Supplementary Information:

Ultrathin CdSe in Plasmonic Nanogaps for Enhanced Photocatalytic Water Splitting

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A) Local photocurrent enhancement in the nanogap

To determine the local enhancement of the photocatalytic activity in the nanogap, the photocurrent obtained on a sample covered with AuNPs was compared to the one measured
on a sample without NPs. The exceeding photocurrent in presence of AuNP is generated only in the highly localized “hot spots” underneath each nanoparticle. The nanoparticle density on the surface is $\sim 5 \times 10^5$ mm$^{-2}$ (Fig. S1). The diameter of the enhanced area underneath the nanoparticle (where $|E| \geq \frac{1}{2}|E_{max}|$) is $\sim 20$ nm, as determined by boundary-element simulations. This results in an “effective plasmon enhanced area” per mm$^2$ of

$$(\text{Number AuNP/mm}^2) \times \text{hot spot size} = 5 \times 10^5 \times (\pi \times (10 \times 10^{-6})^2) = 1.57 \times 10^{-4}.$$ 

As the observed five-fold photocurrent enhancement is generated only in these hot spots, the local enhancement in the gap is estimated to

$$\text{overall enhancement/effective enhanced area} = \frac{5}{1.57 \times 10^{-4}} \approx 3.1 \times 10^4.$$ 

**Figure S1** | DF scattering image of the sample surface covered with AuNPs. AuNPs are identified with red circles.
B) SEM of sample surface

The nanoparticles are well-separated after deposition on the surface (Fig. S2). Aggregation was not observed. This means that the field enhancement usually results only from the enhanced field region in the gap between the NP and the surface.

![Figure S2](image)

**Figure S2** | Scanning electron micrograph, showing the sample surface covered with AuNPs (identified as white spots) which are well-separated.

References

1. Li, L. *et al.* Metal oxide nanoparticle mediated enhanced Raman scattering and its use in direct monitoring of interfacial chemical reactions. *Nano Lett.* **12**, 4242–6 (2012).