

Supporting Information

Modification of Gold Nanorods using Phosphatidylcholine to Reduce Cytotoxicity

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In this supporting information, we discuss the replacement of hexadecyltrimethylammonium bromide (CTAB) on the NR surfaces with alternative stabilizing agents using repeated centrifugation. Polyvinylpyrrolidone (PVP) and polyethyleneglycolthiopyridyldisulfide (OPSS-PEG, Mw: 5,000, Shearwaters polymer) were used as the alternative stabilizing agents. The first centrifugation of the NR solution (1 mL) was carried out at 8000 g for 15 min. Precipitated NRs were redispersed in water, PVP (10 mg/mL) or OPSS-PEG (10 mg/mL) solution (1 mL). The redispersed NR solution was further centrifuged under the same conditions as for the first centrifugation.

Figure S1 shows absorption spectra of the NR solutions after three extractions using phosphatidylcholine-chloroform solution (a; see Figure 3), and after the centrifugation procedures ((b)-(d)). In the absence of polymers (b), the precipitated NRs were well dispersed in water after the first and second centrifugations. After the third centrifugation, however, the peak intensity of the longitudinal SP band obviously decreased (Figure S1 (b)). This spectral change indicates that NRs aggregated in water after the third centrifugation. Thus, centrifugation without alternative stabilizing agents cannot be performed more than three times without forming irretrievable NR aggregates in this experiment. After the third centrifugation, the zeta potential of the NRs was $+27 \pm 2$ mV. This is much smaller than that of the initial NRs before centrifugation ($+67 \pm 1$ mV). Thus, the smaller zeta potential after the third centrifugation indicates partial degradation of the CTAB bilayer, and induced destabilization and sequential aggregation of the NRs.

The curve (c) is the spectrum of NRs redispersed in PVP solution after the first centrifugation. The broadening of the longitudinal SP band indicates the formation of NR aggregates. PVP, which has many positions on its polymer chain that can bind to a gold nanoparticle, is suitable for stabilizing the colloidal dispersion of gold nanoparticles. However, because PVP bridges between some NRs, the addition of PVP induced aggregation of NRs. Thus, PVP is not suitable as an alternative stabilizing agent for the NRs. In the case of OPSS-PEG (d), on the other hand, because PEG chains modify the NR surface by Au-S binding, aggregation of NRs does not occur on addition of OPSS-PEG. The NRs redispersed in the OPSS-PEG solution after the first centrifugation showed an identical spectrum to that before centrifugation. After the second centrifugation, however, the redispersed NRs in the OPSS-PEG solution showed a small SP peak at ~ 900 nm and a remarkable increase in absorbance in the longer wavelength region (Figure S1 (d)). This

spectrum indicates considerable formation of NR aggregates. It is plausible that flexible PEG chains are not effective at preventing aggregation of NRs in the centrifuged precipitates. These results indicate that centrifugation is not a desirable method for removing large amounts of CTAB without aggregation of NRs, even in the presence of polymer.

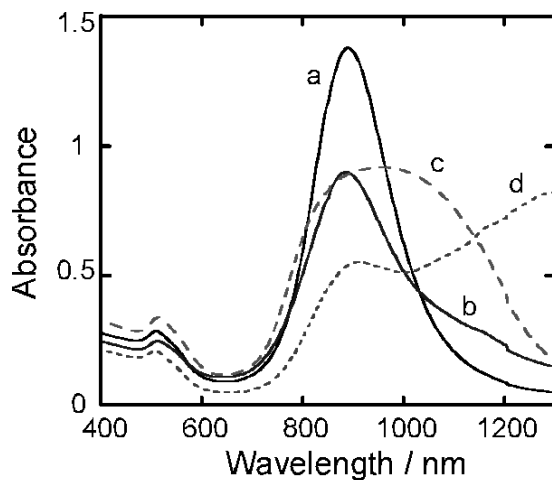


Figure S1. Absorption spectra of NRs after three extractions using phosphatidylcholine-chloroform solution (a) and after repeated centrifugation (b-d). The spectrum (b) shows NRs redispersed in water after the third centrifugation. The spectrum of NRs redispersed in a PVP (10 mg/mL) solution after the first centrifugation is shown as (c). The curve (d) indicates the spectrum in an OPSS-PEG (10 mg/mL) solution after two centrifugations of NRs in the OPSS-PEG solution.