Low-dimensional chainlike assemblies of TiO$_2$ nanorod-stabilized Au nanoparticles†

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A simple and versatile light-based strategy to grow low-dimensional gold superstructures is presented; prolonged UV-irradiation of TiO$_2$ nanorod-stabilized Au nanoparticles in organic media promotes the progressive formation of distinctive chainlike metal assemblies, namely segments of a few gold particles, 2D or quasi-1D large structures composed of interlacing lines of hundreds of metal units over areas of about 500 nm^2

The unique size- and shape-dependent optoelectronic and magnetic properties of semiconductor and metal nanoparticles (NPs) make them extremely attractive as novel structural building blocks for constructing a new generation of innovative materials and solid-state devices.[1–4] In recent years, a growing interest has been devoted to the fabrication of complex Au-based superstructures for both fundamental studies and practical applications.[4–14] Unusual collective properties depending on the nature, dimensions and mutual ordering of the constituent objects can be expected to arise from the programmed organization of metal nanoparticles into one- (1D), two- (2D) or three- (3D) dimensional assemblies. As opposed to the most common low-energy, highly ordered 2D and 3D gold superstructures with isotropic properties,[13,14] a wider potential for functional design and device integration could be offered by a configurational motif with lower symmetry.[5–9] For example, linear metallic structures of nanometre width and possibly up to several micrometres in length could work as future quantum connectors or as sensing nanodevices relying on the dramatic enhancement of many optical effects.[10–12,15]

One of the experimentally simplest and inexpensive approaches for realizing superstructures is self-assembly, which is generally induced by the controlled solvent evaporation from a solution of strictly monodisperse ligand-capped NPs or by particle precipitation upon nonsolvent addition.[1–4,13,14] However, whereas high-symmetry 2D and 3D gold superstructures can be obtained straightforwardly,[13,14] the preparation of 1D or 2D linear assemblies based on NP chains remains prohibited by this method, unless solid or molecular templates possessing extreme specificity to the NPs are employed.[5–9] Exceptions are represented by unidirectional particle alignment promoted by lateral capillary forces in colloidal NPs with anisotropic shapes,[4] or by enhancement of dipolar inter-particle attractions upon controlled removal of the surface organic capping.[16,17]

In this contribution, an original approach to organize Au NPs in low-dimensional assemblies composed of interlacing particle chains is demonstrated. The key strategy stands within the use of TiO$_2$ nanorods (3–4 nm in width, 25–30 nm in length) as "inorganic" stabilizers in place of specific ligands for the metal.[18] Owing to their high solubility in relatively nonpolar media, the TiO$_2$ nanorods can simultaneously initiate the UV-induced photocatalytic reduction of a gold precursor (HAuCl$_4$) and act as colloidal supports for the resulting metallic NPs, thereby providing optically clear TiO$_2$–Au organic solutions.† A characteristic irreversible transition from well-separated gold NPs into progressively more complex chainlike metal assemblies can be easily identified as a function of the irradiation time by TEM (Fig. 1). Moreover, distinguishable absorption changes in the Au surface plasmon (SP) band authenticate the process (Fig. 2). In the early stages (Fig. 1a), individual Au NPs, with a nearly spherical shape (a minor amount of polygonal and flat NPs is also present)† and a broad size-distribution (10–40 nm), can be recognized on an underlying TiO$_2$ film (as confirmed by EDAX analysis). Accordingly, the samples exhibit a single SP band[2] (Fig. 2a), with λ_{max} at 535 nm. By prolonging illumination (Fig. 2b), the gold NPs self-organize into short chains of 3–15 units. The related SP
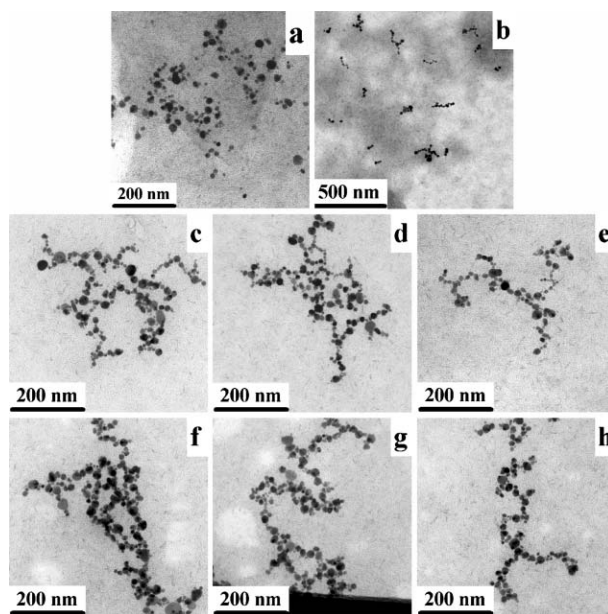

Fig. 1   TEM evolution of Au NP assembly upon UV-photocatalytic reduction of 10^{-3} M HAuCl$_4$ in the presence of 5 × 10^{-2} M TiO$_2$ nanorods in CHCl$_3$–EtOH: (a) 20 min; (b) 60 min; (c–e) 120 min; (f–h) 240 min.
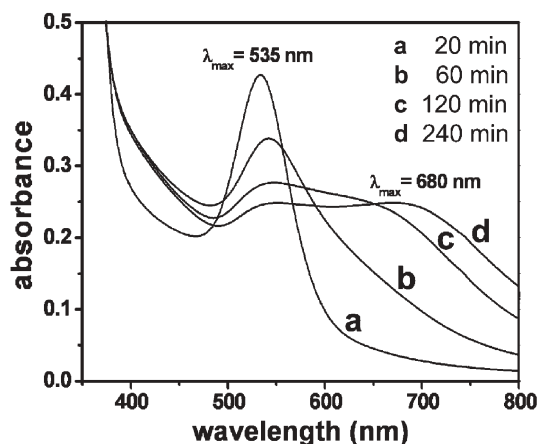
Fig. 2 Temporal evolution of the absorption spectrum of the TiO$_2$ nanorod–HAuCl$_4$ solution corresponding to the experiment in Fig. 1.

undergoes a small red-shift of λ_{max} to 543 nm, being accomplished by simultaneous band broadening and dampening, which results in the appearance of a pronounced shoulder at low energy. Analogous optical changes have been both observed experimentally for small NP assemblies[5–9,20] and predicted theoretically to arise from the SP coupling of neighboring particles.[18,19] In the subsequent illumination period, the samples deposited from the same growth solution display more spectacular changes. 2D particle agglomerates extending over grid areas of about 500 nm^2 are observed (Fig. 1c–e). Several types of NP assemblies coexist at this stage, which, however, possess a common underlying "pearl chain-like" structural motif. In all cases, the Au NPs are accommodated in the chains, irrespective of their size, without signs of coalescence or fusion. The patterns comprise disordered networks of relatively long chains resembling molecular electronic circuit boards (Fig. 1c) as well as more ramified structures being similar to high-generation or low-generation dendritic arrangements (Fig. 1d and e, respectively). Finally, in the latest irradiation stage, superstructures with a higher degree of 1D orientation, as more compact frameworks (Fig. 1f), meander-like (Fig. 1g) or quasi-linear long snake-like (Fig. 1h) branches, are detected. Significantly, the large aggregate-containing samples exhibit further modified absorption features, recognizable by the presence of two broad convoluted SP bands, peaking at $\lambda_{max} = 540$ nm and at 640–680 nm, respectively (Fig. 2c and d). Notably, with increasing irradiation time, the high-energy SP remains virtually unaffected in position with its intensity appearing considerably decreased, whereas the low-energy SP red-shifts to $\lambda_{max} = 680$ nm (Fig. 2d). As for nanowires, the extinction spectra of colloidal Au assemblies composed of single clusters exhibit two absorption peaks, caused by excitation of the SP resonance along the transverse and the longitudinal axes of the superstructure.[19,20] Thus, the red-shift of the low-energy SP can be explained as arising from an extended longitudinal plasmon coupling that is established when the superstructure adopts a more defined unidirectional configuration upon light exposure.[16,17,19,20]

The process of Au NP self-organization should take place under solution-like conditions rather than arise from the process of solvent evaporation upon sample drying onto the TEM grid. This hypothesis was supported by two facts. Firstly, similar NP assemblies were detected by depositing onto substrates with different wettabilities.† Secondly, the progressive formation of various types of assemblies was accomplished by peculiar absorption changes that could not be accounted for solely by the slight modification in the mean NP size/shape and size-dispersion along the course of irradiation. Upon deposition on the TEM grid, the 3D aggregates free-standing in solution obviously collapsed to form nearly monolayer quasi-2D structures reflecting the spatial anisotropy of the parent 3D assembly.

Prolonged UV-light irradiation after completion of the metal precursor photoreduction step is essential in order to produce extensive assembly effects. The aggregation process does not, in fact, occur in the dark and can be stopped at any desired stage by halting irradiation. This evidence indicates a photoactivated assembly process, which may proceed through either surface charge photoneutralization[21] or weak SP excitation.[21,22] In this latter case, charge redistribution on the surface of the NPs may occur and generate dipolar interactions over longer distances than those covered by van der Waals forces in the dark, thus enhancing the sticking probability after Brownian encounters. In this regard, the absence of a repelling layer of surfactant molecules on the gold surface[18]† can be expected to facilitate collisions[16,17] terminating in irreversible agglomeration and to allow the configurational restructuring of the assemblies.

In conclusion, a light-directed strategy for assembling small gold particles into chains to form low-dimensional superstructures has been proposed. The simplicity, flexibility, reproducibility, and low cost are the most attractive characteristics of the synthetic method, which represents an unprecedented example among colloidal approaches. The results herein illustrate an appealing use of light for realizing ordered 2D to 1D metal nanostructures without the constraints of size/shape monodispersity and without the need for specific templates or any surface modification required by other assembling procedures. Finally, the combination of organic-free Au NPs with TiO$_2$ offers the opportunity to explore novel catalytic, sensing and electronic properties of semiconductor–metal nanocomposite systems.[23]

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