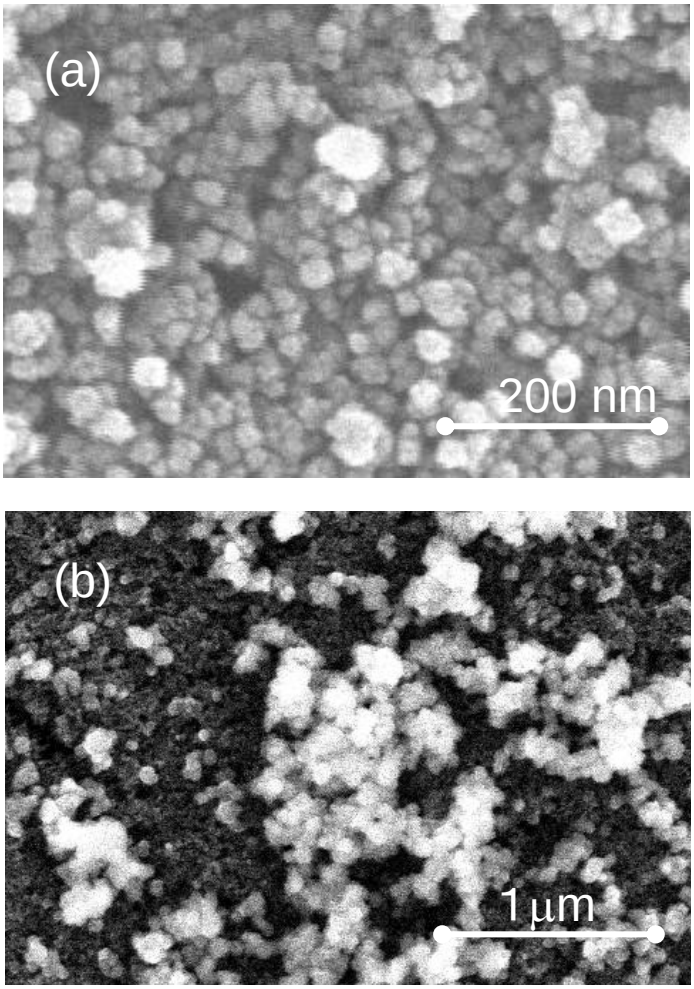

Fig.2S SEM images of the working electrode made of TiO_2 nanoparticles before (a) and after (b) growth of CdSe quantum dots are shown.

The effect of a Pt counter electrode by repeated irradiation of pulsed laser (Fig. 3S)

The photocurrent was measured by repeating the irradiation of the pump pulses. The pump pulses was irradiated with a repetition rate of 0.5 Hz, an intensity of 0.65 mJ/pulse. The wavelength was 570 nm. As the pulses were irradiated, photocurrent was reduced because the reduction reaction at the Pt surface was not fast enough to recover the oxidized species at the working electrode.

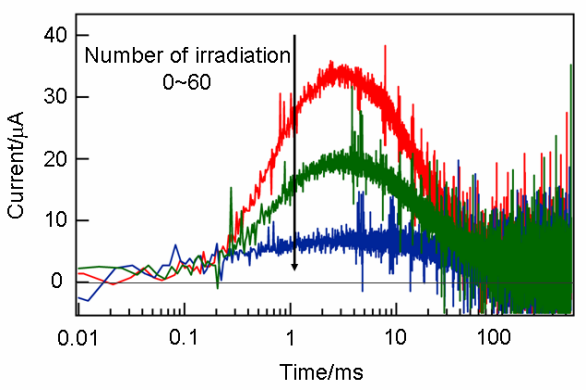

Fig.3S The effect of repeated pulse light irradiation on the photocurrent responses for a Pt counter electrode.

The effect of HD-TG responses for different counter electrodes (Fig.4S)

At the counter electrodes, oxidized redox species are reduced, and if the reaction rate is not fast enough, the oxidized redox species are accumulated in the electrolyte solution and it may affect the HD-TG responses in the slower time region for repeated experiments. It is known that the reaction rate at a Pt counter electrode is slower than that for Cu_2S in polysulfide solution. (ref 41 Hodes et al.) Even after 100 times measurements, the difference was smaller than the error range and the effect of the counter electrode is negligible for HD-TG responses.

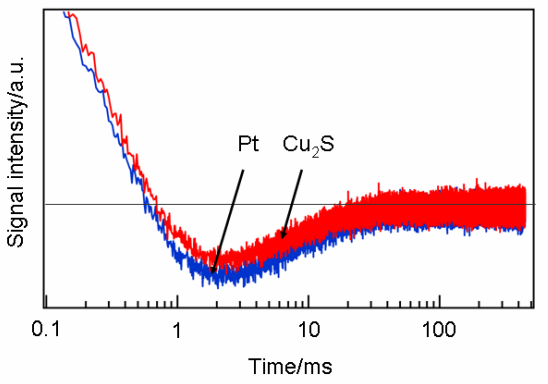

Fig. 4S The effect of the materials of the counter electrode on the HD-TG responses. The counter electrodes were Pt and Cu_2S. The response was taken after 100 times pump pulse irradiation.

IPCE spectra for the QDSSSC (Fig.5S)

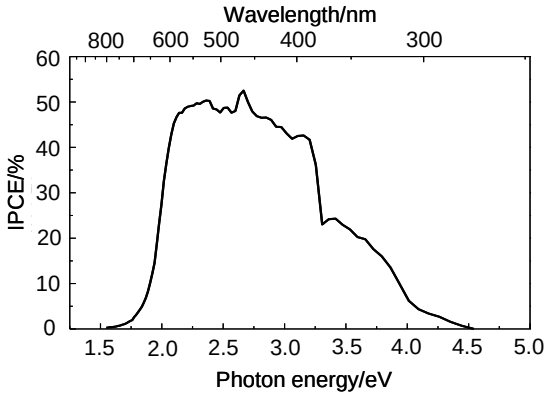

Fig. 5S IPCE spectrum for the QDSSCs used in this experiment is shown. This cell had, Jsc：9.68 mA/cm^2, Voc：0.523 V, FF：0.52, η:2.63 %.