Au/TiO$_2$ plasmon photocatalysis: femtosecond spectroscopy of the hot electron injection into TiO$_2$, bacterial inactivation, bactericide Au-ions and related phenomena


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Au-nanorods synthesized according to the protocol [1].

**Preparation of Au Seeds.** In a typical procedure, 50 μL of an aqueous 0.01 M solution of HAuCl$_4$·3H$_2$O was added to 2 mL of a 0.10 M CTAB solution. The solutions were gently stirred by shaking. Then, 24 μL of an aqueous 0.01M ice-cold NaBH$_4$ solution was added and mixed for 2 min. Care should be taken to allow the escape of the evolved gas during mixing. The solution developed a beige color. Then the solution was kept at 25°C for future use. This seed solution was used 2 h after its preparation.

**Preparation of Au Nanorods.** The 50 mL of 0.10 M CTAB, 2.5 mL of 0.01 M HAuCl$_4$·3H$_2$O, and 0.4 mL of 0.01 M AgNO$_3$ solutions were added in that order consistently into the flask with stirring. Then 0.4 mL of 0.10 M ascorbic acid was added into the reaction mixture with stirring. The solution became colorless at this moment. Finally, 0.5 mL of seed solution was added, and the reaction mixture was gently mixed for 15 s and left undisturbed for at least 3 h. [Sau, T.K. and Murphy, C.J., 2004. Seeded high yield synthesis of short Au nanorods in aqueous solution. *Langmuir*, 20(15), pp.6414-6420.]

The SEM image of particles is presented in Fig.2.
Gold Nanoparticle synthesized according to the protocol [2]. The standard method, as described by Turkevich [Turkevich, J., Stevenson, P.C. and Hillier, J., 1951. A study of the nucleation and growth processes in the synthesis of colloidal gold. *Discussions of the Faraday Society, 11*, pp.55-75.], was used with some changes. The reduction of a hydrogen tetrachloroaurate(III) solution has been initiated by sodium tris-citrate by bringing gold solution to to a temperature of about the boiling. The reaction mixture is vigorously stirred by Teflon-coated magnetic bars. When the solution (147 µl 0.2M HAuCl₄ in water 100 ml) heats up to 95°C, the citrate solution (3 ml 0.034M) was added. After a 20 min the liquid was extracted and cooled to room temperature. The SEM image of particles is presented in Fig. SI1.

Fig. SI1. SEM image of AuNPs synthesized according to the protocol [1]

Fig. SI2. SEM image of AuNPs Nanoparticle according to the protocol [2].
SI2. The spectrum of tungsten-halogen lamp.

Figure SI3. The spectrum of tungsten-halogen lamp.

http://zeiss-campus.magnet.fsu.edu/articles/lightsources/tungstenhalogen.html

SI3. Femtosecond laser photolysis setup.

Transient absorption spectra were measured by the femtosecond pump–
supercontinuum probe setup.12 The pump was performed by the Gauss pulses with a
repetition frequency of 15 Hz, time duration 25 fs, wavelength 740 nm, and energy 15
nJ. The white supercontinuum pulses generated in a quartz cell with H2O were used as
probe pulses. The diameter of a probe spot was ~100 μm. The pump light spot has a
diameter of 300 μm. The relative polarizations of the pump and probe beams were
adjusted to 54.7° (magic angle) configurations. After the sample, the supercontinuum
was dispersed by a polychromator («Acton SP-300») and detected by CCD camera
(«Roper Scientific SPEC-10»). Absorption difference spectra ΔA (t, λ) were recorded
over the spectral range 400–740 nm. The measured spectra were corrected for group
delay dispersion of the supercontinuum.

SI4. The estimation of the local temperature at the surface of AuNPs in Au/TiO2
sample under steady state illumination.

The temperature of the sphere of the radius r in the continuous medium at the distance
r from the center of the sphere T(r) is defined as (1)

\[
T(r) = T_0 + \frac{W}{4\pi\lambda r}
\]

(1)

The T(\text{r}_0) at the sphere surface is (2)
\[ T(r_0) = T_0 + \frac{W}{4\pi \lambda r_0} \]  

(2)

Where \( W = \sigma_{\text{abs}} I \) is the light power absorbing by sphere with the cross-section of the absorption \( \sigma_{\text{abs}} = \pi r^2 Q_{\text{abs}} \). \( I \) is light intensity in W/m\(^2\) units. \( Q_{\text{abs}} \) is equal to 0.0019 for \( r=2.5 \) nm Au nanoparticles at the peak of the plasmon resonance. \( Q_{\text{abs}} \) was calculated according to the Mi theory. The coefficient \( \lambda = \frac{\chi}{c_p \rho} \) is equal to 0.143 \( 10^{-6} \) m\(^2\)/s, where \( \chi \) is heat transfer coefficient, \( c_p \) is heat capacity and \( \rho \) is water density. The temperature increase for \( I= 1 \) W/cm\(^2\) is equal to 0.215 °C according to equation (2).

SI 5. Bright and dark field TEM images of Au/TiO\(_2\) NPs.

![TEM images](image.png)

Figure SI 4. Bright (a) and dark (b) field electron microscopy images of Au/TiO\(_2\) NPs after 24h irradiation with LED green light (300 \( \mu \)W/cm\(^2\)). Red circles indicate fragments of NPs after irradiation. Bright spots in the dark field image suggest the presence of Au fragments.

SI 6. The evaluation of bactericide effect of residual solution after the Au nanorods synthesis.

The reaction mixture for the preparation of gold nanoparticles consisted of reagents:
0.10 M (36.4 g/l) CTAB, 0.47 mM HAuCl\(_4\) (0.16 g/l), and 76 \( \mu \)M AgNO\(_3\) (12.8 mg/l) (Sau, T.K. and Murphy, C.J., 2004). MIC\(_{\text{CTAB}}\) (E. coli AB1157) was determined to be equal to < 50 \( \mu \)g/ml. It is in reasonable agreement with previously reported data (Ishikawa, S. et al. 2002, Guo, L. et al. 2015). MIC\(_{\text{Ag}^+}\)\((E.\ coli\ AB1157) = 0.1 \mu g/ml\) (Radzig M.A. et al. 2013). MIC\(_{\text{Au}^{3+}}\)\((E.\ coli\ AB1157) \)equals 1 \( \mu \)g/ml. The CTAB concentration after Au nanorods synthesis is conserved at the same level. Silver ions are catalyst and Ag\(^+\) concentration apparently is not changed significantly. The CTAB concentration exceeds MIC\(_{\text{CTAB}}\)\((E.\ coli\ AB1157) 7200 \)times, Ag\(^+\) concentration exceeds MIC\(_{\text{Ag}^+}\)\((E.\ coli\ AB1157) 128 \)times. These estimates show that the washing of the synthesized nanoparticles should be carried out very carefully.

