Electronic Supplementary Information

A comparative study of photocatalytic activity of Na⁺-Ag⁺ ion-exchanged glass-ceramics with metallic Ag, semiconductor AgBr, and hybrid Ag-AgBr nanoparticles

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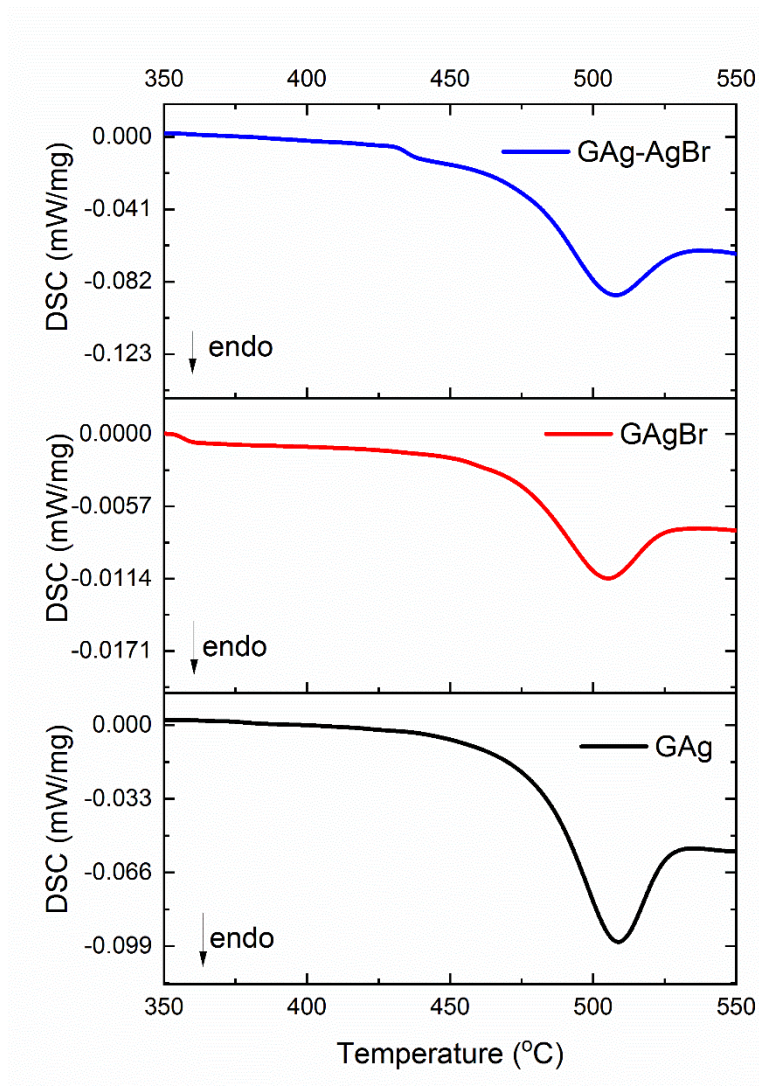[c]*P.N. Lebedev Physical Institute, Moscow, Russia*

Figure S1. DSC curves for as-synthesized GAg, GAgBr, and GAg-AgBr samples.

Estimation of quasi-stationary density of hot electrons in Ag, AgBr and hybrid Ag/AgBr nanoparticles

Let a layer of photoactive nanoparticles of number density ρ is illuminated by external radiation source with the intensity spectrum $I(\omega)$. Under assumption of linear (one-photon)

photoabsorption process, the number density of photo-excited hot electrons (electron-hole pairs) is

$$N_e = \int \rho n_e(\omega)\sigma(\omega)I(\omega)d\omega \tag{1}$$

Where $\sigma(\omega)$ is the absorption cross-section of individual nanoparticle, and $n_e(\omega)$ is the net number density of electrons (electron-hole pairs) per nanoparticle which can be determined from the following rate equation

$$\frac{dn_e(\omega)}{dt} = \frac{\sigma(\omega)I(\omega)}{V\hbar\omega} - \gamma n_e(\omega) \tag{2}$$

Here γ is the characteristic relaxation rate of hot electrons (electron-hole pairs), all nanoparticles are assumed to be of identical shape and volume V. According to this rate equation, the net density of hot electrons (electron-hole pairs) in nanoparticles is given by

$$< n_e > = \frac{1}{V}\int_{\omega_1}^{\omega_2} \frac{\sigma(\omega)I(\omega)}{\hbar\omega\gamma}d\omega \approx \frac{F_0}{\hbar V\gamma}\int_{\lambda_1}^{\lambda_2} \frac{\sigma(\lambda)F(\lambda)}{\lambda}d\lambda \tag{3}$$

with the total intensity of light source given by

$$I = \int_{\omega_1}^{\omega_2} I(\omega)d\omega = 2\pi c F_0 \int_{\lambda_2}^{\lambda_1} \frac{F(\lambda)}{\lambda^2}d\lambda \tag{4}$$

where $\omega_{1,2}$ and $\lambda_{1,2}$ are the boundaries of the light source spectrum in frequency and wavelength domains, respectively. The normalized spectrum $F(\lambda)$ of the mercury lamp used in our experiment is situated between $\lambda_1 = 350$ nm and $\lambda_2 = 600$ nm shown in the Fig. S2,. Taking into account the total intensity of the mercury lamp is 80 mW/cm^2, we find the fitting constant is $F_0 = 2.63 \times 10^{-16}$ Jcm^{-2}
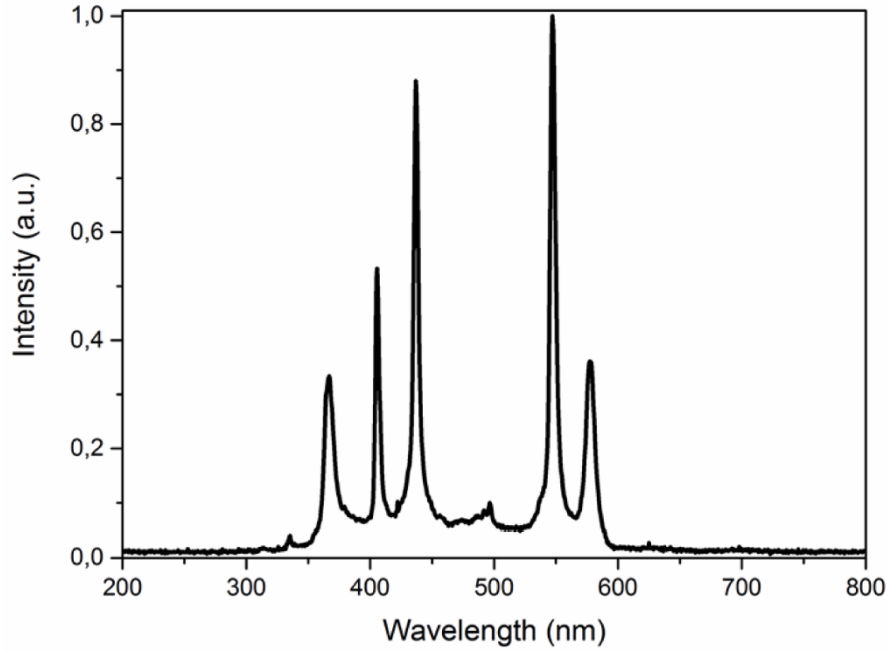
Figure S2. Normalized emission spectrum of the used mercury lamp.

Assuming for estimates the spherical shape of nanoparticles with the effective radius a (i.e., $V = (4/3)\pi a^3$), one can write for the absorption cross section the following relation

$$\frac{\sigma(\omega)}{\pi a^2} = 4ka\,\mathrm{Im}\left(\frac{\varepsilon_o - \varepsilon_n}{\varepsilon_o + 2\varepsilon_n}\right) = 12ka\frac{\varepsilon_o \varepsilon_n{}''}{|\varepsilon_o + 2\varepsilon_n|^2} \tag{5}$$

where $k = 2\pi n_o/\lambda = n_o\omega/c$ is the radiation wavenumber, ε_n and ε_o are the dielectric permittivity of nanoparticle and outer space, respectively. We assume the outer space, i.e. water solution of MO dye, is characterized by low (with respect to the nanoparticle's layer) absorption, so the refraction index is $n_o \approx \sqrt{\varepsilon_o}$. In particular for pure water we have $n_o = 1.347$, $\varepsilon_o = 1.81$

1) Metal Ag nanoparticle.

Let us first make an estimate for Ag nanoparticle. Dielectric permittivity of bulk silver at photon energies below 4eV ($\lambda = 311$ nm) is well described by the Drude model

$$\mathrm{Re}\,\varepsilon_{Ag} = \varepsilon'_{Ag} \approx \varepsilon_L - \frac{\omega_p^2}{\omega^2}, \quad \mathrm{Im}\,\varepsilon_{Ag} = \varepsilon''_{Ag} \approx \frac{\omega_p^2 \Gamma_{Ag}}{\omega^3} \tag{6}$$

with the parameters $\varepsilon_L = 5 \pm 2$ is the limiting short wavelength permittivity value, $\hbar\omega_p = 8.9$ eV is the plasma frequency, and $\Gamma_{Ag}^{-1} \approx 17 \pm 3$ fs is the characteristic relaxation constant [1]. For small nanoparticles, one should take into account additional broadening which is caused by collisions of electrons with the boundary of nanoparticle (so-called Landau damping), so that in (6) one should replace the relaxation rate as follows

$$\Gamma_{Ag} \to \Gamma = \Gamma_{Ag} + \Gamma_{LD}, \quad \Gamma_{LD} = A_K \frac{v_F}{a} \tag{7}$$

where the Kreibig constant $A_K \Box 1$, and $v_F \approx 1.4 \times 10^8$ cm/s is the Fermi velocity of silver. Estimate of the net density of hot electrons for Ag nanoparticles can be made according to relation (3) with the absorption cross section determined by Eqs. (5)-(7). Under assumption of elastic collisions of electrons with nanoparticle's boundary, one should keep $\gamma = \Gamma_{Ag}$ in Eq. (3). Assuming the diameter of metal nanoparticle is 10 nm, we find the net quasi-stationary density of hot electrons is $\Box 3.36 \times 10^7$ cm^{-3}

2) Semiconductor AgBr nanoparticle.

In AgBr nanoparticles absorption of photons proceeds through excitation of electron-hole pairs and thus has a natural threshold determined by the bandgap, $\hbar\omega_{th} = 2.6$ eV ($\lambda_{th} = 477$ nm), absorption of photons below this energy threshold proceeds mainly through impurity levels inside the bandgap and is sufficiently small. Using the known experimental data of linear absorption coefficient $\alpha_{AgBr}(\omega)$ and refraction index $n_{AgBr}(\omega)$, we have recovered the real and imaginary parts of the dielectric permittivity of AgBr as follows

$$\varepsilon''_{AgBr}(\lambda) = n_{AgBr}(\lambda)\alpha_{AgBr}(\lambda)\lambda/2\pi, \quad \varepsilon'_{AgBr}(\lambda) = n^2_{AgBr}(\lambda) - (\alpha_{AgBr}(\omega)\lambda/4\pi)^2 \tag{8}$$
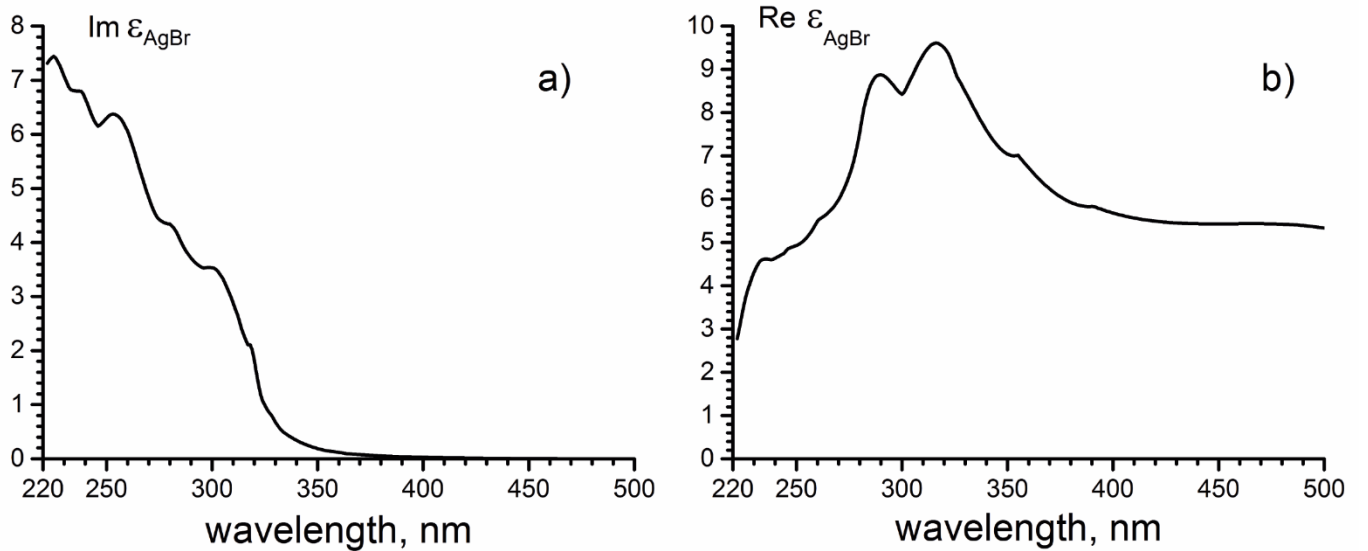
The result is shown in the Fig. S3 below.

Figure S3. The spectra of imaginary (a) and real (b) parts of dielectric permittivity of AgBr recovered according to Eq. (8).

Relaxation of electron-hole pairs in bulk AgBr is caused mainly by radiative recombination with the characteristic time scale of nanosecond domain. In the case of our interest, electrons and holes participate in much faster redox reactions with the components of MO dye solution in water

which are of picosecond time scale. Keeping in mind the general reasons [1], we will take for estimates the characteristic time of electron-hole relaxation in AgBr nanoparticle is $\gamma_{AgBr}^{-1} \simeq 1$ ps. Using the above data, we find from Eqs. (3),(5) the estimate of quasi-stationary electron-hole density in AgBr nanoparticle is $\simeq 0.67 \times 10^8 \text{cm}^{-3}$.

3) Hybrid nanoparticle.

A hybrid nanoparticle with a metallic Ag core and a semiconductor AgBr shell makes it possible to combine the advantages of a high rate of formation of hot electrons in a metal and a large relaxation time of electrons in a semiconductor. Excited in a metal core, hot electrons with an energy E above the potential barrier $E_F + U$ at the metal-semiconductor interface $E - E_F > U$ can relatively easily pass into a semiconductor, where their lifetime will be an order of magnitude longer than in a metal.

To make estimate, we use the Fowler approximation, assuming that hot electrons are uniformly distributed in a spherical layer $[k_F, \sqrt{2m(E_F + \hbar\omega)}]$, $k_F = \sqrt{2mE_F}$ is the Fermi wavenumber, in the space of electron wave vectors. Thus, the fraction of hot electrons that can move into the semiconductor shell is

$$\eta = \frac{(E_F + \hbar\omega)^{3/2} - (E_F + U)^{3/2}}{(E_F + \hbar\omega)^{3/2} - E_F^{3/2}} \tag{9}$$

For an electron with the energy $E > U + E_F$, the effective decrease in the relaxation rate can be estimated as

$$\Gamma_{eff} = \frac{\xi}{1+\xi}\Gamma_{Ag} + \frac{1}{1+\xi}\gamma_{AgBr} \tag{10}$$

where $\xi \approx (R/h)(\mu(E - E_F - U)/E)^{1/2}$ can be conditionally interpreted as the ratio of the net time spent by the electron in the metal core to the time spent in the semiconductor shell. Here, R is the core radius and h is the shell thickness of the hybrid nanoparticle, and $\mu = m/m*$ is the ratio of the effective masses in the metal and semiconductor. When the excess of electron energy above the potential barrier $E - (E_F + U)$ is small, the parameter ξ vanishes and $\Gamma_{eff} \to \gamma_{AgBr}$. Assuming that most of hot electrons in hybrid nanoparticle are excited in metal core, taking into account the fraction η varies as $0.55 < \eta < 0.75$ in the wavelength interval 350 nm$<\lambda<$ 600 nm, we estimate the hot electron density in hybrid nanoparticle exceeds that for AgBr nanoparticle by the factor $20 \div 27$.

Finally, our estimates demonstrate that quasi-stationary net hot electron densities in metal (Ag), semiconductor (AgBr), and hybrid (Ag/AgBr) nanoparticles under conditions of our experiment relates approximately as 0.5:1:20, respectively.
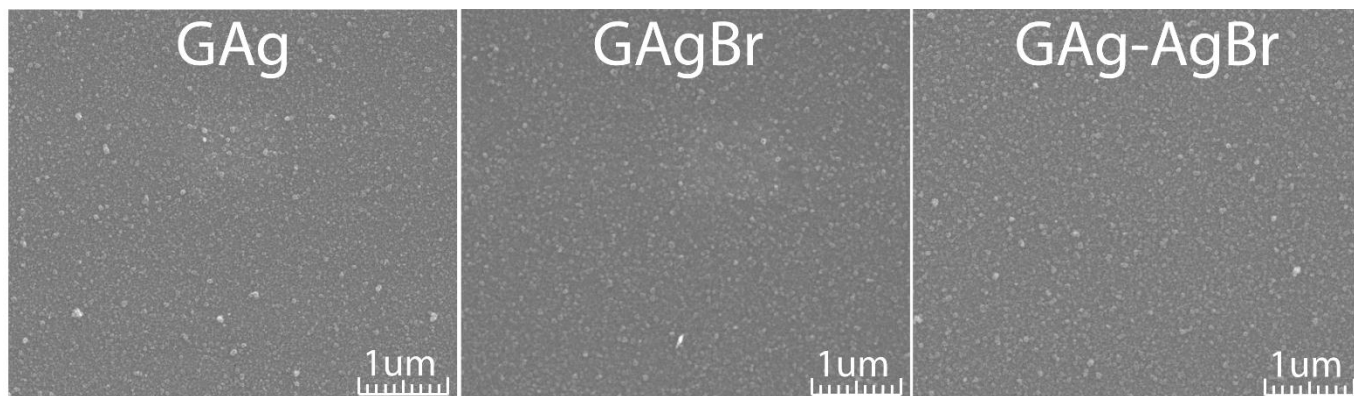
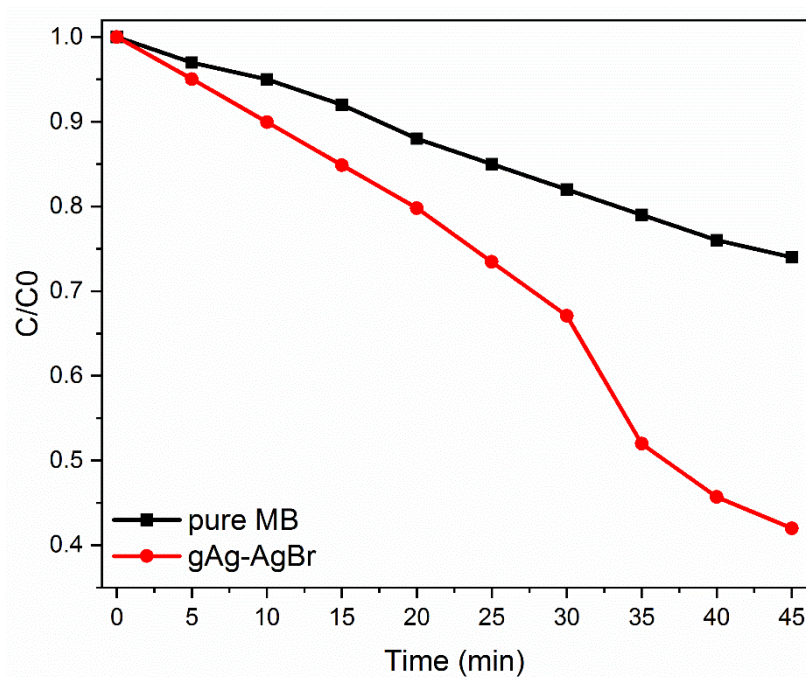Figure S4. SEM images GAg, GAgBr, and GAg-AgBr samples.

Figure S5. Photocatalytic degradation of pure methylene blue aqueous solution (black squares and line) and with GAg-AgBr glass-ceramic photocatalyst (red circle and line).

References

1. Mozumder, A., and John L. Magee. "The early events of radiation chemistry." *International Journal for Radiation Physics and Chemistry* 7.2-3 (1975): 83-93.