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Joo, Ji Bong
Dillon, Robert
Lee, Ilkeun
et al.

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Promotion of atomic hydrogen recombination as an alternative to electron trapping for the role of metals in the photocatalytic production of H$_2$

Ji Bong Joo, Robert Dillon, Ilkeun Lee, Yadong Yin, Christopher J. Bardeen, and Francisco Zaera[1]

Department of Chemistry, University of California, Riverside, CA 92521

The production of hydrogen from water with semiconductor photocatalysts can be promoted by adding small amounts of metals to their surfaces. The resulting enhancement in photocatalytic activity is commonly attributed to a fast transfer of the excited electrons generated by photon absorption from the semiconductor to the metal, a step that prevents deexcitation back to the ground electronic state. Here we provide experimental evidence that suggests an alternative pathway that does not involve electron transfer to the metal but requires it to act as a catalyst for the recombination of the hydrogen atoms made via the reduction of protons on the surface of the semiconductor instead.

photocatalysis | hydrogen production | gold–titania | time-resolved fluorescence | core-shell nanostructures

Photocatalysis is a promising technology to address problems in chemical synthesis (1), environmental remediation (2, 3), and energy utilization (4). The potential for harvesting solar energy and storing it as a chemical fuel using photocatalysts is particularly appealing. Specifically, H$_2$ may be produced via water splitting this way (5–7). In fact, many photocatalysts have been reported already capable of producing hydrogen out of water, even if none of those are yet commercially viable. Such photocatalysis rely on capturing photon energy via excitation of electrons from the valence band to the conduction band of appropriate semiconductors such as titania, which is often cited as a prototypical example (8–10), creating an excited electron–hole pair that is then used to promote redox reactions (11, 12). However, for the photocatalysts to be useful, the lifetime of the electron–hole pair needs to be long enough to be accessible for chemical conversions. The search for photocatalytic systems that fulfill this and other key requirements continues, and would be greatly facilitated by a clearer understanding of the underlying chemical process.

It is well known that the addition of metals such as platinum or gold to semiconductors enhances their activity as photocatalysts, in particular for water splitting to produce H$_2$ (13–15). This effect is currently explained by a mechanism where the excited electrons produced by absorption of light are transferred from the semiconductor to the metal before they have the opportunity to recombine with their corresponding holes and return to the ground electronic state (Fig. 1A) (16–18). In this scheme, the protons from water are reduced on the surface of the metal, in sites physically separated from those on the semiconductor, where oxygen production takes place. Here we present evidence that challenges this conventional explanation, and offer an alternative mechanism for the promotion of photocatalysis by metals. Specifically, using the Au/TiO$_2$ metal–semiconductor pair as a model system, we show that electron transfer to the metal may not play a significant role in photocatalysis. Instead, the data support a model where the excited electron promotes the reduction of protons on the surface of the semiconductor, not the metal, and where the reduced atomic hydrogen then

migrates to the metal and recombines to yield the final molecular hydrogen product (Fig. 1B).

Results and Discussion

The dynamics of photon absorption, electronic excitation, and electron migration was first assessed by using transient absorption and time-resolved fluorescence spectroscopies. Time-resolved fluorescence studies have proven to be particularly useful for the characterization of photocatalysts, because fluorescence is one of the main channels by which the electron–hole pair recombines and the photon excitation is lost. A recent study from our laboratory using well-defined Au@Void@TiO$_2$ yolk-shell nanostructures identified clear correlations among the lifetime of the fluorescence decay, the rate at which hydrogen is produced in photocatalysis, and the crystallinity of the titania shells: the more crystalline catalysts display both longer fluorescence lifetimes and higher hydrogen production rates (Fig. S1) (19). Surprisingly, however, similar fluorescence decay kinetics were seen here with Au@Void@TiO$_2$ versus Void@TiO$_2$ samples [Fig. S1A; synthetic details of the latter catalyst are provided elsewhere (20, 21)], indicating that the photophysics of the titania shells is not affected by the presence of the metal. This behavior proved to be quite general: it was also observed with catalysts made by dispersing either gold or platinum nanoparticles

Significance

The use of catalysis assisted by light is a promising route to convert solar energy into chemical fuels such as H$_2$. Photon absorption promotes electrons in semiconductor catalysts from the valence to the conduction band of those solids, and the excited electrons may be used to reduce protons in water to produce hydrogen gas. Unfortunately, those electrons tend to rapidly return to their ground state instead. The addition of metals has been shown to enhance photocatalytic activity, and that has been explained by their ability to trap the excited electrons and quench the electron–hole recombination process that neutralizes the photoexcitation. Here we challenge the validity of this model and provide an alternative explanation for the enhancement. A new thinking about this mechanism may result in new searches for appropriate cocatalysts.
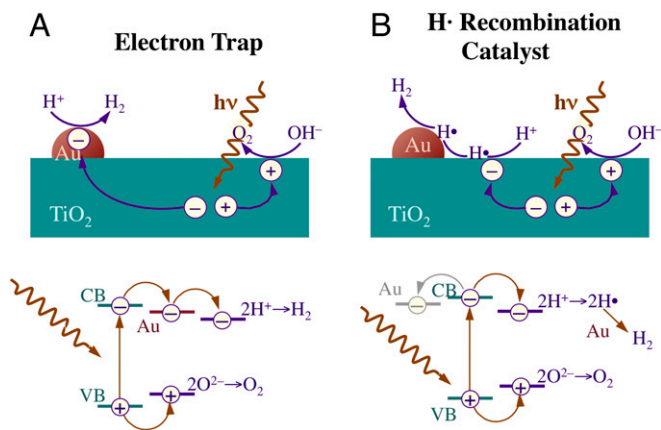
Fig. 1. Schematic representation of the mechanisms (*Upper*) and electronic transitions (*Lower*) proposed to explain the role of metals (Au) in the photocatalytic splitting of water with semiconductors (TiO₂). (*A*) In the conventional model, the metal acts as an electron trap that physically separates the excited electron used for proton reduction from the oxidation step that occurs on the surface of the semiconductor. (*B*) Our alternative model proposes that H⁺ reduction occurs at semiconductor sites but that the resulting hydrogen atoms need to migrate to the metal to recombine and produce the final H₂ product.

on the typical commercial titania P25 used in most photocatalysis studies, and was determined to also hold true in different environments and with various metal loadings, up to 10 wt% (Fig. 2 and Fig. S2). The observation that fluorescence from titania is not modified by the presence of a metal on its surface indicates that such metal does not help quench the radiative decay of the electronic excitation due to photon absorption in any appreciable way, even if it does aid in the photochemical production of H₂. Furthermore, no significant differences were seen in transient absorption experiments with 200-fs resolution, which probe the initial events after photon absorption (Fig. S2*C*), although such transients may be quite fast and perhaps no longer obvious after ~1 ns. Some early reports with Pt, the metal most often used in photocatalytic applications, claimed that the picosecond decay of the electron–hole in either transient absorption or photoluminescence measurements is faster when there is metal present (22, 23). However, the reported differences were small, and many of those experiments were carried out using high laser intensities, where carrier annihilation effects become important. Like with Au, no changes in fluorescence dynamics were seen in our experiments when Pt was added to our TiO₂-P25 samples (Fig. 2*E*). We believe that the lack of changes in TiO₂ carrier dynamics with the addition of metals seen here is general.

The main conclusion from our discussion so far is that the increase in photocatalytic activity seen via the addition of metals to photocatalysts is not due (at least primarily) to quenching of the electron–hole pair decay. However, the photophysics data alone may not be sufficient to fully prove this fact. The time-resolved fluorescence from the TiO₂ samples does follow the electron–hole pair formation and provides one of the main channels for deexcitation, in competition with the photocatalytic reactions, but photon excitation may also be dissipated via competing nonradiative channels, and those may be affected by the metal. The fact that in our measurements the fluorescence decay correlates well with photocatalytic activity (as crystallinity is varied) argues against this possibility, but does not fully rule it out (9). Another shortcoming of the photophysics experiments is that the rates of the photocatalytic processes are orders of magnitude slower than those of the dynamics of photon adsorption and subsequent electronic transitions, which means that it is possible that our measurements may not have the sensitivity

needed to detect the small number of electrons needed to produce the quantity of H₂ detected. However, it was determined that the fluorescence lifetime is sensitive to changes in the reaction environment (Fig. S3), in particular when methanol is added to the liquid phase (as required to promote H₂ production). The interpretation of those data are complex and may involve changes in local electronic structure, but they do provide evidence that the states involved in photocatalysis and photoluminescence are sensitive to the same environmental factors. On the whole, we believe that the time-resolved fluorescence data offer strong, if not irrefutable, support for the lack of participation of semiconductor-to-metal electron transfer steps in the photocatalytic production of H₂.

It should be said that it is well known that metals do accept charge from the semiconductor when photoexcited. In the case of gold, this can be detected by a shift in the frequency at which the plasmon resonance of the metal occurs (24), a fact that was also corroborated in our study (Fig. S4*A*). However, it should be noted that no differences in this shift were observed in our experiments with pure water versus with 10 vol% methanol solutions (Fig. S4*A*), even though the addition of the sacrificial methanol was needed to promote hydrogen production (no H₂ was seen to evolve from pure water). On the other hand, it has also been well established that most transition metals are efficient catalysts for the recombination of adsorbed hydrogen atoms (25), the alternative mechanism proposed in this report. That behavior was probed, and shown to be operative in the H₂-producing photocatalysts, by following the isotope scrambling of H₂ + D₂ mixtures in the gas phase, as illustrated in Fig. S4*B*. The challenge, therefore, is to decouple the two effects in order to determine which one is the most pertinent to photocatalysis. In
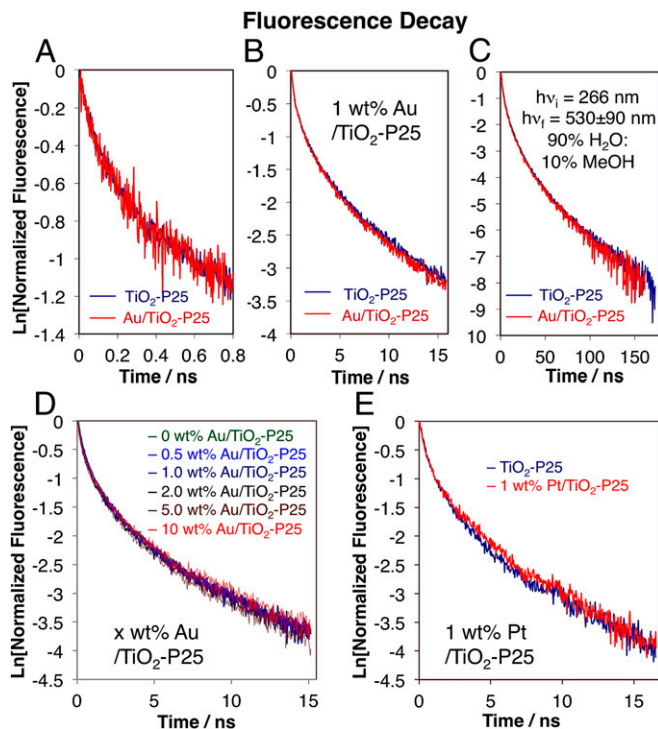
Fig. 2. Time-resolved fluorescence data, integrated over wavenumbers in the range of 530 ± 90 nm, from different TiO₂-P25–based photocatalysts: (*A–C*: three different time regimes) TiO₂-P25 (blue) and 1 wt% Au/TiO₂-P25 (red), (*D*) × wt% Au/TiO₂-P25, x = 0–10 (various colors), and (*E*) TiO₂-P25 (blue) and 1 wt% Pt/TiO₂-P25 (red). All samples display the same time-resolved fluorescence behavior, within experimental error, whether any metal is present on the surface of the titania or not.

the next paragraphs, we report the results from a number of experiments designed to do just that. They provide evidence disputing the traditional model of the role of the metal as a scavenger of the electrons used for hydrogen production, and support our alternative scheme where the metal acts as an atomic hydrogen recombination catalyst instead.

One way to check whether the metal is required as an electron trap in photocatalysis is to eliminate it altogether from the photocatalyst and to assess if any photocatalytic activity is maintained. The H_2 production reaction cannot be used to test this directly because the metal is also needed for H atom recombination, but a different reducible ion can be used instead (26–28). Based on the current model described in Fig. 1A, the prediction is that the addition of reducible ions to the water solution should not alter the photocatalytic rates in any significant way: The metal should still be needed to act as an electron trap, and the reduction step should still occur on the surface of the metal. In our alternative model, however, the reduction step takes place on the titania, and because no atom recombination is required with the reducible ions, there is no longer the need for the metal functionality (Fig. 3A). As a consequence, the production of molecular oxygen, the other half reaction in the photocatalysis of water splitting, should occur on pure titania, without the need of any metal promotion. This is in fact what happens: Measurable amounts of O_2 are generated with TiO_2-P25 when Ce^{4+}, Ag^+, or IO_3^- ions are added to the water phase (Fig. 3B). Similar behavior has been reported previously, but not properly explained (29). It was also found that the O_2-production

Fig. 3. (*A*) Schematic representation of the mechanism by which the addition of reducible ions to water promotes photocatalysis with pure titania according to our model. (*B*) Initial rates of O_2 photoproduction from Ce^{4+}, Ag^+, and IO_3^- solutions using pure TiO_2-P25 as the photocatalyst. The value obtained with 1 wt% Pt/TiO_2-P25 for the iodate solution is also provided for reference. Error bars indicate the range of values expected based on the estimation of experimental errors. (*C*) Rates for H_2 photoproduction from 10 vol% methanol solutions and (*D*) HD production via room temperature scrambling of H_2 + D_2 gas mixtures measured by using pure titania (green) and titania with added carbon (blue), NiO (purple), gold (brown), and platinum (red) nanoparticles. Schematic representations of the mechanisms and electronic transitions for the reaction with Carbon/TiO_2 (*E*) and NiO/TiO_2 (*F*) catalysts.

activity of the pure titania catalyst immersed in reducible-ion solutions is comparable to that with metal-modified catalysts: Almost identical oxygen production rates were measured in iodate solutions with TiO_2-P25 versus Pt/TiO_2-P25 (Fig. 3B). It is interesting to note that whereas both Pt and Ag^+ were reported to act as electron acceptors in a previous publication, O_2 production was only readily observed with the latter (30). This difference in the photocatalytic behavior of Pt versus Ag^+, although difficult to explain with the conventional model, derives naturally from ours. A second study reported a significant increase in the fluorescence decay rate with both the rutile and anatase forms of titania upon the addition of Fe^{3+} ions, another reducible scavenger of excited electrons, to the water solution (31).

An alternative approach to elucidate the mechanism of water-splitting photocatalysis is to focus on the H_2 production, which can be facilitated via the addition of an easy-to-oxidize sacrificial agent such as methanol to the solution (to bypass the O_2 production half reaction) (18, 32). For this, the metal may be replaced with another element capable of performing only one of the two functions being considered in this discussion, namely, electron trapping or atomic-hydrogen recombination. Several samples were prepared in this study with this aim in mind. The first set was based on the dispersion of electrically conductive carbon on the TiO_2-P25 surface, an additive that should be able to trap electrons upon photoexcitation of the titania in much the same way as metals do but should not promote the recombination of hydrogen atoms (Fig. 3E). It was determined that, despite their potential ability to aid in the electron–hole recombination quenching, the carbon/titania catalysts are in fact not capable of producing measurable amounts of H_2 via photoactivation in methanol solutions (Fig. 3C). It was also established that they are not able to promote HD production from H_2 + D_2 mixtures in the gas phase (Fig. 3D), the reaction used here to evaluate the ability of our catalysts to promote the recombination of adsorbed hydrogen atoms. Unfortunately, because of the black nature of the carbon-based samples, the electrical contact between the carbon and titania phases could not be probed directly by spectroscopic means. Instead, four different carbon-based samples were designed and prepared in our study to maximize the chances of forming such contact (see *SI Materials and Methods* for details). The transmission electron microscopy (TEM) images in Fig. S5 show reasonable intermixing between the two materials, yet all of the samples showed the same lack of catalytic activity for either H_2 photoproduction or H–D scrambling. Therefore, it is concluded that, without the ability to facilitate the recombination of hydrogen atoms, the electron-trapping functionality provided by the conducting carbon cannot alone augment the photocatalytic activity of the titania samples.

An example of a sample where the opposite choice of functionality is added to the titania photocatalyst, namely, of a material that facilitates H_2 recombination but cannot act as an electron trap, is nickel oxide. The energy level of the conduction band of NiO is much higher than that of TiO_2, and therefore that band cannot easily receive the electrons photogenerated at the titania sites (Fig. 3F). Although there is some controversy in the literature about where exactly the valence and conduction bands of NiO lie in the energy scale (33), the most accepted values are in the ranges of −4.8 to −5.5 and −0.2 to −2.1 eV from the vacuum level, respectively (34), which are to be contrasted with the −7.6 and −4.4 eV values associated with titania (with anatase, specifically) (12). On the other hand, NiO is likely to be capable of promoting the recombination of adsorbed atomic hydrogen atoms: Theoretical calculations indicate that H + H recombination on NiO(100) is exothermic, with an activation barrier of only about 40 kJ/mol (35), and NiO is used as a H_2 gas sensor, implying that hydrogen can reversibly adsorb and desorb from NiO surfaces (36). Our experiments indicated that, indeed, appreciable activity is possible for gas phase H_2 + D_2 isotope
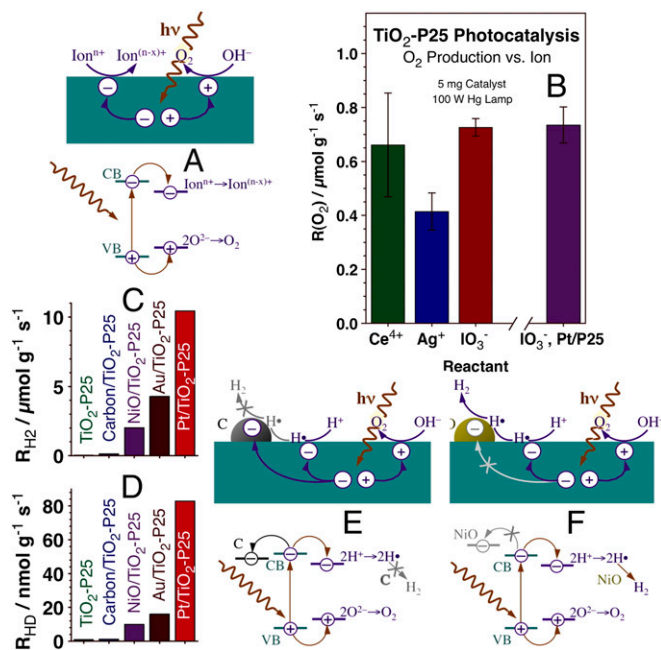
scrambling with our NiO/TiO$_2$-P25 catalyst (~60% of the rate seen with Au/TiO$_2$-P25, Fig. 3D), and additional measurements showed significant photocatalytic H$_2$ production from methanol solutions (~50% of the rate seen with Au/TiO$_2$-P25, Fig. 3C). In fact, a semiquantitative correlation between the H$_2$ photocatalytic production (Fig. 3C) and gas phase H$_2$ + D$_2$ isotope scrambling (Fig. 3D) rates was seen with all of the titania-based catalysts in the set reported in Fig. 3. Again, the ability to promote hydrogen recombination, not the trapping of photogenerated electrons, is the functionality required for the promotion of hydrogen photoproduction in this case.

The promoting effect of NiO in photocatalysis with titania-based materials has been reported before (37–39). A couple of explanations have been put forward for this observation in the past (37), none of them satisfactory. In one, it was suggested that some of the nickel oxide dispersed on the titania surface is reduced to the metallic state, and that protons form water adsorb on the NiO surface but are reduced by direct electron transfer from the Ni metal. However, it is difficult to envision the reduction of the nickel oxide in the oxidizing environment provided by the water solvent, and, as expected, no metallic Ni was detected in our samples with X-ray photoelectron spectroscopy (XPS) (Fig. S6A). The signals in the XPS spectra are weak and noisy, but the peaks from metallic nickel would be expected at ~3-eV lower binding energies than those from NiO, and because there are no other interferences in that region of the spectra, we estimate our sensitivity to metallic Ni to be in the range of a few percent or better. Alternatively, it was also proposed that because NiO is a semiconductor, it may itself be excited via light absorption. In that case, the NiO/TiO$_2$ system may behave as a p–n photochemical diode, where protons are reduced at the nickel oxide sites and oxygen is produced at the titania surface. However, in our experiments, a linear relationship was observed between the rate of H$_2$ production with the NiO/TiO$_2$-P25 catalyst and the power of the light used for the excitation (Fig. S6B), a result that rules out any such two- or multiphoton processes.

Similarly, it was shown that NiO by itself (or dispersed on a silica substrate) is not capable of photoproducing any H$_2$ (Fig. S6C). A third mechanism proposed in the literature states that the nickel and titania oxides may intermix and form new titanate compounds with different electronic properties (39). However, this oxide mixing requires specific synthetic methods, and it is unlikely to be relevant in our case; no evidence of such mixing was observed in the XPS (Fig. S6A), X-ray diffraction (XRD) (Fig. S6D) or TEM (Fig. S6E) data obtained from our samples. Although no satisfactory explanation is, in our opinion, available in the published literature for the promoting effect of NiO based on the conventional model of photocatalysis, that behavior is easily explained by our alternative scheme.

Finally, the effect of removing the electrical contact between the semiconductor and the metal in the standard Au/TiO$_2$-P25 catalyst was examined. This was accomplished by coating the dispersed gold nanoparticles with a thin layer of an insulating porous material to block the electron trapping ability of those nanoparticles while still retaining some of their catalytic hydrogen-recombination capabilities. Three different Au@SiO$_2$ core-shell structures were prepared: two with shells of different thicknesses (~7 and ~15 nm) and a third by aging the thin shells to increase their porosity. Typical TEM images of the core-shell structures as prepared and after having been dispersed on the titania support are shown in Fig. 4 A–D. The shells in all three samples proved to be quite effective at electrically insulating the gold nanoparticles from the titania support, as indicated by the lack of evidence for any shifts in their plasmon resonance upon photoexcitation (Fig. 4E). Nevertheless, they displayed measurable rates, up to an order of magnitude larger or more than with pure TiO$_2$-P25, for both photocatalytic H$_2$ production in 10 vol% methanol solutions (Fig. 4F) and H–D isotope scrambling in the gas phase (Fig. 4G). The rates for the former reaction are low, but that is to be expected because in our model hydrogen atoms are required to migrate from the titania surface, where they are generated, to the gold nanoparticles, where recombination
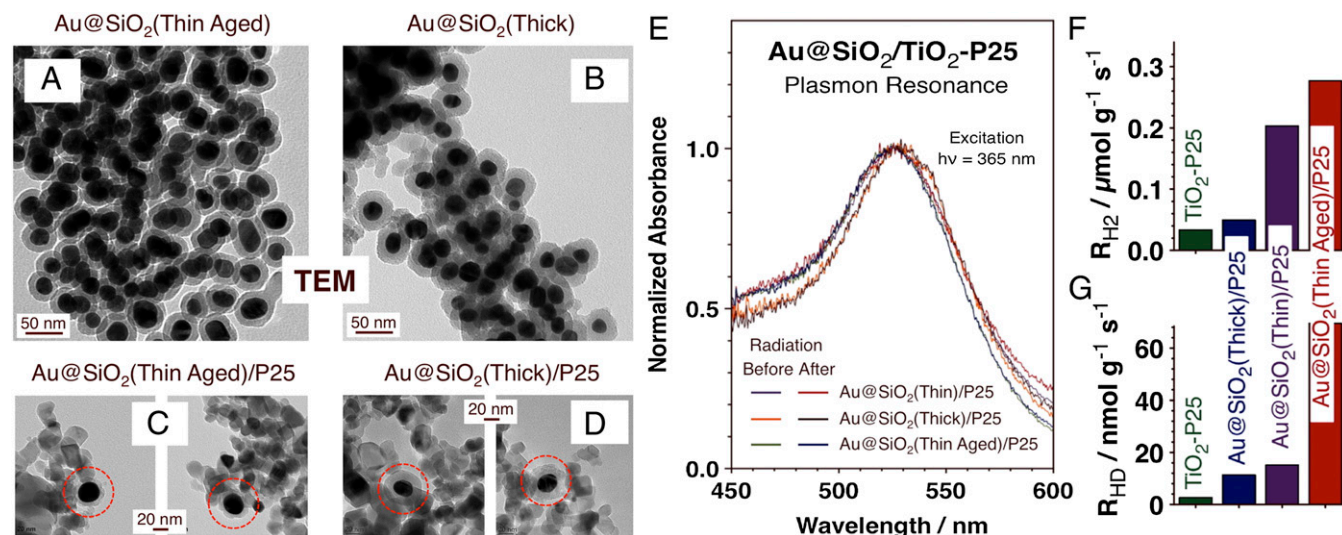
Fig. 4. TEM images of Au@SiO$_2$ core-shell structures by themselves (A and B) and after dispersion on TiO$_2$-P25 (C and D). Images for two types of samples are shown, with different silica shell thicknesses: ~7 (A and C) and ~15 (B and D) nm. The thin-shell samples were also aged in a water:ethanol mixture for 1 d to induce additional gelling. (E) Visible-light absorption spectra for three Au@SiO$_2$/TiO$_2$-P25 samples [with thin (~7 nm, purple and red); thick (~15 nm, orange and brown); and thin/aged (green and blue) silica shells] in 10 vol% methanol:water solutions before (purple, orange, green) and after (red, brown, blue) radiation with 365-nm light. No significant shifts in plasmon resonance frequency are seen with any of these samples upon photon excitation, indicating that the gold nanoparticles are electrically insulated from the titania. (F) Rates for H$_2$ photoproduction from 10 vol% methanol solutions and (G) Rates for HD production by scrambling of H$_2$ + D$_2$ gas mixtures measured with pure titania (green) and the three Au@SiO$_2$/TiO$_2$-P25 samples, with thick (blue), thin (purple), and thin/aged (red) silica shells. The two rates follow similar trends, suggesting that H$_2$ production via photocatalysis depends on the accessibility of the gold surfaces to the H atoms generated on the titania surface.

and H_2 production is to take place, and that requires diffusion through the silica layer. In any case, the trends for H_2 photoproduction mirror those seen in the isotope scrambling experiments, and can be easily accounted for by the expectation of easier H atom migration to the gold surfaces in catalysts with thinner or more porous silica shells leading to higher reaction rates. Therefore, once again, our results with the $Au@SiO_2$/TiO_2-P25 core-shell samples are inconsistent with the standard model of metals as electron traps, and they support our alternative mechanism based on H diffusion and recombination at the metal surface.

In addition to providing evidence for our new model, the data presented in this study are in line with key observations from multiple other articles available in the literature. For instance, Baba et al. reported a kinetic isotope effect for the photoproduction of hydrogen gas from H_2O + D_2O mixtures with Metal/TiO_2 catalysts that they ascribed to a rate-limiting hydrogen atom recombination step (although they did not elaborate on the nature of the sites where the hydrogen atoms are produced) (40). On the other hand, studies under vacuum with rutile single crystals have shown conclusively that no thermal atomic hydrogen recombination to H_2 is possible on TiO_2 surfaces; it was speculated that the surface H atoms (H_{ads}) either penetrate into the bulk or diffuse across the surface instead (41). In support of that observation, theoretical calculations on both rutile (41) and anatase (42) have indicated that H_{ads} recombination on titania is highly unlikely: On anatase, for instance, the activation barrier for that reaction was estimated to be about 200 kJ/mol, whereas the barrier for diffusion on the surface was calculated at only 130 kJ/mol (42). There is also substantial experimental evidence for the migration of hydrogen atoms across oxide surfaces, a phenomenon known as spillover (43, 44). Specifically, Yates and coworkers have in a recent article provided evidence for the spillover of hydrogen on a Au/TiO_2-P25 catalyst quite similar to the ones used in our studies (45). This behavior is usually reported in connection with the dissociation of H_2 molecules on a metal surface and the subsequent spillover of the resulting hydrogen atoms into the oxide, but the reverse migration of H atoms to the metal for recombination, what is sometimes referred to as reverse or back spillover, has been extensively discussed as well (46). All these reports provide further credence to our model.

It has been long known that transition metals, platinum and gold in particular, significantly enhance the activity of semiconductor photocatalysts. However, those metals are expensive; there is an interest in finding more economical alternatives. Based on the widely accepted model for the role of the metal in this photocatalysis, the focus has been on finding cheaper electron scavengers. However, our results lead us to argue that what is needed is a good atomic hydrogen recombination catalyst instead. For instance, we have shown that carbon black, despite its excellent conductive properties (the reason why it is often used as an electrode), is not viable for photocatalytic promotion. On the other hand, nickel oxide, a material that cannot accept excited electrons from the conduction band of most photocatalysts, is nevertheless able to enhance their photoactivity. Our study also suggests that the rate of H–D exchange may be a useful figure of merit for screening water-splitting photocatalysts. In general, we believe that, with a change in focus driven by our new proposed model, it may be possible to identify better promoters for photocatalysis in the near future.

Materials and Methods

The metal nanoparticles and yolk-shell catalysts have been prepared by using colloidal and sol–gel procedures reported previously (20, 21, 47) and described in detail in *SI Materials and Methods*. The titania-P25 support was purchased and used as supplied. The preparation of the catalysts made with NiO, carbon, and $Au@SiO_2$ nanoparticles is also described in detail in *SI Materials and Methods*. The samples were characterized by TEM, XRD, and XPS. TEM images were obtained by using a Tecnai T12 instrument. XRD analysis was done using a Bruker D8 Advance Diffractometer with Cu K_α radiation ($\lambda = 1.5406$ Å). XPS data were acquired by using a Kratos analytical AXIS instrument equipped with a 165-mm-mean-radius semihemispherical electron energy analyzer and a 120-element delay line detector.

Time fluorescence experiments were carried out by using a 40-kHz Spectra Physics Spitfire regeneratively amplified laser system and a Hamamatsu C4334 streak-scope. Monitoring of the shifts of the gold plasmon band was done by using a diffuse reflectance setup and an Ocean Optics USB4000 spectrometer. The H–D isotope-scrambling activity of the catalysts was evaluated by following the formation of HD from H_2 + D_2 gas mixtures with a UTI quadrupole mass spectrometer. The photocatalytic activity was measured in a homemade Pyrex glass reactor using an Opti-Quip 100-W Hg lamp as the source of excitation and gas chromatography for the analysis and quantitation of the products. More details on all of these procedures are provided in *SI Materials and Methods*.

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