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# Light-induced modification of silver nanoparticles with functional polymers†

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**A mild, efficient and ambient temperature photochemical approach for the synthesis of silver nanoparticle core–shell structures employing a zwitterionic polymer as well as polyethylene glycol is presented.**

Polymer nanocomposites have attracted significant interest in recent years due to their unique properties and a broad range of potential applications.[1] Silver polymeric nanoparticles (Ag NPs) are particularly sought after due to the combination of their optical, catalytic and antimicrobial properties.[2] However, bare Ag NPs are so far only of limited use in the biomedical and biosensing field, since contact with the biological media results in fouling causing either loss of colloidal stability or opsonization. In order to prevent such processes, the Ag NPs must be coated with polymers able to prevent the fouling while concomitantly endowing specific functions.[3] By fusing the properties of Ag NPs with a corona of antifouling polymers, a plethora of new applications are accessible.[4] In this context, it is necessary to prepare stable and biocompatible NPs with well-defined surface coatings. Several methods have been employed to prepare polymer-functionalized metallic NPs such as embedment in a polymer matrix[5] or surface coating to form core–shell structures.[6] The latter is particularly interesting as it results in smaller, well-defined nanostructures with significant biomedical potential. Such core–shell structures can be prepared either *via* a one-pot strategy using monomers[7] or a polymer[8] as a reducing/stabilizing agent. Alternatively, a grafting-from approach may be employed, which usually results in heterogeneous particles and ill-defined polymer brushes.[3,9] α-Mercapto-functional polymers have been extensively used for the functionalization of Au NPs.[10,11] However, such composites exhibit poor stability and are prone to ligand exchange with thiol-containing molecules present in reaction buffers or cell media.[12]

With the rapid advances in nanoparticle functionalization, various thermally driven methods are often employed for attaching molecular species to the nanoparticle surfaces.[3] Core–shell polymer NPs have mainly been prepared using gold (Au) NPs as core nanocomposites *via* thermally activated chemical strategies. For instance, Peng and coworkers demonstrated the coupling of alkyne-terminated poly(*N*-isopropylacrylamide) to azide-functionalized Au NPs through a copper-catalyzed Huisgen cycloaddition to form thermoresponsive core–shell Au NPs with high grafting densities.[13] In another approach, Beyer *et al.* employed Diels–Alder chemistry to afford a reversible surface functionalization of Au NPs with poly(styrene),[14] and Aldeek *et al.* prepared highly fluorescent PEG and zwitterion-functionalized Au nanoclusters.[15] There are only limited examples of Ag NP–polymer composites usually containing a poly(ethylene glycol) (PEG) shell.[16] In addition, the current thermally triggered chemical strategies involve the use of additional reagents or catalysts, sensitive functional groups, extensive reaction times (up to several days), the use of elevated temperatures or a combination of all of these, which can impair the NP stability and induce their aggregation.

To overcome the disadvantages associated with thermally controlled reactions, we herein apply a novel light-triggered strategy first described by Barner-Kowollik and coworkers[17] to prepare Ag NP–polymer core–shell NPs using functional polymers. Here, a photoactive group based on *ortho*-quinodimethane (caged diene) is allowed to react with dienophiles such as maleimide groups under UV irradiation (Fig. 1). Light has already been employed for the preparation of tailored nanomaterials,[18,19] however, herein the first example of employing light-triggered

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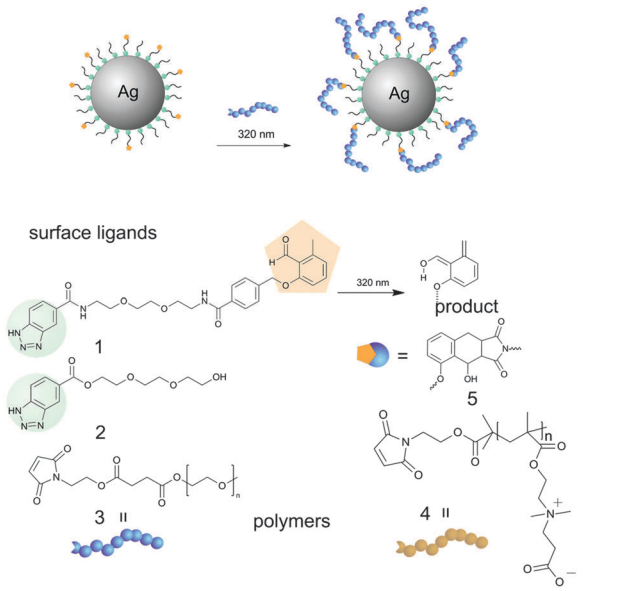


Fig. 1 Light-induced functionalization of Ag NPs with polymers. The novel photoactivable linker **1** and the inert linker **2** are attached to the Ag NP surface. **1** enables the light-induced cycloaddition with either PEG-Mal **3** or pCBMA **4** upon UV-irradiation resulting in cycloadduct **5**.

cycloaddition for the mild, efficient, fast and catalyst-free Ag NP modification with antifouling and biocompatible polymers (*i.e.* poly(carboxybetaine methacrylate) (pCBMA) and poly(ethylene glycol) (PEG)) enabling temporal reaction control is presented. PEG is one of the most widely used water soluble, biocompatible polymers, which can enhance the stability of NPs in aqueous solutions or cell media.[20] Zwitterionic pCBMA, on the other hand, outperforms PEG in terms of resistance to non-specific protein adsorption from blood serum and plasma[21,22] as well as to marine fouling and bacteria. In addition, the *in situ* generation of Ag NPs inside betaine brushes has already been exploited as an effective antibacterial interface.[5,23]

Initially, a novel bifunctional linker **1** containing benzotriazole (BT) as the Ag NP anchoring group and a caged diene (photoenol) moiety for light-induced cycloaddition were prepared (Fig. 1). Benzotriazoles have previously been shown to bind strongly to Ag surfaces and have been employed for the modification of Ag NPs.[16,24] To assess the reactivity of the linker, a model reaction between BT–photoenol **1** and maleimide-functionalized PEG **3** ($M_n \sim 1300$ g mol$^{-1}$) was carried out (Fig. 2a). Low molecular weight maleimide-PEG was chosen due to its excellent dienophile reactivity and the ease of precise ESI-MS characterization of the adduct. A reaction mixture of **1** and **3** was irradiated using a 320 nm light source for 15 min in DMSO. Subsequent analysis by ESI-MS evidenced that a new set of peaks is formed, which was assigned to the product of the light-induced Diels–Alder reaction indicating the complete conversion to photoadduct **6** (Fig. 2a). Subsequently, the successful model reaction was adapted to modify the surface of Ag NPs. First, we explored the one-pot synthesis in which $AgNO_3$ is reduced using sodium borhydride or ascorbic acid in the presence of linker **1** to prepare photoenol-decorated Ag NPs. However, the use of such reducing agents leads to the reduction of the aldehyde group to the hydroxyl group in **1**, which results in the loss of reactivity (data not shown). To circumvent this drawback, a milder ligand exchange methodology was employed in which the linker is added to the citrate-capped Ag NPs (10 000 eq. per NP). To minimize the surface crowding effect, an inert linker **2**, which does not contain the photoenol moiety, was used in a 1 : 10 ratio (linker **1** to linker **2**). The combination of reactive and inert linkers improved the colloidal stability of the nanoparticles and enabled control over the density (and availability) of reactive groups as previously reported.[25] After incubation in DMSO over night at ambient temperature, unbound ligands were removed by centrifugation. The concentration of

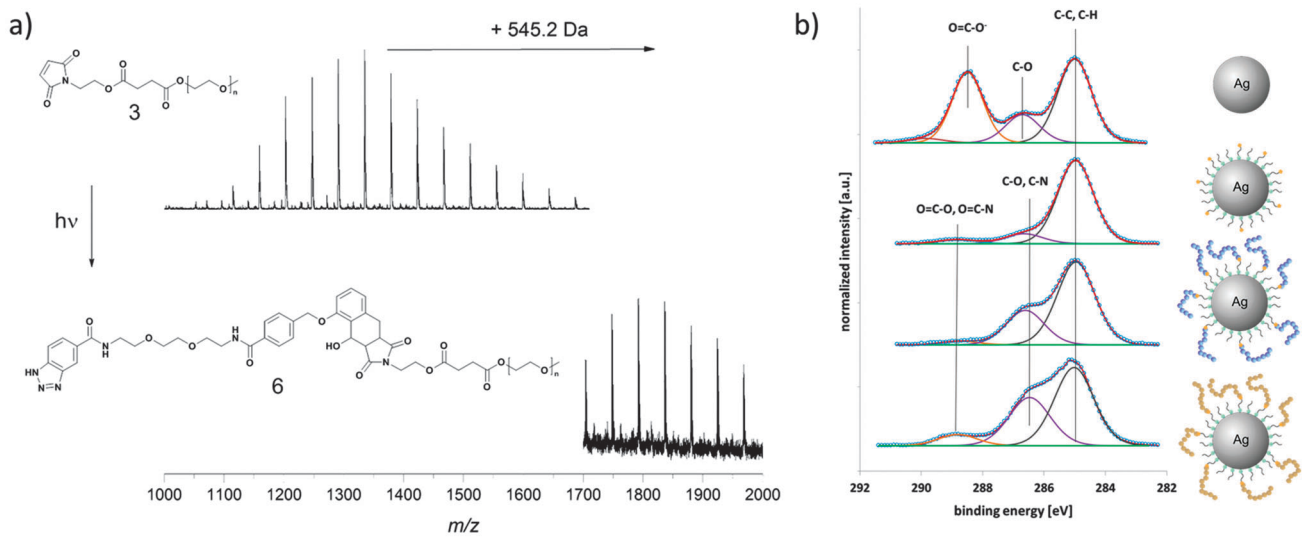


Fig. 2 (a) ESI-MS spectra of PEG maleimide **3** and photoadduct **6** after the light-induced cycloaddition with the bifunctional linker **1**, (b) C 1s XP spectra of untreated citrate-capped Ag NPs (top), modified Ag NPs-**1** (2nd row), PEG-functionalized Ag NPs-**3** (3rd row) and pCBMA-functionalized Ag NPs-**4** (bottom) evidenced successful ligand exchange and photoreactions.

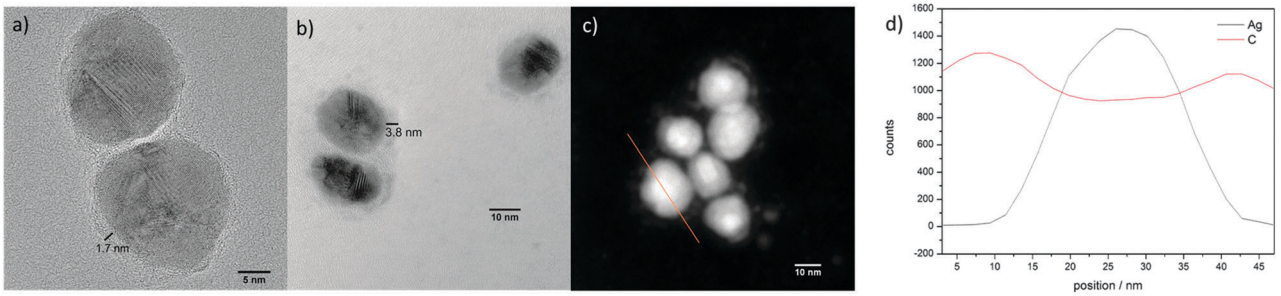


Fig. 3 HRTEM images of (a) PEG-coated Ag-NPs-**3** and (b) pCBMA-coated Ag NPs-**4**. (c) An EDXS line scan (orange) of pCBMA-coated Ag NPs. (d) C and Ag peak intensities along the EDXS line scan showing the Ag-pCBMA core–shell structure. The counts of C and Ag are plotted against the position. The core is close to 20 nm and the shell approx. 4 nm in size.

modified Ag NPs was determined by UV-Vis spectroscopy. The efficient ligand exchange was evidenced *via* a change in the zeta potential (negative charge of citrate Ag NPs decreases, ESI,† Table S2) and X-ray photoelectron spectroscopy (XPS) measurements (Fig. 2b). The C 1s XP spectrum of the modified Ag NPs shows a strong decrease of the peak intensity assigned to O═C–O bonds at 288.5 eV, stemming from the replaced citrate groups. Once the ligand exchange was confirmed, maleimide-PEG **3** was added to the dispersion of modified Ag NPs, purged with nitrogen and irradiated for 15 min at 320 nm (for experimental details please refer to the ESI†). After performing washing steps, UV-Vis spectroscopy was employed to evidence that the NPs remain stable and no aggregation occurs as indicated by the unchanged characteristic plasmonic resonance of Ag NPs at 420 nm (ESI,† Fig. S16). XPS analysis of Ag NPs-**3** shows a strong increase of the peak intensity at 286.6 eV in the C 1s spectrum, which is assigned to C–O bonds, stemming from the ethylene glycol unit. The formation of a corona of PEG was evidenced by high-resolution transmission electron microscopy (HRTEM). As depicted in Fig. 3a, a 1–2 nm PEG shell can be observed around the 20 nm Ag core. To further prove the formation of the corona and its composition, energy-dispersive X-ray spectroscopy (EDXS) was carried out (ESI,† Fig. S22). An EDXS line scan along the core–shell structure recorded a high C content in the shell resulting from the attached PEG layer and a high Ag content at the core resulting from Ag NPs.

Once the successful light-induced modification of Ag NPs with PEG was demonstrated, the more challenging zwitterionic, non-fouling pCBMA **4** ($M_n \sim 21\,700$ g mol$^{-1}$) was also grafted onto the Ag NPs. A longer irradiation time was used for the coupling of pCBMA (1 h *vs.* 15 min for PEG **3**) to compensate for the steric hindrance effects of the longer, highly swollen polymer chain. The successful photografting was unambiguously confirmed by XPS and EDXS analyses and HRTEM measurements. Namely, the C 1s XP spectrum of Ag NPs **4** shows a strong increase of the peak intensity at 288.5 eV assigned to the O═C–O bonds, stemming from the carboxylic acid and ester groups of pCBMA. In addition, the N 1s XPS spectrum shows a new peak assigned to the high-energy quaternary ammonium groups (ESI,† Fig. S25). HRTEM measurements also demonstrated the formation of the core–shell structure consisting of a 20 nm Ag core and a 4 nm pCBMA shell (Fig. 3b), which was additionally ascertained by an EDXS line scan indicating the corresponding Ag and C contents (Fig. 3c and d). It should be noted that control samples – into which both polymers were added without irradiation – did not show any increase in the C content *via* EDX line scans (ESI,† Fig. S26 and S27).

In conclusion, we introduce a novel light-induced route for the covalent functionalization of photoenol-modified Ag NPs with poly(ethylene glycol) and poly(carboxybetaine methacrylate). The novel bifunctional linker containing benzotriazole as the Ag anchoring group and a caged diene (photoenol) moiety enabled photo-grafting of ω-maleimide polymers to Ag NPs as demonstrated by XPS, HRTEM and EDXS. Such a light-induced approach for preparation of the polymer Ag NPs expands the synthetic toolbox for the tailoring of nanomaterials and can be translated to the other molecular species. In addition to the potential that Ag NPs could have in biosensing/biomedicine, photoenol-modified Ag NPs could be used for light-induced pattering onto a range of surfaces – a concept that is the subject of our ongoing studies.

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