Organo-soluble photoresponsive azo thiol monolayer-protected gold nanorods†

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Organo-soluble photoresponsive azo thiol monolayer-protected gold nanorods were synthesized; the resulting gold nanorods encapsulated by thiols on their entire surface with strong covalent Au–S linkages were very stable in both organic solvents and in the solid state without aggregation or decomposition.

Owing to their unusual behavior compared with spherical gold nanoparticles as well as corresponding bulk materials,[1] gold nanorods provide tremendous opportunities as well as challenges for insights into fundamental science that opens the door to applications in optics,[1] sensors,[2] biological imaging,[3] and anticancer agents.[4] So far gold nanorods are mainly prepared in an aqueous solution by a seed-mediated growth method,[5] in which cetyltrimethylammonium bromide (CTAB) is widely used as a shape-directing surfactant to selectively form a densely packed dynamic layer around the sidewall of a growing gold nanorod with its two ends free from CTAB for an anisotropic growth along the longitudinal axis. The resultant gold nanorods covered with a CTAB layer on their longitudinal surface are water-soluble. Unfortunately, the dynamic CTAB layer is not stable. For example, with the removal of excess free CTAB and other components in aqueous solution by centrifugation to obtain the CTAB-covered gold nanorods, the bound CTAB in the dynamic layer will eventually enter the solution leaving a gold surface which will result in irreversible aggregation of gold nanorods into gold clusters. Furthermore, compared with dispersing gold nanorods in water, dispersing them in organic solvents is appealing since their low interfacial energies should allow for a high degree of control during solution and surface processing. So a challenging task is to prevent their aggregation propensity and make them soluble and stable in organic media. Recent progress on thiol monolayer-protected spherical gold nanoparticles[6] provides an intriguing pathway to address this challenge. However, the densely-packed CTAB layer on the longitudinal side obstructs thiol molecules from accessing the gold surface to bind to the gold through a strong

covalent Au–S linkage. For this reason, thiol molecules have been attached only onto the two CTAB-free ends at best.[7] The seemingly trivial work of exchanging CTAB with organic thiol molecules was found to be difficult.[8] To date only a few organo-soluble gold nanorod materials have been reported, mainly achieved by electrostatic binding, polymer adsorption, or forming a thin organo-silane shell on the CTAB-covered gold nanorods.[9] On the other hand, complete functionalization of gold nanorods with thiol monolayers, if realized, will allow thiol surfactants not only to act as a stabilizer/interfacial compatibilizer for the gold nanorods in organic solvents/composites, but also to tune properties by regulating the surface plasmon characteristics of gold nanorods with certain covalently-bound functional organic thiol surfactants containing chromophore center(s), chiral center(s), electron accepting/donating or photoresponsive moieties, for example.

Here, we report the synthesis of organo-soluble photoresponsive azo thiol monolayer-protected gold nanorods by treating the as-synthesized water-soluble gold nanorods with the photoresponsive azo thiol surfactant **1** (Fig. 1). As expected, the resulting gold nanorods encapsulated by thiols on their entire surface with strong covalent Au–S linkages are very stable in both organic solvents and in the solid state without aggregation or decomposition. To the best of our knowledge, these are the first organo-soluble photoresponsive azo thiol monolayer-protected gold nanorods to be reported.

The azo thiol surfactant **1** was synthesized starting from 4-aminophenol **2** which was reacted with sodium nitrite in aqueous HCl to give diazonium salt followed by coupling with phenol to obtain azo intermediate **3**. The azo intermediate was treated with 1-bromohexadecane in the presence of K_2CO_3 to give **4**. The phenol intermediate **4** was reacted with 11-thio-acetoxy-1-bromoundecane to yield the intermediate **5** which was de-protected in the presence of tetrabutylammonium cyanide (TBACN) to afford azo thiol **1** (Fig. 2). The structure of azo thiol surfactant **1** was well identified by ^1H NMR, ^{13}C NMR, FT-IR, and elemental analysis.[10]

A solution of freshly prepared CTAB-covered gold nanorods in water, prepared by the seed-mediated growth method in the presence of CTAB,[5] was added to a solution of azo thiol surfactant **1** in dry THF under stirring and nitrogen protection. The mixture was stirred for 4 days at room temperature, and then dried by solvent evaporation under reduced pressure. Thereafter, CH_2Cl_2 was added to the above mixture followed by centrifuging to remove free CTAB and thiol. The resulting gold nanorods were treated with excess azo thiol surfactant **1** in CH_2Cl_2, stirred overnight, and

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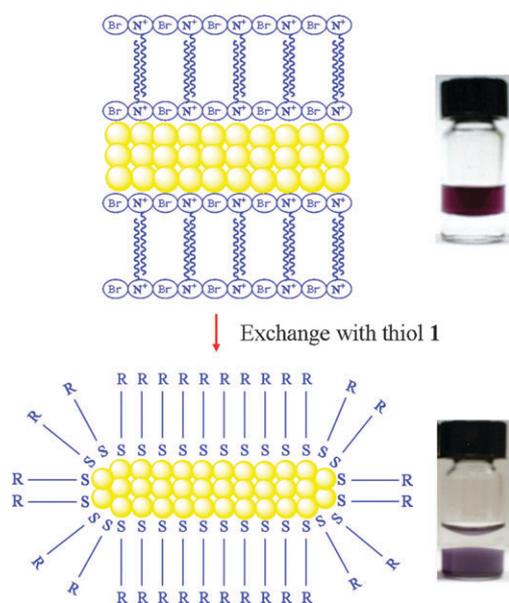
Fig. 1 Schematic synthesis of organo-soluble azo thiol monolayer-protected gold nanorods by treating the water-soluble gold nanorods covered with a CTAB layer on their longitudinal surface with azo thiol surfactant **1** (R–SH). Note: thiols adsorb on the entire surface of the gold nanorod. Photographs showing the solubility of corresponding gold nanorods in the two phases (top layer: water; bottom layer: CH$_2$Cl$_2$).
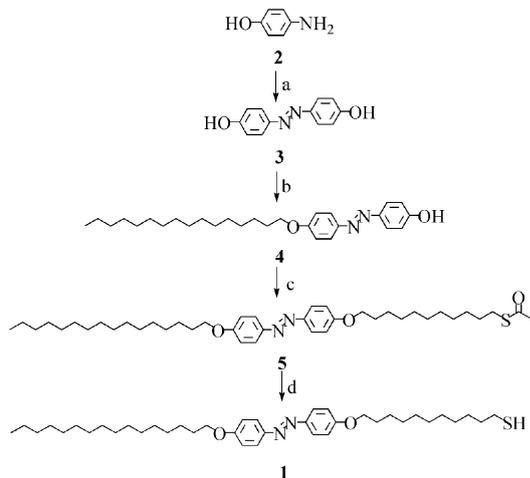

Fig. 2 Synthesis of azo thiol surfactant **1**. a: (1) NaNO$_2$, aq. HCl, (2) phenol, NaOH; b: n-C$_{16}$H$_{33}$Br, K$_2$CO$_3$, KI, acetone; c: 11-thioacetoxy-1-bromoundecane, K$_2$CO$_3$, KI, acetone; d: tetrabutyl-ammonium cyanide, CH$_3$OH, CHCl$_3$.

centrifuged. Since the dynamic CTAB layer is not stable under the above conditions, this procedure was repeated three times to ensure that the gold nanorods were encapsulated by the thiol molecules completely. The solubility of the resultant gold nanorods in organic solvent was improved with continued CTAB–thiol exchange until complete thiol monolayer-protected gold nanorods were achieved. Finally, the as-prepared azo hybrid gold nanorods were centrifuged and washed with CH$_2$Cl$_2$ several times until the disappearance of the IR absorption of thiol surfactant **1** from the top layer.
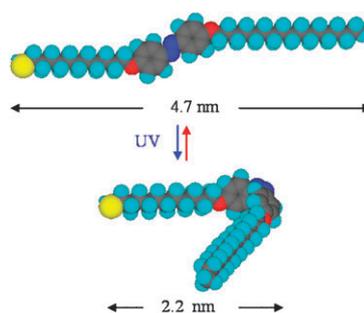

Fig. 3 *trans–cis* Isomerization of azo thiol surfactant **1** (3D-ChemDraw space filling model).

Interestingly, upon UV irradiation of the modified gold nanorods, some azo thiol surfactants were released into the solution whereas no precipitation was observed. After the sample was irradiated and centrifuged a few times, there was no IR absorption of thiol surfactant **1** in the top layer while the azo hybrid nanorods clearly exhibited the IR peaks characteristic of the ether linkage at 1247 cm^{-1} and the benzene rings at 1602–1881 cm^{-1} in the surface-bound thiol surfactant **1**. It is worth noting here that the resulting photoisomerized gold nanorods are still soluble after UV irradiation, albeit with a reduced solubility as some of the thiol azo surfactants turned into the shorter *cis*-configuration (Fig. 3). Thus, UV irradiation offers a simple and efficient method for purification of the photoresponsive azo hybrid gold nanorods from excess thiol surfactants and even their unirradiated counterparts.

Our experiment further shows that the azo thiol monolayer-protected gold nanorods were individually isolated and no aggregation was observed (Fig. 4 left). They are very stable in both organic media and the solid state while the CTAB-covered gold nanorods easily precipitated and aggregated in CH$_2$Cl$_2$ (Fig. 4 right). Raman spectra of the raw CTAB-covered gold nanorods and the azo thiol monolayer-protected gold nanorods are shown in Fig. 5. The disappearance of the characteristic Au–Br band at 170 cm^{-1} present in the raw CTAB-covered gold nanorods in the Raman spectrum of the azo hybrid gold nanorods provides clear evidence that there is no CTAB in the organo-soluble thiol monolayer-protected gold nanorods, whereas additional Raman peaks characteristic of the azo hybrid gold nanorods are seen. No IR absorption in the top layer of the azo hybrid gold nanorods after centrifugation also provides clear evidence that there is no free thiol surfactant in the organo-soluble monolayer-protected gold nanorods. Furthermore, the azo thiol
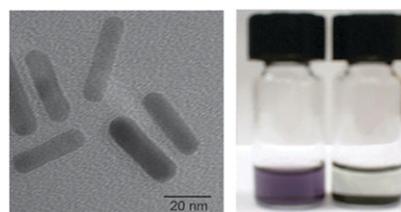

Fig. 4 Left: TEM image of organo-soluble azo thiol monolayer-protected gold nanorods. Right: photograph of the azo thiol mono-layer-protected gold nanorods (left bottle) and the CTAB-covered gold nanorods (right bottle) in CH$_2$Cl$_2$.
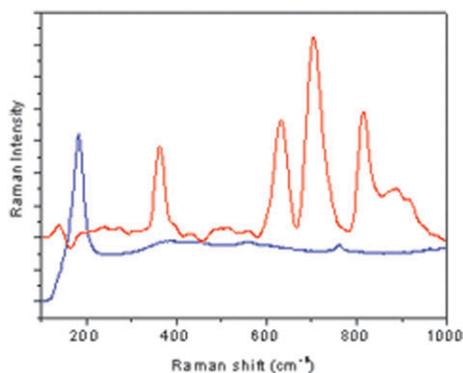
Fig. 5 Raman spectra of the CTAB-covered gold nanorods (blue) and organo-soluble azo thiol monolayer-protected gold nanorods (red).
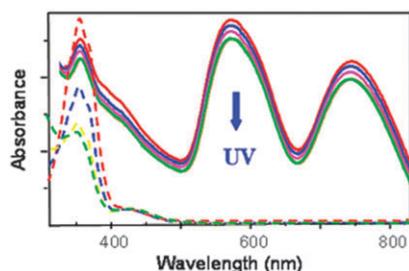

Fig. 6 UV-Vis-NIR spectra of photoswitchable thiol monolayer-protected gold nanorods under UV irradiation at 365 nm (solid line) for 0 min (red), 10 min (blue), 20 min (pink) and 40 min (green), and free thiol azo surfactant **1** under UV irradiation at 365 nm (dash line) for 0 min (red), 2 min (blue), 5 min (yellow) and 6 min (green).

monolayer-protected gold nanorods exhibit the expected reversible photoresponsive behavior in organic solvent. Dark incubation of a solution of the azo hybrid gold nanorods in $CHCl_3$ maximized the two distinct plasmonic absorptions at approximately 546 and 733 nm, together with the absorption at 356 nm originating from the surface-bound azo thiol surfactants in the *trans*-isomer (solid red line in Fig. 6). Irradiation of the solution with 365 nm light resulted in the occurrence of photoisomerization, as evidenced by a decrease in their absorbance accompanied with a small blue shift of 6 nm in the longitudinal band (solid line in Fig. 6) while the free azo thiol surfactant **1** in solution did not have any response above 500 nm upon UV irradiation (dash line in Fig. 6). This indicates that the covalently bound organic surfactants can directly affect the surface plasmon characteristics of gold nanorods. The tendency to revert to gold nanorods with the *trans*-azobenzene configuration was observed after the removal of UV light, as evidenced by the recovery of the original unirradiated absorption spectrum.

In summary, organo-soluble photoresponsive azo thiol monolayer-protected gold nanorods were, for the first time, synthesized and characterized. The resulting gold nanorods encapsulated by thiols on their entire surface with strong covalent Au–S linkages is very stable in both organic solvents and in the solid state without aggregation or decomposition. UV irradiation was also found to be a simple and highly efficient technique for purification of the photoresponsive gold nanorods due to the solubility change accompanied with the

photoisomerization. The synthetic approach demonstrated above is versatile and effective for preparing other organo-soluble thiol monolayer-protected gold nanorods. This study provides new insight for stabilizing gold nanorods in organic solvents/composites and tuning their properties of practical significance by using functionalized thiol surfactants.

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10 Data for the azo thiol surfactant **1**: yellow solid; ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 3H), 1.30 (m, 42H), 1.78 (m, 4H), 2.51(t, 2H, J = 7.1 Hz), 4.03 (t, 4H, J = 6.4 Hz), 6.97 (m, 4H), 7.85 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 14.12, 22.70, 24.65, 26.03, 28.38, 29.07, 29.23, 29.37, 29.49, 29.6; IR (KBr) ν_{max} (cm^{-1}): 2917.21, 2848.60, 1604.11, 1463.74, 1253.00, 1151.63, 1107.21, 1019.79, 843.89, 823.02, 750.00, 603.49, 555.52; Anal. calcd for $C_{39}H_{64}N_2O_2S$: C, 74.95; H, 10.32; N, 4.48; S, 5.13. Found: C, 74.74; H, 10.58; N, 4.42; S, 5.09.