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Surface Functionalization

Molecular Camouflage: Making Use of Protecting Groups To Control the Self-Assembly of Inorganic Janus Particles onto Metal–Chalcogenide Nanotubes by Pearson Hardness**

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One of the goals in current nanoscience is to develop strategies for assembling nanoscale components into large-scale, organized structures with desired properties and functionalities.[1] However, unlike in molecular chemistry, where bond specificity and directionality are inherent to different types of atoms, nanoparticles mostly interact through symmetric interaction potentials (e.g. electrostatic,[2] van der Waals,[3] or dipole–dipole interactions)[4] and typically assemble into bulk, three-dimensional aggregates[4,5] or crystals.[2,4,5] The available methods of directional bonding and assembly at the nanoscale are, to date, limited to either the use of directional organic templates (e.g. DNA,[6] proteins,[7] small molecules[8]) or the formation of topological defects at the "poles" of metal nanoparticles[8b] or nanorods,[9] which then assemble into short, linear oligomers. Herein, we show that the toolbox of "nanosynthesis" can be greatly enhanced by extending the all-important chemical concepts of protecting groups and steric hindrance to the nanoscale.

Surface functionalization is a stringent requirement for controlling the assembly of nanoparticles to aggregates with hierarchical structure. Most nanoparticles (metals, metal sulfides, or oxides) can be surface-treated in a straightforward fashion by using established concepts of coordination chemistry. In general surface ligands contain an anchor group (phosphines,[10] thiols,[11] carboxylates,[12] phosphates,[13] or catecholates[14]), which strongly attaches to the surface of the respective nanomaterial, and a (long) hydrocarbon or polyether chain, which confers solubility in apolar or polar solvents.[15] A terminal group (e.g. an amino group) provides connectivity to additional functional ligands.[14d] As a result, a dense ligand shell is formed around each nanoparticle, thereby preventing particle aggregation as well as providing chemical protection against oxidation and long-term solvent stability.

Inorganic nanotubes[16] (NT-MQ_2) and inorganic fullerenes (IF-MQ_2)[17] of layered metal chalcogenides are the inorganic congeners of carbon fullerenes and nanotubes that exhibit analogous mechanical[18] and electronic properties.[19] Their excellent lubrication properties[20] are related to their crystal structures. In contrast to other inorganic nanoparticles, layered chalcogenide nanotubes (NT-MQ_2 with M = tungsten, molybdenum, niobium and Q = sulfur, selenium) and inorganic fullerenes (IF-MQ_2) have long resisted functionalization by using methods of standard surface chemistry. The inert chalcogenide layers sandwich the metal atoms and provide efficient steric shielding from nucleophilic attack by organic ligands and thus make chalcogenide nanoparticles inert and notoriously difficult to functionalize. While the covalent surface modification of their carbon congeners (fullerenes and nanotubes) is achieved through acid-induced oxidation of the carbon-nanotube surface defects,[21] the covalent surface functionalization of layered chalcogenides needs anion coordination: metals with a high sulfur affinity, the coordination sphere of which is partially blocked by chelating groups, must serve as "glue" for anchoring organic ligands to the sulfur surface.

This approach has been demonstrated by employing chalcophilic transition metals in combination with multidentate surface ligands: The 3d metals "wet" the sulfur surface of the chalcogenide nanoparticles, while the multidentate surface ligands partially block one hemisphere of the metal coordination environment. This steric shielding prevents an aggregation of the chalcogenide nanoparticles through interparticle cross-linking.[22]

An alternative strategy is to attach nanoparticles directly to the chalcogenide nanoparticles.[23] In this case the sulfur atoms of the chalcogenide particles outcompete the protecting ligand on the nanoparticle surface. The affinity is based on the acid/base properties or Pearson hardness of the incoming nanoparticles,[24] and the right affinity allows their attachment without the aid of linkers or ligands. It has also been observed that the density of binding of different nanoparticles to the chalcogenide particles is related to the degree of Pearson hardness of their respective metal cations.[24e]

An interesting group of asymmetric nanoparticles composed of two distinct building blocks are Janus particles.[25]

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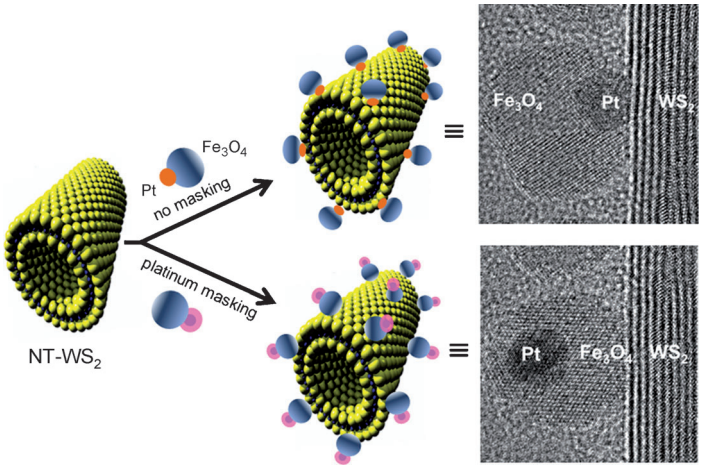
Their inorganic counterparts[26] consist of domains with different Pearson hardnesses, which may allow comparison of reaction behavior based on the Pearson HSAB (hard–soft acid–base) principle with a single particle. Moreover, the perception that anisotropic shape and interactions through chemical "patchiness" are powerful tools for engineering the assembly of specific targeted structures has fuelled the discovery of new chemical, physical, and biosynthetic methods for the synthesis of anisotropic nanoparticles and colloidal building blocks.

Herein we report a synthetic strategy that allows the customized binding of inorganic Pt@Fe_3O_4 Janus particles onto WS_2 nanotubes (NT-WS_2) either through their Pt or Fe_3O_4 domains. According to Pearson's HSAB principle, a hard Lewis acid has the tendency to bind to a hard Lewis base and vice versa.[27] Thus, in the case of the metal chalcogenides, the soft sulfur surface layer will tend to bind to nanoparticles that contain soft acid cations. The customized binding was achieved by making use of the Pearson hardness of the Janus particles: the soft Pt block (3.5 eV)[24e] has a higher sulfur affinity than the magnetite face. This binding preference could be reversed by masking the Pt face with an organic ligand (Scheme 1). In the absence of a masking ligand the binding of the Pt@Fe_3O_4 Janus particles proceeded preferentially through the Pt face.



Scheme 1. Customized binding of Pt@Fe_3O_4 Janus particles onto NT-WS_2 through their Pt and Fe_3O_4 faces and corresponding HRTEM images.

NT-WS_2 nanotubes were prepared by sulfidization of tungsten oxide nanorods with H_2S.[28] Pt@Fe_3O_4 Janus particles were synthesized by a modified one-step method.[29] Figure 1 shows representative TEM images of NT-WS_2 (Figure 1 a) and Pt@Fe_3O_4 particles (Figure 1 b). The high-resolution TEM (HRTEM) image in the inset of Figure 1 b reveals the distinct Pt and Fe_3O_4 nanodomains. The oleic acid capping agents make the Pt@Fe_3O_4 Janus particles soluble in most nonpolar solvents (hexane, toluene, etc.). X-ray diffraction (XRD) patterns of NT-WS_2 and Pt@Fe_3O_4 are provided in Figures S1 and S2 in the Supporting Information.

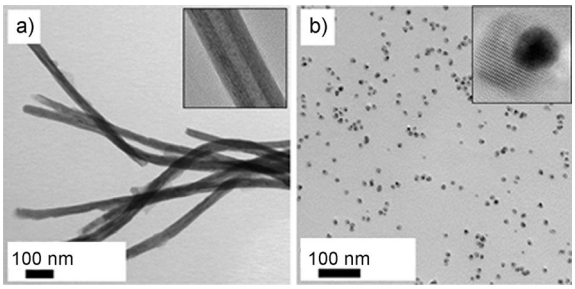


Figure 1. TEM images of a) NT-WS_2 and b) Pt@Fe_3O_4 Janus particles. The inset in (b) shows a HRTEM image of a single Pt@Fe_3O_4 particle; Pt dark and Fe_3O_4 light contrast.

Functionalized NT-WS_2 was produced by mixing the NT-WS_2 and Pt@Fe_3O_4 nanoparticles in chloroform under strong mechanical shaking. During this process, the Pt@Fe_3O_4 Janus particles assembled on the NT-WS_2 surface through ligand exchange. In this process, the oleic acid capping ligands on the surface of the Janus particles are substituted by the surface sulfur atoms of the chalcogenide nanotubes, and the Janus particles bind through their Pt face (Figure 2). The optimum concentration to make a monolayer of Janus particles on NT-WS_2 was found by varying the concentration (1, 0.1, or 0.025 mg mL^{-1}) of Janus nanoparticles while keeping the concentration of NT-WS_2 (1 mg mL^{-1}) constant. The samples were characterized using TEM (Figure S3 in the Supporting Information) without washing away the unbound nanoparticles. These TEM images reveal that the nanoparticles tend to adhere to NT-WS_2 rather than stay in $CHCl_3$. Upon decreasing the Pt@Fe_3O_4 Janus-particle concentration, careful examination of the TEM images shows that the amount of unbound Janus particles decreases to zero at a concentration of 0.025 mg mL^{-1} (Figure S3c in the Supporting Information), which may be considered to be the critical concentration for monolayer coverage. At higher concentrations, free nanoparticles exist in the $CHCl_3$ solution, while at lower concentrations all nanoparticles were bound to the surface of NT-WS_2. This critical concentration depends on the relative size of NT-WS_2 and of the nanoparticles.

Inorganic Janus particles in general have two chemically distinct surfaces, which can be exploited selectively for the formation of hierarchical assemblies. In the case of Pt@Fe_3O_4 particles the platinum domain may be considered synonymous with other soft coinage metals such as Au, Ag, or Cu,[30] the surfaces of which can be tailored with thiol ligands,[31] whereas the surface properties of the magnetite domain are comparable to those of other metal oxide nanoparticles such as MnO, TiO_2, or ZrO_2, which can be tailored with ligands containing suitable anchor groups (e.g. catechol).[32] Pt is one of the softest metals (Pearson hardness 3.5 eV);[24e] thus in the absence of any masking ligands the Pt domain will have a higher tendency to bind to the soft sulfur layer of the metal chalcogenide than will the magnetite domain, which contains either hard Fe^{3+} (Pearson hardness of Fe^{+3} 13.1) or intermediate Fe^{2+} (Pearson hardness of Fe^{+2} 7.2 eV).[24e]

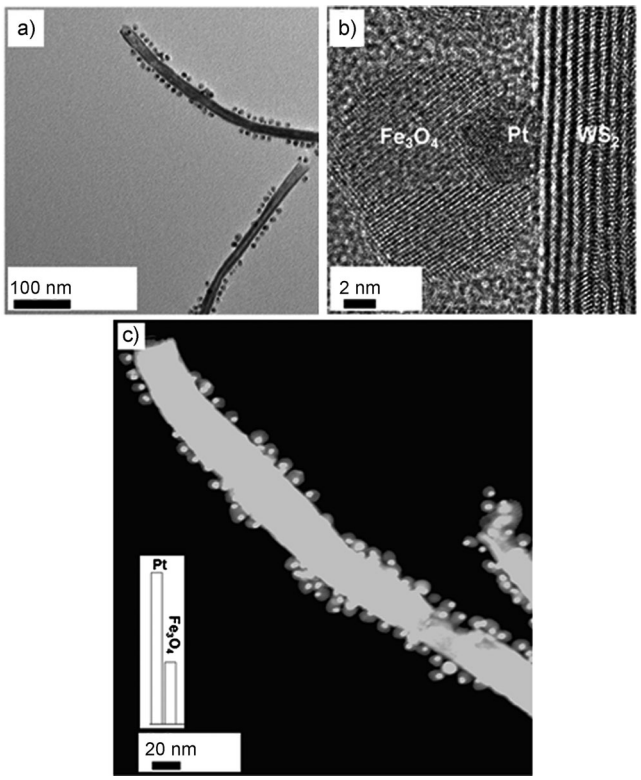
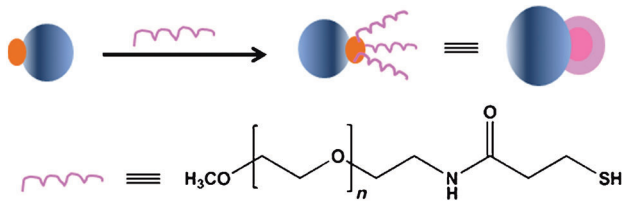


Figure 2. a) Overview TEM image of a WS_2 nanotube having a monolayer with nearly full coverage of Pt@Fe_3O_4 Janus particles. b) HRTEM image showing the binding of the Pt face of a single Pt@Fe_3O_4 Janus particle to the surface of NT-WS_2. c) STEM (scanning TEM) image showing the quantitative binding of the Pt Janus faces onto NT-WS_2. The histogram in the inset shows the binding ratio of Pt and Fe_3O_4 domains (65:35, average from 70 individual particles).



Scheme 2. Selective masking of the Pt domain of the Pt@Fe_3O_4 Janus particle by the SH-PEG-OCH_3 ligand.

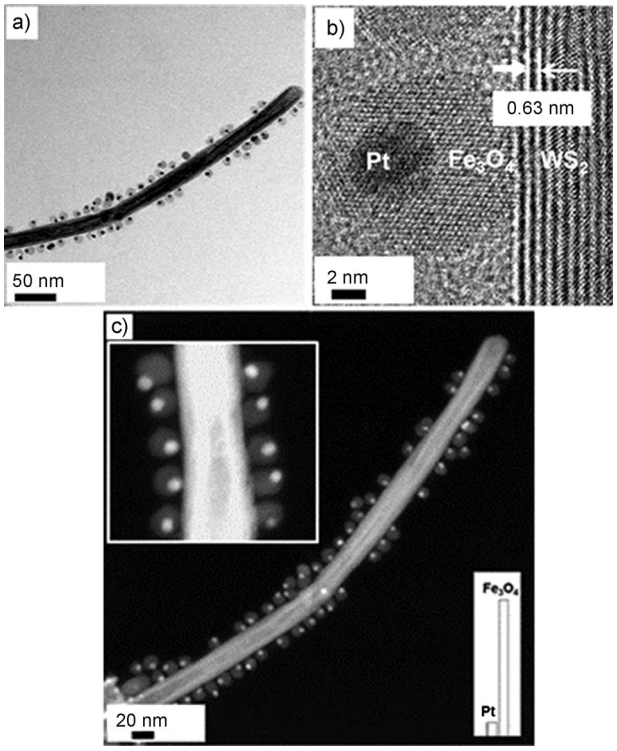


Figure 3. a) TEM image of Pt@Fe_3O_4 Janus particles, the Pt domain of which was masked with an organic ligand and immobilized on NT-WS_2. b) HRTEM image showing binding of the Fe_3O_4 magnetite face of the Janus particle to NT-WS_2. c) STEM image showing the preferred binding of the Fe_3O_4 faces to NT-WS_2. The histogram in the inset shows the binding ratio of Pt and Fe_3O_4 domains (Fe_3O_4/Pt 90:10; average from 80 individual particles).

Owing to the chemically distinctive Janus particle surfaces it is possible to selectively camouflage each Janus face with an organic ligand that facilitates the binding of the other domain to the chalcogenide surface. As discussed above, Pt is one of the softest metals (Pearson hardness 3.5 eV)[24e] and is more likely to bind to sulfur. We masked the Pt face (or similarly Au, Ag, Cu, etc.) with *O*-[2-(3-mercaptopropionylamino)ethyl]-*O*′-methylpolyethylene glycol 5000 (SH-PEG-OCH_3), a soft thiol anchor group (i.e. replacing the oleic acid originally present on the Pt face), which inverts the binding pattern of the Janus particle: now it binds almost exclusively through the Fe_3O_4 face.[33] The PEG moiety confers stability to the particle in polar solvents, and—together with the terminal methoxy group—camouflages the Pt domain and facilitates the binding of the Janus particle through its unmasked Fe_3O_4 domain (Scheme 2).

Figure 3a shows a representative TEM image of the Pt@Fe_3O_4/NT-WS_2 nanocomposite, and the HRTEM image in Figure 3b demonstrates the attachment of the Pt@Fe_3O_4 through their magnetite domains. The interlayer distance in NT-WS_2 is 0.63 nm, as reported for other WS_2 nanotubes. The STEM image in Figure 3c shows the preferential orientation of the magnetite domain towards the outer NT-WS_2 sulfur layer, with a magnified image given as an inset (top left); the second inset (bottom right) summarizes the orientation of different Janus domains with respect to the outer NT-WS_2 layers. Now more than 90% of the Janus particles stick to the NT-WS_2 sidewalls through their magnetite domains. This unprecedented result can be explained by the masking of the Pt domains which enforces binding through the Fe_3O_4 domains. The corresponding energy-dispersive X-ray spectrum (Figure S4 in the Supporting Information) confirms the composition of the nanocomposites (W, S, Pt, Fe, and O). The presence of carbon and copper can be attributed to the carbon-coated copper grids used for electron microscopy. Moreover, the magnetic domains of the Janus nanoparticles can be reversibly detached from the NT-WS_2 surfaces by adding competing ligands that contain catechol groups. In contrast, the binding of the Pt domain to NT-WS_2 surfaces is irreversible, as is the reported binding of Au domains. A study

revealing the binding of gold nanoparticles chemisorbed onto NT-WS_2 surfaces by Tenne and co-workers showed a strong aggregation of Au nanoparticles and NT-WS_2. We expect a similar trend for Pt and NT-WS_2 because of the similar Pearson hardness of Au and Pt (3.5 eV).[33]

In summary, we have demonstrated that the hierarchical assembly of Pt@Fe_3O_4 Janus particles on WS_2 nanotubes is dictated by the principles of Pearson's HSAB concept, that is, Pt is the preferred binding partner over Fe_3O_4. However, the preferential binding of Fe_3O_4 domains can be enhanced by protecting[34] the Pt face of the Janus particle with an organic ligand. The assembly of the Pt@Fe_3O_4 particles onto WS_2 nanotubes in $CHCl_3$ solution can be quantitatively controlled by varying the particle concentration below a critical value. Owing to the magnetism of the magnetite domain, Pt@Fe_3O_4/NT-WS_2 can be retrieved from solution with a permanent magnet (Figure S5 in the Supporting Information). The Pt@Fe_3O_4/NT-WS_2 aggregates reported herein may be viewed as molecular analogues of metal oxide gated layered chalcogenide transistors.[35] Traditional metal oxide semiconductor (MOS) structures are obtained by growing a layer of metal oxide on top of a semiconductor substrate and depositing a layer of metal (or silicon). Recently, Kis and co-workers[35] used a HfO_2 gate dielectric to demonstrate room-temperature single-layer MoS_2 mobility, similar to that of graphene nanoribbons, and to demonstrate transistors with room-temperature on/off current and ultralow standby power dissipation. Chalcogenide nanotubes or graphene layers "gated" by metal oxide particles (such as Fe_3O_4, Fe_2O_3, or Al_2O_3) epitaxially connected to conductive metals (such as Pt or Au) might therefore exhibit interesting properties that require thin transparent semiconductors, such as optoelectronics and energy harvesting.

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